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DEVELOPMENT OF SCHEMATIC ANALYTICAL PROCEDURES FOR SYNTHETIC LUBRICANTS AND THEIR ADDITIVES

Part IV. Laboratory Manual for the Analysis of Synthetic Lubricants, Greases and Their Additives

FRANCIS S. BONOMO
JOSEPH J. E. SCHMIDT

DENVER RESEARCH INSTITUTE

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FOREWORD

This report was prepared by the Denver Research Institute, University of Denver, under USAF Contract Nos. AF 33(616)-2204 and AF 33(616)-3336. These contracts were initiated under Project No. 3044, "Aviation Lubricants", Task No. 73314, "Lubricants." It was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Mr. John B. Christian acting as project engineer.

This report is a laboratory manual based on research programs under the above contracts, initiated in July 1953 and continuing through November 1956.

ABSTRACT

Laboratory methods and techniques for the analysis of certain synthetic lubricants, greases, and their additives are described in detail, including drawings and photographs of equipment when necessary. As stipulated by WADC, none of the methods includes optical or elaborate instrumental techniques of analysis. Most of the methods employ simple wet chemical manipulations, or such techniques as adsorption or partition paper or column chromatography. The individual methods are numbered and patterned after Federal Test Method Standard No. 791.

The manual is divided into five major sections:

(1) Preliminary qualitative examination of the lubricant or grease, including solubility, elemental analysis, identification of grease type, and behavior of the lubricant (or base-oil from a grease) upon adsorption on a column of silica gel.

(2) Qualitative detection and quantitative determination of antioxidants.

(3) Qualitative detection and quantitative determination of corrosion preventive compounds.

(4) Separation and quantitative determination of gelling agents and thickeners.

(5) Separation, identification, and determination of base-oils from lubricants and greases.

In a number of instances parts of existing ASTM methods have been incorporated into the analytical procedures, where applicable, to avoid the use of parallel methods to the same goal.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

R. T. SCHWARTZ
Chief, Organic Materials Branch
Materials Laboratory

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INTRODUCTION

This laboratory manual is intended to provide a guide toward the analysis of synthetic lubricants, greases, and their additives by non-optical, non-instrumental techniques. The purpose of the restricted scope of analysis was designed to provide analytical methods for those laboratories throughout the world which are not equipped with the most modern analytical equipment, and whose staffs do not necessarily have personnel trained in the use of complex analytical instruments. The manual is in no sense complete with respect to all of the various types of compounds which may be found in these lubricants. In fact, the rapid rate of change in the lubrication field, with new types of base-oils and additives being continuously developed to meet more stringent operational requirements of the Air Force, has already out-moded some of the compounds covered in this manual. However, many of the more recently developed compounds, both in the base-oil and in the additive classes, can probably be adapted to the described techniques with a minimum of preliminary experimentation; or the procedures might be modified slightly to provide means for including these newer compounds.

The manual is divided into five major SECTIONS, concerned with (1) preliminary examination and classification, (2) antioxidants, (3) corrosion preventive compounds, (4) thickeners and gelling agents, and (5) base-oils. The various methods set forth in each of the sections are patterned after the format of Federal Test Method Standard No. 791, currently in use by the Air Force. In several instances, parts of existing ASTM methods have been incorporated into the analytical procedures, where applicable, to avoid the unnecessary use of nearly identical methods for the same type of analysis, and to avoid needless referral to ASTM Methods or parts of Methods.

In a few instances (for example the "hindered" phenol antioxidants), no satisfactory non-instrumental technique could be found for detection and determination of the compound directly in a lubricant or grease, or for separation of the compound from the grease for analysis. In these cases the manual usually gives methods

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of determination of the non-compounded material, which may prove useful occasionally as a control measure in analyzing the material before compounding. Silicone oils are a case where simple, non-instrumental techniques are not available for quantitative determinations. A technique such as wet oxidation may be employed, which is time-consuming; however, these base-oils may be separated from other base-oils and identified by qualitative color reactions; therefore it was felt unnecessary to include additional quantitative methods which would lengthen the procedure and produce little more information about the compounds than was already known by qualitative tests and quantitative separations.

Instances where currently popular compounds in lubricant or grease formulation are omitted from the manual are due to the fact that (1) WADC did not specify their inclusion in the research program, (2) these compounds have been developed since the research program was well under way, or (3) there were insufficient time or funds under the contract to study their properties and incorporate them into the analytical procedures.

SECTION I

PRELIMINARY EXAMINATION OF SYNTHETIC LUBRICANTS AND GREASES

COLOR AND SOLUBILITY CLASSIFICATION OF SYNTHETIC LUBRICANTS AND GREASES

1.0 SCOPE.

1.1 This method is intended to suggest the first step toward successful analysis of a synthetic lubricant or grease. It is intended primarily to point out that by casual inspection of an oil or grease as received, a number of characteristics concerning the chemical composition may be deduced, with the result that it will not be necessary to perform a number of the tests and procedures given in this manual. An experienced analyst may avail himself of this information to save time in the ultimate analysis of a synthetic lubricant or grease (Note 1). The experience of the analyst in handling these materials and moreso his knowledge of the chemical properties of the compounds involved is important in this casual examination. An analyst with less experience may resort to comparison of known samples of oils and greases as an aid in examining samples submitted for analysis.

Note 1. As an example of the type of short cut which prelimimary examination will effect, an oil or grease which exhibits a brilliant blue fluorescence under ultra-violet irradiation is likely to contain the antioxidant N-phenyl-alpha-naphthylamine; therefore, an immediate test for this compound would be suggested. If a grease has a deep blue color it probably contains phthalocyanine-type gelling agents; these could be isolated and examined immediately by the techniques given in the appropriate methods. Finally, if a grease is completely soluble in concentrated sulfuric acid without carbonization, a silicone thickened with a urea-type gelling agent should be sought.

2.0 OUTLINE OF METHOD.

2.1 The sample is inspected in daylight, in artificial light, and under ultraviolet irradiation. Small portions of the sample are tested for solubility in a variety of solvents designed to extract certain groups of compounds according to their chemical properties.

3.0 APPARATUS.

3.1 Ultra-violet lamp. A Blak-Ray Model XX-4 long-wave ultra-violet lamp (Ultra-Violet Products, Inc., South Pasadena, California) has proven satisfactory for illuminating samples of oil and grease.

4.0 REAGENTS.

4.1 A variety of solvents should be employed for solubility studies, the number being limited only by the experience of the analyst in ascertaining which types of solvents are most useful in determining basic information about the oil or grease. Reagent grade chemicals should be employed. The following are suggested, but this should not be taken as a definitive list:

4.2 Benzene, reagent grade.

4.3 Ethanol, absolute, purified.

4.4 Acetic acid, glacial, reagent grade.

4.5 Sulfuric acid (sp. gr. 1.84), reagent grade.

4.6 Sodium hydroxide solution (10 percent aqueous).

4.7 Hydrochloric acid solution (10 percent aqueous).

4.8 Water, distilled.

5.0 PROCEDURE.

5.1 COLOR CHARACTERISTICS. Inspect the sample in daylight, in artificial light, and under ultra-violet irradiation. Note the color in each of these media, record, and compare (if possible) to samples of known composition.

5.2 SOLUBILITY CLASSIFICATION. Place about 0.1 gram of the sample in a 3-inch, 10-milliliter test tube, and fill the tube half full with a solvent. Close with a clean polyethylene or cork stopper, and shake vigorously for several minutes. Set the tube aside to clear, and make observations concerning the apparent solubility of the sample. Withdraw about 1 milliliter of solvent with a medicine dropper pipette,

and place the drop on a clean watch glass on a steam bath. Evaporate to dryness and observe whether there is a residue on the glass, and if so note the appearance of the material (for example oil, crystals, color, etc.). Repeat this procedure with all solvents which are felt to be necessary by the analyst. The results of these solubility tests should be compared with those obtained with oils and greases of known composition (Paragraph 5.3 below). In the case of aqueous acid and alkaline solvents, neutralize the solution in the test tube after noting solubility behavior, using indicator test paper (such as litmus paper) to indicate the degree of acidity or alkalinity. Note whether any soluble materials are precipitated, color changes, etc., and draw conclusions from the observed results. When using concentrated acid, first dilute the acid with water (Caution!) to precipitate any soluble materials; if there is no precipitate, neutralize and record results. The analyst must know the basic chemical characteristics of the compounds with which he is dealing, in order to interpret these results correctly, bearing in mind the fact that traces of impurities usually present in these oils and greases can contribute to erroneous interpretation of the observed results.

5.3 COMPARISON WITH KNOWN OILS AND GREASES.

Whenever the analyst suspects the presence of certain compounds because of the color and/or solubility behavior of the sample, it is useful to obtain, if possible, samples of oils or greases which contain these compounds and to compare the behavior of these known samples to the unknown with respect to color and solubility.

QUALITATIVE ELEMENTAL ANALYSIS OF SYNTHETIC LUBRICANTS AND GREASES

1.0 SCOPE.

1.1 This method is intended to point out procedures for the qualitative elemental analysis of synthetic lubricants and greases. Elements which are included in this analysis are: nitrogen, phosphorus, silicon, sulfur, selenium, copper, nickel, sodium, potassium, lithium, calcium, barium, strontium, aluminum, and iron. Elemental qualitative analysis assists the analyst by eliminating specific compounds and groups of compounds, thus obviating the need for only a selected few methods in this manual for the analysis of a lubricant or grease (Notes 1 and 2).

Note 1. Qualitative elemental analysis either on a macro, semimicro, or micro scale is dealt with in full detail in numerous textbooks and reference books. If the analyst is in the habit of using other techniques than those given in this method, they may be substituted. In addition, at the end of this method a short bibliography is appended which includes a small number of the total reference works which may be employed for these analyses (13.0).

Note 2. In addition to standard reference and textbooks on the subject of elemental analysis, a number of the analyses are included in this manual in pertinent sections. These are tabulated below:

TABLE I. Qualitative Elemental Analyses Given In Other Methods In This Manual

Element	Method	Paragraph
Nitrogen	15	13.2.1
Phosphorus	14	2.0
Silicon	15	7.4.1
Selenium	28	4.1 and 4.2
Copper	15	13.4.5.1
Nickel	15	13.4.5.2
Sodium	15	11.2
Potassium	15	11.2
Lithium	15	11.2
Calcium	15	14.2.3
Barium	15	14.2.1
Strontium	15	14.2.1
Aluminum	15	13.2.2.1 and 13.2.2.2

1.2 If the tests described in this method are employed for elemental analysis on the as-received lubricant or grease, the analyst must determine the pre-treatment of the sample required to obtain the particular element in detectable form. Usually ashing of the sample is required, either wet or dry, before the above elements can be detected.

1.3 Following is a list of compounds in synthetic lubricants and greases which are indicated by elemental analysis. This list is followed by a list of compounds for which elemental analysis is useless, because these compounds contain only carbon, hydrogen, and oxygen:

TABLE II. Compounds Indicated By Elemental Analysis

Positive Test	Compounds Indicated by Positive Test
Nitrogen	Phenothiazine, N-Phenyl-Alpha-Napthylamine, p,p'-Dioctyl-diphenylamine, Mineral Oil, Bentones, Urea Thickeners, Phthalocyanines
Silicon	Silicone Oils, Silicate Esters, Disiloxanes, Silica Gel, Bentones
Sulfur	Phenothiazine, Barium Sulfonates, Calcium Sulfonates, Metallic Sulfides, Mineral Oil
Phosphorus	Phosphate Ester Base-Oils
Copper	Phthalocyanines
Nickel	Phthalocyanines
Selenium	Dilauryl Selenide
Sodium	Sodium Stearate Thickener
Potassium	Potassium Stearate Thickener
Lithium	Lithium Stearate or Hydroxystearate Thickener
Calcium	Calcium Sulfonate, Calcium Stearate Thickener
Barium	Barium Sulfonate, Barium Stearate Thickener
Strontium	Strontium Stearate Thickener
Aluminum	Aluminum Stearate Thickener, Bentones
Iron	Bentones, Iron Contamination
	Compounds Not Detected by Elemental Analysis
	2,6-Ditertiarybutyl-4-Methylphenol, 2,4-Dimethyl--6-Tertiarybutylphenol, Quinizarin
	Sorbitan Mono-Oleate, Graphite Filler
	Dibasic Acid Esters, Polyglycols, Methacrylates

2.0 OUTLINE OF METHOD.

2.1 Individual tests on the original sample of oil or grease are performed for nitrogen, sulfur, and selenium. Silicon, alkali metals, copper, nickel, and phosphorus are determined in the ash of the sample. Following these tests, alkaline-earth metals, aluminum, and iron are detected by the standard qualitative analytical scheme.

3.0 PREPARATION OF SAMPLE.

3.1 LUBRICANTS. Heat the sample of oil to about 50°C., and agitate in the original container vigorously until all sediment is homogeneously suspended in the oil. If a sediment is present and separate analyses are desired on the oil and on the sediment independently, filter the sample through a coarse filter paper to obtain clean oil. Wash the filter and precipitate with clean hexane to remove traces of oil, discarding the wash liquid. Collect the sediment for qualitative elemental analyses.

3.2 GREASES. The sample of grease shall be made as uniform as possible. If the grease is soft, stir and mix with a glass or wood paddle in a glass beaker until uniform. If the grease is hard, scrape off the surface layers with a clean spatula, discard, and take samples from the freshly exposed surfaces.

4.0 APPARATUS.

4.1 Centrifuge. A centrifuge equipped for small test tube or centrifuge tube (75 x 10 millimeter) centrifugation.

4.2 Muffle furnace. Furnace equipped with control to provide a variable temperature range of 200° to 1100°C.

5.0 REMOVAL OF ORGANIC MATERIAL.

5.1 REAGENTS.

5.1.1 Sulfuric acid solution (18N).

5.1.2 Sodium carbonate, anhydrous, reagent grade.

5.1.3 Hydrochloric acid solution (6N).

5.2 LUBRICANTS. Transfer to a clean 90-millimeter diameter porcelain dish approximately 10 grams of the homogeneous sample. Heat with a Bunsen burner until the contents ignite and burn readily. Move the dish and flaming contents to a hot plate and maintain them at such a temperature that only ash and carbon remain after burning ceases. If any liquid or tarry material remain, heat with the burner until smoking ceases. Ignite over the burner, or in a muffle furnace at 550° to 600°C. Cool, add to the residue 1 to 2 drops of 18N H_2SO_4, evaporate the acid, and ignite at 650° to 700°C., until the oxidation of carbon is complete. Repeat the acid treatment and ignition, if necessary (Note 3).

5.3 GREASES. Transfer to a clean 50 millimeter diameter porcelain crucible approximately 5 grams of the sample. Heat the crucible with a Bunsen burner to burn combustible matter off slowly, and finally ignite the residue until the ash is free of carbonaceous matter either over the burner or in a muffle furnace at not over 600°C. If the residue is not free of carbon, cool, add to the residue 1 to 2 drops of 18N H_2SO_4, evaporate the acid, and ignite at 650° to 700°C., until the oxidation of carbon is complete. Repeat the acid treatment and ignition, if necessary (Note 3).

Note 3. If the oil or grease contains an appreciable quantity of silicone oil or silicate ester, it is difficult to obtain a carbon-free ash, due to entrapment of carbon in the silica formed during ashing. Evidence of the presence of these compounds is the formation of a gray, spongy mass of large volume which will not "cook down" or turn white, even with prolonged heating. In the event that these compounds are present, they may be separated from remaining components by solvent extraction (Methods 41 through 45) or adsorption chromatography (Method 16). The other components may then be analyzed for metal constituents by the procedures given below.

5.4 TREATMENT OF RESIDUE AFTER ASHING. Transfer the ash of the oil (5.2) or grease (5.3) to a mortar, and grind the material into a fine powder. Divide the powder into two approximately equal portions. Place one portion of about 0.1 gram in a small platinum crucible with five times its weight of anhydrous Na_2CO_3. Mix thoroughly with a spatula and heat over a strong burner flame until the mixture

melts. Keep the mixture molten for 5 to 10 minutes. Cool, and digest with hot water until the entire fusion cake has gone into solution. Transfer the solution to a small test tube, centrifuge, and remove the supernatant liquid with a medicine dropper pipette. Dissolve the residue in the test tube in warm dilute HCl for further analysis (12.0). Acidify the filtrate with HCl, and evaporate to dryness on a water bath. Allow the residue to remain on the bath for 30 minutes to dehydrate precipitated SiO_2. Moisten the residue with a few drops of dilute HNO_3, and evaporate just to dryness. Moisten the residue with a few drops of dilute HCl, add a few milliliters of water to dissolve soluble salts, and centrifuge to remove silica. Withdraw the supernatant solution from the test tube and combine it with the solution resulting from HCl solution of the residue from the basic fusion above for cationic analysis (12.0). Reserve the residue for a silica test (6.0). The second portion of the original ash should be reserved for individual tests for silicon, phosphorus, sodium, potassium, and lithium (6.0, 7.0, 10.0, and 11.0).

6.0 DETECTION OF SILICON.

6.1 REAGENTS.

6.1.1 Sodium carbonate, anhydrous, reagent grade.

6.1.2 Sodium peroxide, anhydrous, reagent grade.

6.1.3 Hydrochloric acid solution (6N).

6.1.4 Ammonium molybdate solution. Dissolve 5 grams of the salt in 100 milliliters of water, and pour into 35 milliliters of HNO_3 (sp. gr. 1.2).

6.1.5 Benzidine solution (0.5 percent in glacial acetic acid).

6.1.6 Ammonium hydroxide (sp. gr. 0.90), reagent grade.

6.1.7 Oxalic acid solution (1 percent aqueous).

6.1.8 Sodium acetate solution (saturated aqueous).

6.2 PEROXIDE FUSION PROCEDURE.

6.2.1 Detection of Silicon in the Absence of Phosphorus. Mix about 0.1 gram of anhydrous Na_2CO_3, 0.1 gram of Na_2O_2, and 0.01 gram of the residue after ashing (5.4) into a homogeneous mixture in a small test tube. Make a 1/8 inch diameter loop in the end of a platinum wire, and clean the wire thoroughly by alternately dipping in dilute HCl and heating to redness in a Bunsen burner flame until no color is imparted to the flame by the wire. Dip the hot loop into the reaction mixture and heat in the flame until all reaction has ceased. Repeat this procedure until a 1/16 inch thick bead is formed. Heat for several minutes until it becomes water-white. Cool, unwind the wire, and drop the bead into a small platinum crucible containing 2 to 3 milliliters of distilled water. Warm over a burner until the bead has completely dissolved. Cut a 1 inch square piece of ashless filter paper and moisten the paper with the solution. Place a drop of ammonium molybdate solution on the paper, and warm over a burner or in an oven to evaporate excess moisture. With the paper still damp, place a small drop of benzidine solution over the ammonium molybdate spot. Wait one minute, then hold the paper over a watch glass containing a few drops of concentrated NH_4OH. The appearance of a blue spot indicates silicon, unless phosphorus compounds have been identified in the oil; in this case, the procedure must be modified as indicated in the following paragraph.

6.2.2 Detection of Silicon in the Presence of Phosphorus. If phosphorus-containing compounds are present in the sample, the ash will contain some phosphates, which give the same benzidine blue reaction as silicon. The test for silicon may be performed in the presence of phosphorus compounds as follows: mix a few drops of the solution from dissolution of the fusion bead (6.2.1) with several drops of ammonium molybdate solution in a small centrifuge tube, and centrifuge. Transfer the supernatant liquid with a medicine dropper pipette to a microcrucible, and warm gently. Cool and add several drops of oxalic acid solution (which destroys traces of ammonium phosphomolybdate). Add a drop of benzidine solution and a few drops of sodium acetate solution. Appearance of a blue color indicates the presence of silicon. This procedure should be employed for testing any suspected material or precipitate for the presence of silicon.

7.0 DETECTION OF PHOSPHORUS.

7.1 OUTLINE OF METHOD.

7.1.1 Phosphates react with molybdates to form salts of phosphomolybdic acid, which in turn may be used to oxidize benzidine, the products of the reaction being benzidine blue and molybdenum blue. Silicates also give this reaction, but their effect is eliminated either by removing as insoluble silica or by complexing with tartaric acid.

7.2 REAGENTS.

7.2.1 Ammonium molybdate solution. Dissolve 5 grams of the salt in 100 milliliters of water, and pour into 35 milliliters of HNO_3 (sp. gr. 1.42).

7.2.2 Benzidine solution (0.5 percent in glacial acetic acid).

7.2.3 Sodium acetate solution (saturated aqueous).

7.2.4 Ammonium hydroxide (sp. gr. 0.90), reagent grade.

7.2.5 Tartrate-ammonium molybdate solution. Dissolve 15 grams of reagent grade tartaric acid in the ammonium molybdate solution (7.2.1).

7.3 PROCEDURE.

7.3.1 Procedure in the Absence of Silicates. Place one drop of the combined acidified filtrates (5.4) (from which silica has been removed by digestion with HCl) on a square of quantitative filter paper, followed by a drop of ammonium molybdate solution and a drop of benzidine solution. Pour a few drops of ammonium hydroxide onto a watch glass, and hold the paper in the fumes of ammonia. If phosphates are present, a blue stain will appear. If there is doubt as to whether the spot could have been caused by silica, repeat the test as given in Paragraph 7.3.2 below.

7.3.2 Procedure in the Presence of Silicates. Place one drop of the combined acidified filtrates (5.4) (from which silica has been removed by digestion with HCl) on a square of quantitative filter paper, followed by a drop of tartrate-ammonium molybdate solution.

Place the paper in an oven at 110°C., or hold over a heating plate for a moment, to increase the reaction rate. Now place a drop of benzidine reagent on the original spot. Pour a few drops of ammonium hydroxide onto a watch glass, and hold the paper in the fumes of ammonia. If phosphates are present, a blue stain will appear; if the first spot (7.3.1) was caused only by silicates, no spot will appear, and the absence of phosphates is confirmed.

8.0 DETECTION OF SELENIUM.

8.1 OUTLINE OF METHOD.

8.1.1 This analysis is performed on the as-received oil or grease. Organic components are oxidized by sodium peroxide and sodium carbonate fusion in a platinum wire loop, converting selenium to selenate ion. The resulting melt is dissolved in dilute HCl, and a drop of the solution is treated with asymmetric diphenylhydrazine and glacial acetic acid to form a bright red-violet color in the presence of selenate ion.

8.2 REAGENTS.

8.2.1 Asymmetric diphenylhydrazine (1 percent in glacial acetic acid).

8.2.2 Acetic acid, glacial, reagent grade.

8.2.3 Hydrochloric acid solution (2N).

8.2.4 Sodium peroxide, anhydrous, reagent grade.

8.2.5 Sodium carbonate, anhydrous, reagent grade.

8.2.6 Hydrochloric acid solution (1:1). Pour one volume of HCl (sp. gr. 1.19) into an equal volume of distilled water.

8.3 PROCEDURE.

8.3.1 Removal of Organic Material. Mix 0.1 gram of anhydrous Na_2CO_3, 0.1 gram of Na_2O_2, and 10 drops of the synthetic

lubricant or an equivalent quantity of grease into a smooth paste with a spatula in a spot plate depression. Form a clear bead as described in Paragraph 6.2.1 of this method. After dissolving the bead in water in a small beaker, add 2 or 3 milliliters of HCl (1:1), heat to boiling, and cool. This reduces selenic acid to selenious acid, H_2SeO_3, which can be detected by any one of several sensitive color reactions.

8.3.2 Asymmetric Diphenylhydrazine Reaction for Selenium. Place several drops of the H_2SeO_3 solution in the depression of a spot plate, and add four or five drops of asymmetric diphenylhydrazine solution. Mix with a stirring rod and allow to stand for several minutes. If a violet color has not appeared after this time, add one drop of dilute HCl to increase the acidity. The appearance of a red-violet color indicates the presence of selenium, the intensity of the color deepening when the concentration of selenium is high (Note 4). Caution: keep oxidizing agents from the vicinity of the spot plate during this reaction.

Note 4. The concentration of selenium in synthetic lubricants is so low that care must be taken to have enough sample in the bead to give the test for selenium. If only one drop of oil or an equivalent amount of grease is mixed with the fusion mixture, the test is likely to be questionable, but if about ten drops or the equivalent amount of grease are mixed and a large bead is made, a definite test will be obtained. Because of these low concentrations, the color will not appear for several minutes; therefore, it is necessary to wait at least 5 minutes to be sure that the color reaction is negative or positive.

9.0 DETECTION OF ORGANIC NITROGEN AND SULFUR.

9.1 OUTLINE OF METHOD.

9.1.1 A small sample of the original oil or grease is reacted with hot metallic sodium, destroying the bulk of the organic matter and forming NaCn, Na_2S, etc. from nitrogen and sulfur present in the sample. Nitrogen is detected in a solution of the decomposition products by its reaction with iron salts to form the blue ferric ferrocyanide, "Prussian Blue", which is collected by filtration. Sulfur is detected in the solution of the decomposition products by its reaction with freshly prepared sodium plumbite solution, giving a black PbS precipitate.

9.2 REAGENTS.

9.2.1 Sodium metal, reagent grade.

9.2.2 Ferrous sulfate solution (0.5N). Dissolve 8 grams of $FeSO_4 \cdot 7H_2O$ in 100 milliliters of distilled water with a few drops of concentrated H_2SO_4.

9.2.3 Ferric chloride solution (1 percent aqueous).

9.2.4 Sulfuric acid solution (5 percent).

9.2.5 Sodium hydroxide solution (10 percent).

9.2.6 Lead acetate solution (0.1 molar).

9.3 PROCEDURE.

9.3.1 Detection of Nitrogen. Place a small (1/8 inch diameter) piece of clean, dried metallic sodium in a dry 2-inch test tube which is suspended by its lip in a small hole in an asbestos board or wire screen. Add a small drop of the sample oil or a small piece of the grease, and heat the tube slowly until the sodium melts and its vapors form a layer 1/2 inch up the test tube. Drop about 0.05 gram of the oil or grease directly into the sodium vapor (avoid standing over the test tube, as some compounds react violently, sending a jet of flame out of the tube). Continue heating the mixture to oxidize residual sodium and to remove decomposition products. Remove the flame and with forceps quickly lift the hot tube from the board or screen and lower it into a small beaker containing 10 milliliters of water. Take special care during this operation not to stand over the beaker. Touch the bottom of the hot tube to the water to crack the glass, then wait a moment for the glass to cool. Tap the cracked tube against the side of the beaker to open the reaction mixture to the air. When all of the pieces of glass are in the water, bring the water to boiling, with stirring to break up solid particles. Filter through a coarse paper. The filtrate should be colorless; otherwise, repeat the decomposition. Test for alkalinity with litmus or indicator test paper. The solution should be strongly alkaline. To about 5 milliliters of the alkaline filtrate add 5 or 6 drops of $FeSO_4$ solution and 2 drops of $FeCl_3$ solution. Heat to boiling for a minute or

two, cool, and acidify by the dropwise addition of dilute H_2SO_4 with shaking. Stop the addition of acid when the solution becomes acidic and the hydroxide precipitate dissolves. A brilliant blue color (actually a precipitate) will appear immediately if nitrogen is present. If the concentration of nitrogen is low, the blue color may be faint and may require several moments to appear. After ten minutes, filter the solution through a fine-texture paper; the Prussian blue precipitate should be visible against the white paper background. If no color appears, the nitrogen content of the sample is negligible.

9.3.2 Detection of Sulfur. Prepare a fresh solution of sodium plumbite by adding dilute NaOH solution to 0.2 milliliters of lead acetate solution until the precipitate just dissolves. Add this solution to about 1 milliliter or less of the alkaline solution from the sodium fusion (9.3.1). A black precipitate or suspension of PbS indicates the presence of sulfur. If selenium is present in the oil or grease, it also will give this reaction; therefore the presence of selenium must be ascertained before the sulfur test may be considered conclusive (8.0).

9.3.3 Detection of Halogens. Halogens may also be detected in the alkaline solution from the sodium fusion (9.3.1) by standard techniques; however, none of the compounds considered in this study contain halogen, and therefore this technique is omitted here.

10.0 DETECTION OF SODIUM, POTASSIUM, AND LITHIUM.

10.1 OUTLINE OF METHOD.

10.1.1 Alkali metals impart characteristic colors to flames when their salts are heated on a platinum wire. By using a cobalt glass the color caused by sodium, if it is present in the sample, may be masked out to permit observation of the colors given by lithium and potassium.

10.2 REAGENTS.

10.2.1 Hydrochloric acid solution (5 percent aqueous).

10.3 PROCEDURE.

10.3.1 Place a small portion (about 0.1 gram or less) of the ash of the oil or grease (5.4) in a small test tube, add about 5 milliliters of dilute HCl, heat the tube to boiling, and keep at the boiling point for about 5 minutes to dissolve as much of the residue as possible. Centrifuge to obtain a clear supernatant liquid. Transfer this liquid with a medicine dropper pipette to a second small test tube. Clean a platinum wire by repeated heating in a Bunsen burner flame, followed by immersion in dilute HCl. The wire is clean when it imparts no color to the flame when glowing red hot (sodium salts are the usual source of impurity on the wire, giving a bright orange-yellow flame). When the wire is clean, dip it in the solution obtained from dissolving the ash, hold the wire in the flame, and observe any color imparted to the flame. If sodium is present, an orange-yellow color will be seen, and the colors from lithium or potassium will be masked. If potassium is present without sodium, a violet flame occurs; when sodium is present, the potassium color may be seen through a cobalt glass. Lithium gives a carmine-red flame which tends to mask the violet potassium flame. This lithium color may also be observed through a cobalt glass. If there is doubt about interpretation of the flame tests, the aqueous solution may be concentrated by evaporation, and the tests repeated. If there is still doubt, a number of sensitive spot reactions for these metals are described in standard analytical texts. It is likely, however, that the alkali metals will appear singly in an oil or grease; the flame tests will therefore be clear and easily interpreted.

11.0 DETECTION OF COPPER AND NICKEL.

11.1 OUTLINE OF METHOD.

11.1.1 Copper in the ash of the oil or grease is detected either by its reaction with ammonia or by the more sensitive benzoin oxime reaction. Nickel is detected by the standard dimethylglyoxime test, which must be modified if copper has already been detected in the solution.

11.2 REAGENTS.

11.2.1 Ammonium hydroxide (sp. gr. 0.90), reagent grade.

11.2.2 Ammonium hydroxide solution (5 percent aqueous).

11.2.3 Benzoin oxime solution (5 percent in ethanol).

11.2.4 Ethanol (95 percent), reagent or purified grade.

11.2.5 Rochelle salt solution (sodium potassium tartrate) (10 percent aqueous).

11.2.6 Dimethylglyoxime solution (1 percent in ethanol).

11.2.7 Dimethylglyoxime solution (saturated, in acetone).

11.3 PROCEDURE.

11.3.1 The tests for copper and nickel should be performed on a portion of the acidified filtrate obtained after basic fusion of the ash of the oil or grease (5.4). If this filtrate is distinctly blue, copper is present; if the filtrate is green, nickel is present. Color of the filtrate, however, should not be taken as proof of the presence of these metals; the filtrate should be reserved and checked with the following color reactions:

11.3.2 Detection of Copper. Place about 1 milliliter of the acidified filtrate (5.4) in a small test tube and add NH_4OH (sp. gr. 0.90) dropwise. A precipitate will appear when the solution becomes slightly alkaline, but if copper is present the precipitate will re-dissolve with the appearance of a dark blue-violet color, due to the $Cu(NH_3)_4^{++}$ complex. If nickel only is present, a light blue complex, $Ni(NH_3)_6^{++}$, will form. If both ions are present, the copper complex will mask the nickel color. Centrifuge the solution to permit clear inspection of color of the filtrate. If there is doubt about the presence of copper, the benzoin oxime test may be applied: impregnate a piece of filter paper with 5 percent alcoholic benzoin oxime solution by dipping in the solution and drying. Lower the acidity of a few milliliters of the filtrate (5.4) with concentrated NH_4OH to a pH of 5 or 6, using indicator test paper. Place a drop of the filtrate on the impregnated paper and hold the paper over a watch glass containing a few drops of concentrated NH_4OH. Appearance of a green coloration indicates the presence of copper. If nickel is suspected, repeat the test using untreated filter paper: place a drop of the filtrate (after lowering the pH to 5 or 6) on the paper, add a drop of a 10 percent

solution of Rochelle salt, and a drop of benzoin oxime solution on the previous spots. A green coloration due to copper will appear, and nickel will not interfere. (Note 5).

11.3.3 Detection of Nickel. If copper has not been detected in the filtrate (11.3.2), use the following test for nickel: lower the acidity of a few milliliters of the filtrate (5.4) with concentrated NH_4OH to a pH of 5 or 6, using indicator test paper. Place a drop of the neutralized filtrate on a piece of dry, clean filter paper. Add a drop of 1 percent alcoholic solution of dimethylglyoxime to the first spot, and hold the paper over a watch glass containing a few drops of concentrated NH_4OH. A red circle or coloration on the paper indicates the presence of nickel. If the test is questionable, impregnated paper may be employed to increase the sensitivity of the method, using a warm saturated solution of the dimethylglyoxime reagent in acetone to impregnate the paper, followed by drying. The test with impregnated paper is carried out by placing a drop of filtrate on the paper and holding the paper over NH_4OH in a watch glass. If copper has been detected in the filtrate, the test must be modified in the following way: place a drop of the filtrate on filter paper impregnated with dimethylglyoxime. Wait a moment, then immerse the paper in a Petri dish or large watch glass containing about 20 milliliters of 5 percent NH_4OH solution, keeping the paper in constant motion to wash out the soluble copper dimethylglyoxime compound. The red nickel dimethylglyoxime compound will remain on the paper. (Note 5).

Note 5. If there is iron in the oil or grease sample (introduced usually as a result of the manufacturing process, and not as a part of any of the compounding ingredients except bentone), the iron will be precipitated from the filtrate (5.4) when NH_4OH is added, giving a brown coloration to the filtrate at the same time that the copper and nickel ammonia complexes are formed. It is well to separate out this precipitate either by centrifugation or filtration before continuing with the specific tests for copper and nickel.

12.0 DETECTION OF ALUMINUM, IRON, CALCIUM, BARIUM, AND STRONTIUM.

12.1 OUTLINE OF METHOD.

12.1.1 The standard qualitative inorganic scheme of analysis is employed to detect and identify aluminum, iron, calcium, barium and strontium in the ash of the oil or grease sample. Copper and nickel, discussed in the previous paragraphs, may also be detected in this scheme, if the analyst prefers to identify them at this point in the analysis.

12.2 REAGENTS.

12.2.1 Nitric acid (sp. gr. 1.42) (16N), reagent grade.

12.2.2 Hydrochloric acid solutions (1N, 6N, 12N).

12.2.3 Hydrogen sulfide generator. H_2S gas may be generated from solid commercially available synthetic materials which simply require heating, or from dilute acid and FeS. If the latter method is employed, the gas should be passed through a trap in the line to prevent acid from being swept into the sample solution.

12.2.4 Ammonium hydroxide (sp. gr. 0.90)(15N), reagent grade.

12.2.5 Ammonium molybdate solution. Dissolve 5 grams of the salt in 100 milliliters of water, and pour the solution into 35 milliliters of concentrated HNO_3 (sp. gr. 1.42).

12.2.6 Bismuth nitrate solution (0.1M aqueous). Add 31 milliliters of concentrated HNO_3 to 49 grams of $Bi(NO_3)_3 \cdot 5H_2O$, dilute to 1 liter.

12.2.7 Lead acetate solution (0.5M aqueous). Dissolve 190 grams in water and dilute to 1 liter.

12.2.8 Ammonium chloride solutions (3N, 6N), 160 and 320 grams, respectively, of the salt per liter of solution.

12.2.9 Sodium hydroxide solution (6N), 240 grams per liter.

12.2.10 Sodium peroxide (solid), anhydrous, reagent grade.

12.2.11 Ammonium acetate solution (3N), 250 grams per liter.

12.2.12 Aluminon solution. Dissolve 0.1 gram in 100 milliliters of water.

12.2.13 Ethanol (95 percent), reagent or purified grade.

12.2.14 Sodium chlorate solution (saturated aqueous).

12.2.15 Ammonium thiocyanate solution (1M), 76 grams per liter.

12.2.16 Acetic acid solution (6N). Pour 350 milliliters of glacial acetic acid into 650 milliliters of distilled water.

12.2.17 Dimethylglyoxime solution (1 percent in ethanol).

12.2.18 Ammonium carbonate solution (3M), 340 grams per liter.

12.2.19 Potassium chromate solution (0.5M), 97 grams per liter.

12.2.20 Triethanol amine solution (20 percent aqueous).

12.2.21 Ammonium sulfate solution (1M), 120 grams per liter.

12.2.22 Ammonium oxalate solution (0.1M), 14 grams per liter.

12.2.23 Barium hydroxide solution (saturated aqueous).

12.2.24 Acetone, reagent grade.

12.2.25 Sodium cobaltinitrite solution. Dissolve 230 grams of $NaNO_2$ in 500 milliliters of water, add 165 milliliters 6N acetic acid and 30 grams of cobalt nitrate, $Co(NO_3)_3$. Allow to stand 12 hours, filter, and dilute to 1 liter.

12.2.26 Zinc uranyl acetate solution. Dissolve 10 grams of uranyl acetate in 65 milliliters of water containing 6 grams of 30 percent acetic acid. Prepare a second solution of 30 grams of zinc acetate in 65 milliliters of water containing 3 grams of 30 percent acetic acid. Heat to dissolve the solids. Mix the solutions, cool to 20°C. Filter after standing overnight.

12.3 PROCEDURE.

12.3.1 Separation of Group II Metals. Place 5 milliliters of the acidified filtrate from basic fusion of the ash of the oil or grease (5.4) in an evaporating dish and add 1 milliliter of concentrated HNO_3. Evaporate just to dryness, taking care not to overheat the residue. Take up the residue in 3 milliliters of 3N HCl. Transfer to a small test tube and heat to boiling to decompose HNO_3. Add 1/2 milliliter of water and neutralize the solution with concentrated NH_4OH, using indicator test paper. Bring back to pH 7 with 6N HCl, and add two drops in excess. Pass H_2S into the cold solution for 5 minutes, then place the tube in boiling water and continue passage of the gas for 5 more minutes. Centrifuge the solution, separate the filtrate with a medicine dropper pipette, and test the filtrate for completeness of precipitation by passing in further H_2S gas for several more minutes. If more precipitate appears, re-centrifuge, adding the precipitate to the first precipitate. Wash the precipitate with two successive 1/2 milliliter portions of hot water, shaking, centrifuging, and discarding the wash water. The precipitate should be black CuS and may be tested for copper according to Paragraph 12.3.2 below. Reserve the filtrate for analysis of Groups III, IV, and V.

12.3.2 Detection of Copper. To the black precipitate obtained in Paragraph 12.3.1 add 1/2 milliliter of concentrated HNO_3 and 1/2 milliliter of water. Stir for a moment, then heat gently. Remove any particles of free sulfur which appear. Cool the solution, centrifuge to remove any residue, transfer the filtrate to a small test tube, and neutralize with NH_4OH, using indicator test paper. Add 1/2 milliliter of NH_4OH in excess, and observe the color of the filtrate; if it is deep blue in color, the presence of copper is confirmed. If further confirmatory tests for copper are desired, employ those tests given in Paragraph 11.3.2 of this method.

12.3.3 Detection and Removal of Phosphate. The presence of phosphate in the solution should already have been established by Paragraph 7.3 of this method. If this test has not been performed, the following test may be utilized: to 1/2 milliliter of the filtrate reserved after the precipitation of Group II compounds, add 1/2 milliliter of concentrated HNO_3, and boil to remove residual H_2S.

Add 1/2 milliliter of ammonium molybdate solution and warm to 60°C. A bright yellow precipitate, which should appear within 5 minutes, indicates the presence of phosphates in the sample. If phosphate is present, evaporate the solution nearly to dryness. Add 1/2 milliliter of concentrated HNO_3 and evaporate nearly to dryness. Again add 1/4 milliliter of HNO_3 and repeat the evaporation. Add a few drops of water, transfer to a 10 milliliter test tube and dilute to about 2 or 3 milliliters. Neutralize the solution with concentrated NH_4OH, using indicator test paper to indicate neutrality; then acidify carefully with concentrated HNO_3. Add 4 drops in excess and dilute to 3 milliliters with water. Place the tube in a boiling water bath and add 0.1M $Bi(NO_3)_3$ solution, a few drops at a time, until precipitation of $BiPO_4$ is complete, then add several drops in excess. Digest for about 5 minutes, and centrifuge. Test for completeness of precipitation by adding a further drop of $Bi(NO_3)_3$. Continue addition of this reagent until precipitation is complete. When no further precipitate appears, withdraw the supernatant liquid and discard the precipitate. Saturate the filtrate with H_2S gas to precipitate Bi_2S_3. Centrifuge, remove the filtrate with a medicine dropper pipette, and add 2 or 3 drops of concentrated NH_4OH, but do not neutralize completely. Repeat the addition of H_2S; if further precipitate forms, remove by centrifugation and discard the precipitate. Evaporate the solution down to about 2 milliliters for analysis of Groups III, IV, and V.

12.3.4 Separation of Group III Metals. Boil the filtrate from the separation of Group II metals (12.3.1) (or the filtrate after separating out phosphates (12.3.3)) until a strip of filter paper moistened with $Pb(C_2H_3O_2)_2$ solution and held in the vapors is not darkened, indicating the absence of H_2S in the solution. Add NH_4OH dropwise with stirring until a faint but permanent precipitate is formed, or until the solution is neutral, using indicator test paper. The volume of the solution should be about 3 to 5 milliliters. Add an equal volume of 6N NH_4Cl solution. Heat nearly to boiling, and add NH_4OH dropwise until the solution is barely alkaline, using indicator test paper. Pass in H_2S for several minutes, until precipitation is complete. Check completeness by centrifuging, separating the filtrate, and adding further H_2S to the filtrate until no further precipitate appears. Reserve the filtrate for the analysis of Groups IV and V. Wash the precipitate with 1/2 milliliter portions of NH_4OH, centrifuging and discarding the washings. The precipitate should consist of nickel and iron sulfides, and aluminum hydroxide.

12.3.5 Separation of Iron and Aluminum Sub-Groups. Digest the precipitate of Group III metals (12.3.4) in a few milliliters of 1N HCl, with stirring and with addition of a few drops of 6N HNO_3 and heating to dissolve the precipitate completely. Transfer the solution to an evaporating dish, add an excess of 6M NaOH, using indicator test paper, and about 0.1 gram of Na_2O_2 in small increments. After evolution of gas has subsided, heat to boiling for several minutes. Replace any liquid which boils away. Filter the solution through a hardened filter paper, washing the precipitate with small portions of hot water, discarding the washings. Reserve the filtrate for detection of aluminum (12.3.6). The precipitate contains iron and nickel.

12.3.6 Detection of Aluminum. Acidify the filtrate after separating the iron and aluminum sub-groups (12.3.5) with 6N HCl, using indicator test paper. Neutralize the solution with NH_4OH (indicator test paper), then acidify carefully with 6N HCl, and add one drop in excess. Add 5 drops of 3N $NH_4C_2H_3O_2$ and 3 drops aluminon reagent. Heat to boiling, then cool. Add 2 milliliters of ethanol and shake vigorously. Add 3 drops 6N HCl and shake again. If a pink color remains, aluminum is present; if the solution is completely decolorized, aluminum is absent. Two other tests for aluminum are given in this manual, one employing morin (Method 15, Paragraph 13.2.2.1) and the other employing alizarin sulfonic acid (Alizarin S) (Method 15, Paragraph 13.2.2.2).

12.3.7 Detection of Iron. Dissolve the precipitate after separating the iron and aluminum sub-groups (12.3.5) with 2 milliliters of hot HNO_3 to which 1 drop of $NaClO_3$ has been added. If any precipitate remains, centrifuge, separate, and discard the precipitate. Pour the filtrate into 1 milliliter of concentrated NH_4OH and stir. Test the alkalinity with indicator test paper; if the solution is not strongly alkaline, add another milliliter of concentrated NH_4OH. A red-brown precipitate should develop at this point if iron is present. Centrifuge and separate the filtrate with a medicine dropper pipette. Reserve this filtrate for the detection of nickel (12.3.8). Dissolve the precipitate in 6N HCl, but without an excess of acid. To several drops of the solution in a small test tube, add a few drops NH_4CNS solution. A deep red color indicates the presence of iron.

12.3.8 Detection of Nickel. Neutralize the filtrate obtained after separating out ferric hydroxide (12.3.7) with 6M $HC_2H_3O_2$, using indicator test paper. Place a few drops of the solution on a spot plate and add several drops of dimethylglyoxime solution. A bright red precipitate indicates nickel. A more sensitive test for nickel is given in Paragraph 11.3.3 of this method.

12.3.9 Separation of Group IV Metals. Acidify the filtrate after the separation of Group III metals (12.3.4) with 6N HCl, and boil to remove traces of H_2S. Transfer the liquid to an evaporating dish, evaporate to dryness, and ignite until all ammonium salts have been volatilized (do not heat to redness). Cool the dish, moisten the residue with 2 drops of 12N HCl, dilute with 1 milliliter of water, and transfer the solution to a large test tube. Add 6 drops 3N NH_4Cl, neutralize with concentrated NH_4OH, using indicator test paper, and add 1 drop in excess. Heat to boiling in a water bath and add 5 drops of 3M $(NH_4)_2CO_3$. Continue heating for 5 minutes, and test for completeness of precipitation by adding another drop of $(NH_4)_2CO_3$. Centrifuge and wash the precipitate twice with distilled water. Reserve the filtrate for analysis of Group V metals (12.3.13).

12.3.10 Detection of Barium. Dissolve the washed carbonates in 2 drops of acetic acid with gentle heating. Add a drop of 3N $NH_4C_2H_3O_2$ solution for each drop of acid used, dilute to a volume of about 20 drops, warm, and add 2 drops of K_2CrO_4. A bright yellow precipitate of $BaCrO_4$ proves the presence of barium. If the test is doubtful, centrifuge the solution to observe whether any yellow precipitate is thrown down. Separate the filtrate with a medicine dropper pipette, and reserve for the detection of strontium (12.3.11) and calcium (12.3.12). A further test for barium is had by moistening the precipitate of $BaCrO_4$ with 6N HCl, and making a flame test with a clean platinum wire. A green flame confirms the presence of barium.

12.3.11 Detection of Strontium. Neutralize the yellow filtrate after separating any barium precipitate (12.3.10) with 6N NaOH, heat, and precipitate carbonates with a few drops of Na_2CO_3 solution. Centrifuge, and wash the residue until practically white. Dissolve the carbonates in a few drops of $HC_2H_3O_2$ solution, warming gently to remove carbon dioxide. Neutralize the solution with NH_4OH, using indicator test paper, and add 1 drop in excess. Dilute to a volume

of about 15 drops. Add 8 drops of triethanol amine solution, then 3 to 4 drops of 1M $(NH_4)_2SO_4$ solution. Warm the solution to about 60-70° C. for 5 minutes. A fine white precipitate, $SrSO_4$, indicates strontium. If this precipitate is large, add an additional drop of 1M $(NH_4)_2SO_4$ to insure complete removal of strontium. Centrifuge, separate, and reserve the filtrate for the detection of calcium (12.3.12).

12.3.12 Detection of Calcium. To the filtrate obtained after separating out strontium (12.3.11), add 2 drops of 0.1M $(NH_4)_2(COO)_2$ solution. A white cloudy precipitate indicates calcium.

12.3.13 Preparation For Group V Analysis. Place the filtrate after the removal of Group IV metals (12.3.9) in an evaporating dish, evaporate to dryness, and heat until ammonium salts are completely fumed off. Cool, moisten the residue with 1 drop of concentrated HCl, let stand a few moments, then dissolve the residue in 1/2 milliliter of distilled water. Neutralize the solution with $Ba(OH)_2$ solution, using indicator test paper, and centrifuge any precipitate which appears. Remove the clear filtrate with a medicine dropper pipette, and heat nearly to boiling. Add 2 drops of $(NH_4)_2CO_3$ solution; centrifuge and discard the precipitate. Evaporate the clear filtrate to dryness and ignite to remove all traces of ammonium compounds.

12.3.14 Detection of Lithium. Treat the dry residue (12.3.13) with 1/2 milliliter of acetone with stirring. Transfer the acetone solution to a clean evaporating dish with a medicine dropper pipette, and extract the residue with 2 more 1/2 milliliter portions of acetone, adding these to the first extract. Reserve the residue after extraction with acetone for the detection of sodium and potassium (12.3.15 and 12.3.16). Evaporate the acetone on a warm water bath, and take up the residue in a few drops of water. Clean a platinum wire by repeated immersion in dilute HCl solution, until no yellow flame is imparted to the Bunsen burner flame by the wire. Dip the wire in the solution and place the moist wire in the flame. A deep crimson color indicates the presence of lithium.

12.3.15 Detection of Potassium. Take up the residue remaining after acetone extraction of lithium salts (12.3.14) with 1/4 milliliter of water. Divide the solution into two parts. To one part add 3 drops

of $Na_3Co(NO_2)_6$ solution, wait a few minutes, and centrifuge. A bright yellow precipitate proves the presence of potassium.

12.3.16 Detection of Sodium. The second portion obtained from the residue after acetone extraction of lithium salts (12.3.14 and 12.3.15) is treated with 3 drops of zinc-uranyl acetate solution. After a few moments, centrifuge. A crystalline precipitate indicates sodium. However, this test should not be taken as definitive until a blank is run, since a certain amount of sodium is present in almost all reagents; a precipitate of small extent should be expected during this test from sodium introduced as impurity in the reagents. The blank run is made by preparing a 0.1 percent NaCl solution. Using 1 drop of this solution, add the same amount of reagent as above. If the quantity of precipitate obtained from the unknown does not exceed substantially that from the check test, the metal should be assumed to be due to impurities.

13.0 BIBLIOGRAPHY. The following reference texts are representative of the many works available on the subject of qualitative inorganic analysis:

Feigl, F., Spot Tests, I. Inorganic Applications, New York: Elsevier Publishing Company, 1954, 518 pp.

Hildebrand, J. H., Principles of Chemistry, Fourth Edition, New York: The Macmillan Company, 1940, 493-500.

Hogness, T. R., and Johnson, W. C., Qualitative Analysis and Chemical Equilibrium, Revised Edition, New York: Henry Holt and Company, 1940, 538 pp.

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Kelsey, E. B., and Dietrich, H. G., Fundamentals of Semimicro Qualitative Analysis, New York: The Macmillan Company, 1940, 350 pp.

Scott, W. W. (Furman, N. H., editor), Standard Methods of Chemical Analysis, Fifth Edition, Volume One--The Elements, New York: D. Van Nostrand Company, Inc., 1939, pp. 1105-12.

Wiig, E. O., Line, W. R., and Flagg, J. F., Semimicro Qualitative Analysis, New York: D. Van Nostrand Company, Inc., 1954, 238 pp.

The methods of analysis given in this method have been extracted in part from these reference works.

QUANTITATIVE ELEMENTAL ANALYSIS FOR METALS IN OILS AND GREASES

1.0 SCOPE

1.1 These methods of chemical analysis are intended for the quantitative determination of aluminum, iron, calcium, barium, sodium, potassium, lithium, and silicon (with a qualitative confirmatory test for copper) in oils and greases which do not contain silicone oils or silicate esters (see Note 2). Other metallic elements, sulfur, selenium, phosphorus, and chlorine in amounts commonly found in lubricating oils do not interfere in this method. (Note 1).

Note 1. These methods do not include the quantitative determination of lead, nickel, copper, zinc, and cadmium. For the quantitative determination of phosphorus and selenium see Methods 14 and 28, respectively.

2.0 OUTLINE OF METHOD.

2.1 The analytical procedures follow established schemes for separating the metals into groups for more convenient determination, as shown in Figure 0. This procedure is adapted from Federal Test Method Standard No. 791 (15 December 1955), Method 5601.1 (ASTM No. D811-48). This scheme provides a rapid and accurate method for the determination of one or all of the metals, as the analyst may deem necessary from initial qualitative examination of the oil or grease (for preliminary qualitative inspection and tentative classification of greases, see Method 15).

2.2 To avoid its interference throughout the procedure, barium is separated with the metals of the hydrogen sulfide group. The 8-hydroxyquinoline serves to remove iron and aluminum from phosphate interference. Phosphate and sulfate ions are removed after the calcium determination to provide more accurate determinations of lithium, sodium, and potassium.

3.0 PREPARATION OF SAMPLE.

3.1 LUBRICANTS.

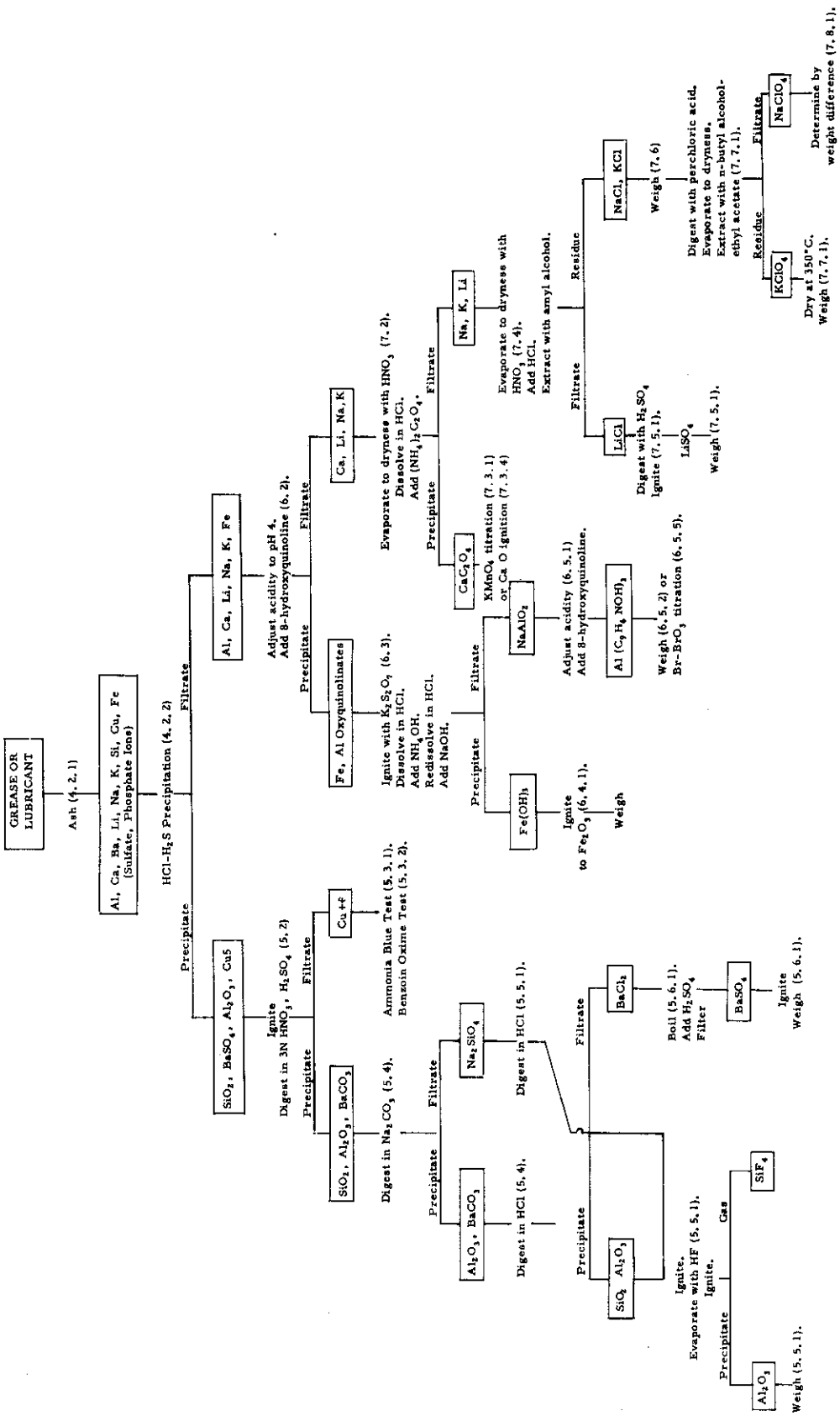

Figure 0. Outline of Method For Quantitative Elemental Analysis.

3.1.1 Heat the sample of oil to 60°±10°C., and agitate in the original container until all sediment is homogeneously suspended in the oil. If the original container is of opaque material, or if it is more than three quarters full, transfer the entire sample to a clear glass bottle having a capacity at least one-third greater than the volume of the sample. Transfer all traces of sediment from the original container to the bottle by agitation of portions of the sample in the original container. After complete suspension of all sediment, strain the sample or a convenient aliquot through a 100-mesh screen for the removal of large contaminating particles. Heat and thoroughly mix the strained oil or aliquot before taking each portion of the sample for test. Homogeneity will be indicated by the precision of the analyses.

3.2 GREASES. The original sample of grease shall be made as uniform as possible. If the grease is soft, stir and mix with a glass or wood paddle in a glass beaker until uniform. If the grease is hard, scrape off the surface layers with a clean spatula, discard, and take the sample from the freshly exposed surfaces.

4.0 PRELIMINARY SEPARATIONS.

4.1 REAGENTS.

4.1.1 Sulfuric acid (18N).

4.1.2 Hydrochloric acid solutions (0.3N, 6N, 12N).

4.1.3 Ammonium hydroxide solution (7N).

4.1.4 Ethyl alcohol (95 percent).

4.1.5 Alcoholic methyl red indicator solution (0.1 percent). Dissolve 0.5 gram of methyl red in 300 milliliters of ethyl alcohol and dilute with water to 500 milliliters.

4.1.6 Ammonium sulfate, reagent grade.

4.1.7 Hydrogen sulfide (gas). This gas may be generated either by reaction of FeS with dilute mineral acid, or by heating commercial preparations designed to produce H_2S.

4.1.8 Hydrogen sulfide wash solution. Saturate 0.3N HCl with H_2S.

4.2 PROCEDURE.

4.2.1 Removal of Organic Material.

4.2.1.1 Lubricants. Transfer to a clean 90-millimeter diameter porcelain dish 10 grams of the homogeneous sample, weighed to the nearest 0.01 gram. Heat with a Bunsen burner until the contents ignite and burn readily. Move the dish and flaming contents to a hot plate and maintain them at such a temperature that only ash and carbon remain after burning ceases. If any liquid or tarry material remain, heat over a burner until smoking ceases. Ignite over a burner, or in a muffle furnace at 550° to 600°C. Cool, add to the residue 1 to 2 drops of 18N H_2SO_4, evaporate the acid and ignite at 650° to 700°C., until the oxidation of carbon is complete.

4.2.1.2 Greases. Transfer to a clean, weighed, 50-millimeter diameter porcelain crucible 5 grams of the sample weighed to the nearest 0.01 gram. Heat the crucible with a Bunsen burner to burn combustible matter off slowly, and finally ignite the residue until the ash is free of carbonaceous matter either over the burner or in a muffle furnace at not over 600°C. The crucible and contents shall then be cooled in a desiccator and weighed.

Note 2. If the oil or grease contains an appreciable quantity of silicone oil or silicate ester, it is difficult to obtain a carbon-free ash, due to entrapment of carbon in the silica formed during ashing. Evidence of the presence of these oils is the formation of a gray, spongy mass of large volume which will not "cook down" or turn white, even with prolonged heating. In the event that these oils are present, they must be separated from remaining components by solvent extraction (Methods 41 through 45) or adsorption chromatography (Method 16). The other components may then be analyzed for metal constituents by the procedures given below.

4.2.2 Separation of Barium, Copper, and Silica From Iron, Aluminum, Calcium, Lithium, Sodium, and Potassium. Treat the residue after ashing (4.2.1.1 or 4.2.1.2) with 20 milliliters of 6N HCl, and evaporate almost to dryness. Add 25 to 30 milliliters of water

to the residue, transfer quantitatively to a 400-milliliter beaker and dilute to 100 milliliters with water. Add 7N NH_4OH drop by drop until the solution is just neutral to methyl red, and then add 6 to 8 milliliters of 12N HCl and 1 gram of $(NH_4)_2SO_4$. Heat to boiling and pass in a vigorous stream of H_2S until the solution has cooled to room temperature, add 200 milliliters of water, and again saturate with H_2S. Filter through an ashless close-texture paper into a 600-milliliter beaker, and wash with H_2S wash solution. Reserve the precipitate for the determinations of silica and barium as described in Paragraph 5, and reserve the filtrate for the determinations of aluminum, calcium, lithium, sodium, and potassium as described in Paragraphs 6 and 7.

Note 3. While the major portion of the aluminum will be in the filtrate, smaller amounts may appear in the precipitate, owing to partial conversion to an acid-insoluble form of aluminum oxide.

5.0 SEPARATION OF COPPER, SILICA, ALUMINUM, AND BARIUM.

5.1 REAGENTS.

5.1.1 Nitric acid solutions (3N, 16N).

5.1.2 Sulfuric acid solutions (4N, 18N).

5.1.3 Sodium carbonate solution (2N).

5.1.4 Hydrochloric acid solutions (0.2N, 2N, 6N).

5.1.5 Alcoholic α-benzoin oxime (5 percent in ethyl alcohol).

5.1.6 Hydrofluoric acid (48 percent).

5.1.7 Ammonium hydroxide solutions (7N, 15N).

5.1.8 Alcoholic methyl red indicator solution (0.1 percent). See Paragraph 4.1.5.

5.1.9 Hydrogen sulfide (gas). See Paragraph 4.1.7.

5.1.10 Hydrogen sulfide wash water. Saturate distilled water with H_2S.

5.2 SEPARATION OF COPPER FROM BARIUM, ALUMINA, AND SILICA. Transfer the paper and precipitate (4.2.2) to a platinum crucible, burn off the paper at 400° to 500°C., cool, add 1 to 2 drops of 18N H_2SO_4, evaporate the acid, then gradually raise the temperature to 870°±25°C., and ignite for 25 to 30 minutes. Transfer the residue to a 100-milliliter beaker and add 25 to 30 milliliters of 3N HNO_3. Dissolve any residue which remains in the crucible with 3N HNO_3, and combine this with the acid solution of the residue. Digest on a hot plate for 5 to 10 minutes, and add 0.5 milliliter of 18N H_2SO_4. Cover the beaker and continue the digestion for 35 minutes just below the boiling point. Cool to room temperature, filter through a small ashless medium-texture paper into a 250-milliliter beaker, and wash thoroughly with cold water. Preserve the filtrate for the detection of copper (5.3) and the precipitate for the determination of silica and barium (5.5.1) and (5.6.1).

5.3 DETECTION OF COPPER.

5.3.1 Ammonia Blue Reaction. Transfer approximately 10 milliliters of the filtrate (5.2) to a large test tube and add carefully dropwise 7N NH_4OH until an excess of the reagent is present, as indicated by litmus or other indicator paper.[1] The appearance of a blue precipitate which dissolves in the excess NH_4OH to form a deep violet-blue solution is a positive test for copper.

5.3.2 Benzoin Oxime Test For Copper. If the ammonia blue reaction is questionable and a further confirmatory test is desired, transfer 1 milliliter of the filtrate (5.2) to a small test tube and add 7N NH_4OH until the pH of the solution is about 3 to 5, using indicator test paper. Place a drop of α-benzoin oxime solution on a piece of clean filter paper. Add a drop of the weakly acid test solution, and hold the paper over a watch glass containing a few drops of concentrated NH_4OH. The appearance of a green coloration indicates copper (Note 4).

Note 4. This test may be carried out on quantitative filter paper such as S & S No. 589, which has been impregnated with a saturated solution of α-benzoin oxime and dried. If this test is carried out in the presence of other metallic salts which form precipitates with ammonia, the influence of these ions may be eliminated by the addition of a drop of 10% solution of Rochelle salt to the paper before adding the test solution.

[1] Alkacid or Hydrion papers or equivalent are satisfactory for this purpose.

5.4 SEPARATION OF BARIUM FROM ALUMINA AND SILICA. Transfer the filter paper and residue (5.2) to a platinum crucible, burn off the paper at 450° to 500°C., and burn off the carbon at 500° to 600°C. Cool, and brush the residue into a 250-milliliter platinum beaker. Add 25 to 30 milliliters of 2N Na_2CO_3, cover the beaker, and boil for 60 to 75 minutes, adding water to maintain volume as the solution evaporates. Filter through a small ashless close-texture paper, and wash thoroughly with water. Reserve the filtrate for the determination of silica (5.5.1). Transfer the paper and residue from the carbonate digestion to a 100-milliliter beaker, add 25 milliliters of 2N HCl, cover the beaker, and simmer for 20 to 25 minutes, adding water when necessary to maintain a volume of 25 to 30 milliliters. Filter through a small ashless close-texture paper into a 250-milliliter beaker, and wash thoroughly with water. Reserve the filtrate for the determination of barium (5.6.1), and reserve the residue and combine with any precipitate obtained in Paragraph 5.5.1.

5.5 DETERMINATION OF SILICA AND ALUMINA.

5.5.1 PROCEDURE. Acidify the filtrate obtained in the carbonate digestion (5.4) with 6N HCl and evaporate to dryness. Heat gently for 20 minutes, and cool. Add 25 milliliters of water and simmer for 20 minutes. If a precipitate appears, filter through an ashless medium-texture paper, wash thoroughly with 0.2N HCl, and add the paper and precipitate to the silica residue obtained in Paragraph 5.4. Transfer the papers and residues (5.4) to a weighed, previously ignited platinum crucible. Burn the paper at 450° to 500°C., allowing sufficient air to reach the sample so that carbon is completely burned off at this temperature. Add 1 to 2 drops of 18N H_2SO_4, evaporate the acid and ignite the residue at 950° to 1,000°C. for 30 to 40 minutes, cool to room temperature in a desiccator, and weigh. Moisten the residue in the crucible, add 5 to 7 milliliters of HF (48 percent) and 2 to 3 drops of 18N H_2SO_4. Taking care to avoid spattering, evaporate to dryness, and ignite the crucible for 1 to 2 minutes at 800° to 900°C. Cool to room temperature in a desiccator and weigh the crucible and remaining alumina. The loss in weight during the HF ignition represents the total silica content. Record the weight of residual alumina and add this to the weight of aluminum determined as described in Paragraphs 6.5.2 or 6.5.5.

5.5.2 Blank. In order to compensate for the amount of silica in the reagents or apparatus, make a blank determination following the same procedure and using the same amounts of all reagents. Subtract the amount of silica found from that obtained from the sample.

5.5.3 Calculation. Calculate the percentage of silica as follows:

$$\text{Silica (percent)} = \frac{(A-B) \times 100}{W}$$

where: A = loss in weight in HF ignition (5.5.1).
B = correction for blank in grams.
W = weight of sample in grams.

5.6 DETERMINATION OF BARIUM.

5.6.1 Procedure. To the filtrate from the acidified carbonates (5.4), add 7N NH_4OH until just basic to methyl red, then add 6N HCl until the solution is just acid to methyl red. Saturate the solution with H_2S while maintaining the solution at boiling. Filter, wash with H_2S wash water, and discard any precipitate. Boil the filtrate for several minutes, and while boiling, add 10 to 15 milliliters of 4N H_2SO_4. Digest near the boiling point for 1 to 2 hours. If the precipitate is very small or slow to form, allow the solution to stand overnight. Filter through a previously dried and weighed Gooch crucible, or a porcelain filter crucible (fine porosity). Wash the precipitate with hot water, dry, and ignite at 500° to 600°C. Cool in a desiccator and weigh the crucible and $BaSO_4$ precipitate.

5.6.2 CALCULATION. Calculate the percentage of barium as follows:

$$\text{Barium (percent)} = \frac{C \times 0.5884 \times 100}{W}$$

where: C = grams of $BaSO_4$ precipitate.
W = weight of sample in grams.

6.0 SEPARATION AND DETERMINATION OF IRON AND ALUMINUM.

6.1 REAGENTS.

6.1.1 Hydrogen peroxide (30 percent).

6.1.2 8-Hydroxyquinoline solution. Dissolve 25 grams of 8-hydroxyquinoline in 58 milliliters of glacial acetic acid and dilute to 500 milliliters with water. The resulting solution contains 5 percent of 8-hydroxyquinoline in 2N acetic acid.

6.1.3 Ammonium acetate solution (2N).

6.1.4 Potassium pyrosulfate (reagent grade).

6.1.5 Ammonium chloride (reagent grade).

6.1.6 Ammonium hydroxide solutions (7N, 14N).

6.1.7 Ammonium chloride solution (0.4N).

6.1.8 Hydrochloric acid solutions (1N, 6N, 12N).

6.1.9 Sodium hydroxide solution (6N).

6.1.10 Alcoholic methyl red indicator solution (0.1 percent). See Paragraph 4.1.5.

6.1.11 Standard sodium thiosulfate solution (0.1N).

6.1.12 Standard potassium bromide--potassium bromate solution (0.2N). Dissolve 20.0 grams of pure KBr and 5.6 grams of pure $KBrO_3$ in water, and dilute to 1 liter. Standardize against 0.1N $Na_2S_2O_3$.

6.1.13 Potassium iodide solution (0.6N).

6.1.14 Starch solution, iodine indicator (0.25 percent). Dissolve 2.5 grams of soluble starch in cold water. Dilute to 1 liter, and boil for a few minutes. Store in a glass-stoppered container.

6.2 SEPARATION OF ALUMINUM AND IRON FROM CALCIUM, LITHIUM, SODIUM, AND POTASSIUM.

Boil for 4 to 5 minutes the filtrate from the sulfide precipitation obtained in Paragraph 4.2.2, add 1 to 2 milliliters of H_2O_2 (30 percent), and boil for an additional 4 to 5 minutes to remove excess peroxide. Cool the

solution to 50° to 60°C., and add 20 milliliters of 8-hydroxyquinoline solution. Add 2N $NH_4C_2H_3O_2$, while stirring constantly, until a precipitate is formed which does not redissolve on further stirring, then add an excess of 25 milliliters of 2N $NH_4C_2H_3O_2$. If no precipitate forms, add 2N $NH_4C_2H_3O_2$ until the pH of the solution is approximately 4, as measured by indicator paper, and then add an excess of 25 milliliters of 2N $NH_4C_2H_3O_2$. Heat the solution at 60° to 80°C. until the precipitate coagulates, and allow to cool. Filter through a medium-texture paper into a 600-milliliter chemically resistant glass beaker and wash well with water. Reserve the filtrate for the determinations of calcium, lithium, sodium, and potassium as described in Paragraphs 7.0 through 7.8.

6.3 SEPARATION OF ALUMINUM FROM IRON. Transfer the hydroxyquinolate precipitate and paper to a platinum crucible. Burn off the organic matter at 400° to 500°C., then ignite at 500°C. for 10 minutes or until all carbon is oxidized. Add 5 to 7 grams of $K_2S_2O_7$ to the crucible and mix well with a platinum wire. Fuse the mixture at a relatively low heat until no solid material remains. Cool to room temperature and dissolve the melt in 200 to 250 milliliters of water. Add 5 grams of NH_4Cl, then add 7N NH_4OH drop by drop until the solution is faintly ammoniacal. Digest the solution for 10 to 15 minutes or until the iron and aluminum hydroxide precipitate has coagulated. Filter through a medium-texture paper into a 600-milliliter beaker, and wash the paper and precipitate with 0.4N NH_4Cl. Discard the filtrate. Transfer the paper and hydroxide precipitate to the original precipitation beaker, and add 20 milliliters of water and 10 milliliters of 6N HCl. Heat the mixture almost to boiling and macerate the paper with a stirring rod. Dilute to 150 to 200 milliliters and neutralize to methyl red with 6N NaOH. Add 6 milliliters of NaOH in excess and digest until the precipitate coagulates. If a precipitate does not form immediately, allow the solution to stand overnight. Filter through a medium-texture ashless filter paper and wash with three 20 milliliter portions of water. The filter contains iron hydroxide and the filtrate is analyzed for aluminum according to Paragraph 6.5.

6.4 DETERMINATION OF IRON.

6.4.1 Procedure. Place the still moist filter paper containing iron hydroxide in a small weighed porcelain crucible and ignite with a very

low flame, gradually increasing the heat. Do not blast, or the black magnetic oxide of iron, Fe_3O_4, will form with high heating. After the crucible reaches dull red heat, maintain this rate of heating for 20 minutes. Remove the flame, cool the crucible in a desiccator, and weigh the crucible and Fe_2O_3 residue.

6.4.2 Calculation. Calculate the percentage of iron in the sample as follows:

$$\text{Iron (percent)} = \frac{D \times 0.6994}{W}$$

where: D = weight of Fe_2O_3 precipitate.
W = weight of sample in grams.

6.5 DETERMINATION OF ALUMINUM.

6.5.1 Preliminary Procedure. Adjust the volume of the filtrate from the NaOH precipitation (6.3) to a volume of 200 to 250 milliliters and add 6N HCl until the solution is just neutral to methyl red, then add 12 to 13 milliliters in excess. Warm until any precipitate has dissolved. Add 1 milliliter of 8-hydroxyquinoline solution for every 3 milligrams of aluminum present, then add 3 milliliters in excess (if the quantity of aluminum is not known, add 5 milliliters of 8-hydroxyquinoline solution). Warm the solution to 70° to 80°C., and add 14N NH_4OH slowly and while stirring constantly, until a pH of 7 or 8 is obtained, as indicated by indicator paper. Allow the precipitate to digest at 70° to 80°C. for 1 hour or until the supernatant liquid is clear (the digestion may require as long as 5 to 6 hours, if the aluminum content is low). If the supernatant liquid is colorless or only very faintly yellow after coagulation of the precipitate, add 12N HCl slowly and while stirring until the precipitate just dissolves. Add an additional 5 milliliters of 8-hydroxyquinoline solution, and neutralize with 14N NH_4OH as before. If the supernatant liquid still does not show an excess of hydroxyquinoline, repeat the dissolving of the precipitate, addition of 5 milliliters of 8-hydroxyquinoline solution, and neutralization until a yellow supernatant liquid is obtained (Note 5). Reserve the hydroxyquinoline precipitate for the determination of aluminum as described in Paragraphs 6.5.2 or 6.5.5.

Note 5. The appearance of long needle-like crystals indicates too large an excess of 8-hydroxyquinoline solution, and will lead to high results.

6.5.2 Gravimetric Method. Decant the supernatant liquid through a previously dried and weighed Gooch crucible or fine porosity porcelain filter crucible, then wash the precipitate into the crucible. Wash the beaker, crucible, and precipitate three times with cold water. Dry at 120° to 130°C., and weigh the aluminum oxyquinolate.

6.5.3 Blank. In order to compensate for the amount of aluminum in the reagents and apparatus, make a blank determination following the same procedure and using the same amount of all reagents. Subtract the amount of aluminum found from that obtained from the sample.

6.5.4 Calculation. Calculate the percentage of aluminum as follows:

$$\text{Aluminum (percent)} = \frac{((E-C) \times 0.0587) + 0.5291\ M}{W} \times 100$$

where: E = weight of aluminum oxyquinolate in grams.
C = correction for blank in grams.
M = alumina, if any, found in silica determination (5.5.1).
W = weight of sample in grams.

6.5.5 Volumetric Method. Decant the supernatant liquid (6.5.1) through a Gooch crucible (Note 6), then wash the precipitate into the crucible. Wash the beaker, crucible, and precipitate three times with cold water. Transfer the asbestos filter pad and as much of the adhering precipitate as possible back into the original beaker used for the precipitation. Measure out 25 milliliters of 12N HCl and, holding the crucible over the beaker, pour just enough of the acid down the walls of the crucible to moisten the entire inner surface. Wash the crucible thoroughly with water. Repeat the alternate washings with acid and water until all adhering precipitate is removed from the crucible. Pour the remainder of the acid into the beaker, allowing it to wet the walls in order to dissolve any adhering precipitate, then wash down the walls of the beaker with water. Allow the beaker to stand, while stirring occasionally, until all the precipitate has been dissolved. Dilute the solution to 250 milliliters with water, and add 8 to 10 drops of alcoholic methyl red indicator. While stirring constantly, add 0.2N $KBr-KBrO_3$ solution from a burette at a rate of 2 to 5 drops per second. Continue to add

0.2N KBr-$KBrO_3$ until a freshly added drop of indicator is decolorized within 2 seconds, then add 0.5 to 1.0 milliliter of 0.2N KBr-$KBrO_3$ solution in excess. Immediately add 20 milliliters of 0.6N KI, and titrate the liberated iodine to the starch end point with 0.1N $Na_2S_2O_3$.

Note 6. A porcelain filter crucible may be used in place of the Gooch crucible, if desired. If such a crucible is used, dissolve all visible precipitate with 12N HCl, then place the crucible in the beaker and allow it to remain there during the titration.

6.5.6 Blank. In order to compensate for the amount of aluminum in the reagents and apparatus, make a blank determination following the same procedure and using the same amounts of all reagents. Subtract the amount of aluminum found from that obtained from the sample.

6.5.7 Calculation. Calculate the percentage of aluminum as follows:

$$\text{Aluminum (percent)} = \frac{((I-H)K \times 0.00225) + 0.5291M}{W} \times 100$$

where: H = milliliters of $Na_2S_2O_3$ solution required to titrate the sample.
I = milliliters of $Na_2S_2O_3$ solution required to titrate the blank.
K = normality of the $Na_2S_2O_3$ solution.
M = alumina, if any, found in silica determination (5.5.1).
W = weight of sample in grams.

7.0 SEPARATION AND DETERMINATON OF CALCIUM, LITHIUM, SODIUM AND POTASSIUM.

7.1 REAGENTS.

7.1.1 Nitric acid (sp. gr. 1.42).

7.1.2 Hydrochloric acid solution (6N).

7.1.3 Ammonium chloride, reagent grade.

7.1.4 Ammonium oxalate, reagent grade.

7.1.5 Ammonium hydroxide, (sp. gr. 0.90).

7.1.6 Alcoholic methyl red indicator solution (0.1 percent). See Paragraph 4.1.5.

7.1.7 Sulfuric acid solutions (4N, 18N).

7.1.8 Standard potassium permanganate solution (0.1N).

7.1.9 Amyl alcohol, reagent grade, boiling point 132°C.

7.1.10 Perchloric acid (60-70 percent) reagent grade, free from non-volatiles.

7.1.11 n-Butyl alcohol, reagent grade, boiling range 116°-118°C.

7.1.12 Ethyl acetate, reagent grade, anhydrous, ethyl alcohol-free.

7.2 SEPARATION OF CALCIUM FROM LITHIUM, SODIUM AND POTASSIUM. Evaporate the filtrate from the hydroxyquinoline precipitation (6.2) until salts begin to settle out, add 15 to 20 milliliters of 16N HNO_3 to aid in the elimination of ammonium salts, and evaporate to dryness. Add 0.5 milliliter of 16N HNO_3 and evaporate to complete dryness. Repeat this procedure until all ammonium salts have been removed, all organic matter has been oxidized, and the remaining salts are white in color (Note 7). Cool the beaker, moisten the residue with water, and add 10 milliliters of 6N HCl. Warm until the residue has dissolved and dilute to 200 to 225 milliliters. Add 2 grams of NH_4Cl and 2 grams of $(COONH_4)_2$, heat the solution almost to boiling, add 15N NH_4OH until the solution is just basic to methyl red, and add 2 milliliters in excess. Digest without boiling for 1 hour or until the precipitate has settled. If the precipitate is small and slow to form, allow the solution to stand overnight. Filter by decantation through an ashless close-texture paper into an 800-milliliter beaker and wash several times with hot water, transferring the precipitate (Note 8) to the filter during the washing. Place the original precipitation beaker under the funnel, and dissolve the precipitate on the paper with hot 6N HCl. Wash the paper thoroughly with hot water, dilute the solution to 200 to 225 milliliters, and add 2 grams of NH_4Cl and 2 grams of $(COONH_4)_2$. Heat

the solution almost to boiling, and stir until the salts are completely dissolved. Add 14N NH_4OH until the solution is just basic to methyl red, then add 2 milliliters in excess. Digest without boiling for 1 hour or until the precipitate has settled out. If the precipitate is small and slow to form, allow to stand overnight. Filter through an ashless close-texture paper, combining the filtrate with the filtrate from the first oxalate precipitation (7.2) and wash well with hot water. Reserve the precipitate for the determination of calcium as described in Paragraphs 7.3.1 and 7.3.4.

Note 7. Do not bake or ignite the residue, as appreciable amounts of calcium may be lost in the insoluble residue.

Note 8. If less than 10 milligrams of calcium are present, omit the second precipitation described in 7.2.

7.3 DETERMINATION OF CALCIUM.

7.3.1 Volumetric Method. In a 250-milliliter beaker, heat 150 milliliters of water and 15 milliliters of 18N H_2SO_4 to 80° to 90°C. Transfer the filter paper containing the calcium oxalate precipitate (7.2) to the hot H_2SO_4 solution with the aid of a stirring rod. Wash the funnel with a portion of the H_2SO_4 solution. Allow the acid to react with the precipitate, then partially remove the paper and allow it to rest on the side of the beaker. Immediately titrate the solution with 0.1N $KMnO_4$ until the end point is nearly reached (do not mistake the initial slow disappearance of the permanganate color for the end point.) Place the paper in the solution and continue the titration until a pink color, permanent for at least 15 seconds, is obtained.

7.3.2 Blank. Make a blank determination following the same procedure and using the same volume of hot acid solution.

7.3.3 Calculation. Calculate the percentage of calcium as follows:

$$\text{Calcium (percent)} = \frac{(L-P)N \times 0.020}{W} \times 100$$

where: L = milliliters of $KMnO_4$ solution required to titrate the sample.
P = milliliters of $KMnO_4$ solution required to titrate the blank.
N = normality of the $KMnO_4$ solution.
W = weight of sample in grams.

7.3.4 Gravimetric Method. Transfer the precipitate and paper (7.2) to a weighed platinum crucible, and heat so as to char but not inflame the paper. When fully charred, increase the flame, and when the carbon has disappeared, set the crucible upright, cover with a close-fitting cover, and heat at 1,100° to 1,200°C. for 5 minutes. Remove the lid for a moment to permit the escape of entrapped CO_2, place the covered crucible in a desiccator containing anhydrous $CaSO_4$[1] or P_2O_5 (not $CaCl_2$), and weigh as soon as cool. Reheat the crucible, cool, and reweigh (Note 9).

Note 9. The second weighing must be made as rapidly as possible. This should be done by placing the required weights on the balance pan before removing the crucible from the desiccator. Calcium oxide will not gain in weight on exposure to air for periods up to 1 minute if kept in a well-covered crucible.

7.3.5 Calculation. Calculate the percentage of calcium as follows:

$$\text{Calcium (percent)} = \frac{R \times 0.7147}{W} \times 100$$

where: R = grams of CaO.
W = weight of sample in grams.

7.4 SEPARATION OF LITHIUM FROM SODIUM AND POTASSIUM. Combine the filtrates obtained in accordance with Paragraph 7.2, add 6N HCl until just acid to methyl red, and evaporate the solution to low volume. Transfer the solution to a 400-milliliter beaker. Evaporate the solution until salts begin to precipitate, add 15 to 20 milliliters of 16N HNO_3 to aid in the elimination of ammonium salts, and evaporate to dryness. Fume off the remaining ammonium salts by heating over a Bunsen

[1] Drierite is satisfactory for this purpose.

burner. Cool the beaker, add 2 to 3 drops of 6N HCl and 10 to 15 milliliters of water and warm for 2 to 3 minutes. Transfer the solution quantitatively to a 50 milliliter Erlenmeyer flask. Add about 5 milliliters of amyl alcohol and heat slowly with stirring on a hot plate until the water has evaporated and the boiling point of the solution reaches that of pure amyl alcohol (132°C.) (Note 10). When water has been completely removed, NaCl, KCl, and some LiOH will separate from the solution. Filter through a medium porosity filter paper, leaving the bulk of the residue in the flask. Wash the residue in the beaker with three successive 5 milliliter portions of hot amyl alcohol, filtering the liquid through the filter after each washing. Add about 1 milliliter of 6N HCl to the flask, and just enough water to dissolve the residue completely (about 3 to 5 milliliters). Repeat the extraction with amyl alcohol. If much LiCl is present, it will be necessary to repeat the extraction procedure several more times. Reserve the filter paper and residue for the determination of sodium and potassium as described in Paragraphs 7.6 through 7.8.

Note 10. To prevent bumping of the solution while evaporating off the water, a slow current of small bubbles of dried air may be passed through the solution, in addition to the stirring. When the water has been removed, as indicated by the rise in temperature of the solution, and by the cessation of bumping, the bubbler capillary may be removed from the solution, the tip being washed several times with fresh amyl alcohol.

7.5 DETERMINATION OF LITHIUM.

7.5.1 Procedure. Evaporate the combined filtrates and washings (7.4) to dryness on a hot plate, cool, and dissolve the residue of LiCl with a few milliliters of 4N H_2SO_4. Filter through a medium porosity filter paper into a weighed platinum crucible, evaporate slowly to dryness, and cautiously heat until sulfuric acid fumes are no longer given off. Ignite the residue at a dull red heat for about five minutes, cool in a desiccator, and weigh as Li_2SO_4.

7.5.2 Calculation. Calculate the percentage of lithium as follows (Note 11):

$$\text{Lithium (percent)} = \frac{S \times 0.1262}{W}$$

where: S = grams of Li_2SO_4.
W = weight of sample in grams.

Note 11. For very accurate work, account must be taken of the fact that small amounts of potassium and sodium sulfates may be found in the Li_2SO_4. To correct for this, deduct 0.00041 gram for every 10 milliliters of filtrate (exclusive of the washings) in case only NaCl was present, or 0.00051 gram if only KCl was present, and 0.00092 if both sodium and potassium chlorides were present. If this correction is applied to the lithium percentage, it should also be applied to the sodium and potassium values obtained (7.7.3 and 7.8.3).

7.6 SEPARATION OF POTASSIUM AND SODIUM. Transfer the residue from the lithium extraction (7.4) to a 100-milliliter weighed beaker and add 10 milliliters of water. Heat the mixture almost to boiling and macerate the paper with a stirring rod. Filter through a small medium-texture paper into a previously dried and weighed 100-milliliter beaker. Wash the beaker and macerated paper with three successive 10 milliliter portions of warm water, filtering the washings into the weighed beaker. Evaporate the solution to dryness on the steam bath. Heat the beaker gently with a burner to complete dryness, cool, and weigh the beaker plus alkali chlorides.

7.7 DETERMINATION OF POTASSIUM.

7.7.1 Procedure. Re-dissolve the mixed alkali chlorides with about 10 milliliters of water in a 150-milliliter beaker, and add twice as much perchloric acid as is required to convert all the bases present into perchlorates (but not less than 1 milliliter), and evaporate on the steam bath to a syrupy consistency with occasional stirring. If there is any acid on the side walls, warm the beaker gently with a flame to remove it. Cool, add 2 or 3 milliliters of water and evaporate again to dryness on a hot plate at less than 350°C. Stir continuously until all the hydrochloric acid is expelled and fumes of perchloric acid are given off. Add 20 milliliters of a mixture of equal parts of anhydrous n-butyl alcohol and ethyl acetate, and digest with stirring near the boiling point for several minutes. Cool to room temperature and decant the supernatant liquid through a weighed porcelain filter crucible. Wash the residue in the beaker with three successive 3 to 5 milliliter

portions of n-butyl alcohol-ethyl acetate, filtering the washings through the crucible. Dissolve the residue in 10 milliliters of hot water containing about 1/2 milliliter of perchloric acid, evaporate until fumes of perchloric acid are given off, and extract as before, using 10 milliliters of solvent. Transfer the precipitate to the crucible, using a jet of the mixed solvent from a wash bottle. Wash the crucible several times with 1 milliliter portions of mixed solvent. Dry the beaker, and brush any particles of precipitate which might still be in the beaker into the crucible. Place the crucible in an oven at 110°C. for ten minutes, and finally heat in a muffle furnace for 15 minutes at 350°C. Cool in a desiccator and weigh as $KClO_4$.

7.7.2 Blank. In order to compensate for the amount of potassium in the reagents and apparatus, make a blank determination following the same procedure and using the same amounts of all reagents. Subtract the amount of potassium or potassium chloride found from that obtained from the sample.

7.7.3 Calculation. Calculate the percentage of potassium as follows:

$$\text{Potassium (percent)} = \frac{(T-U) \times 0.2822}{W}$$

$$\text{Potassium Chloride (percent)} = \frac{(T-U) \times 0.5381}{W}$$

where: T = grams of potassium perchlorate.
U = correction for blank in grams of potassium perchlorate.
W = weight of sample in grams.

7.8 DETERMINATION OF SODIUM.

7.8.1 Procedure. The amount of sodium chloride in the sample is determined by subtracting the weight of potassium chloride found by calculation (7.7.3) from the total weight of alkali chlorides found in the sample which was determined before separating potassium chloride from sodium chloride (7.6).

7.8.2 Blank. In order to compensate for the amount of sodium in the reagents and apparatus, use the same determination as was used for the potassium blank (7.7.2). Subtract the amount of sodium chloride found from that obtained from the sample (7.8.1).

7.8.3 Calculation. Calculate the percentage of sodium as follows:

$$\text{Sodium (percent)} = \frac{(V - X) \times 0.3934}{W}$$

where: V = grams of NaCl.
X = correction for blank in grams.
W = weight of sample in grams.

DETECTION AND DETERMINATION OF PHOSPHORUS IN LUBRICANTS AND GREASES

1.0 SCOPE.

1.1 This method is applicable to the detection and determination of phosphorus in unused lubricating oils, lubricating oil additives, and their concentrates. The quantitative method is not restricted with respect to the type of phosphorus compounds which may be present (for example, tri- or penta-valent phosphorus compounds, phosphines, phosphates, phosphonates, phosphorus sulfides, etc.), since all phosphorus present is quantitatively converted to orthophosphate ion in aqueous solution by oxidation of the sample. This procedure is adapted from Federal Test Method Standard No. 791 (15 December 1955), Method 5661.3 (ASTM No. D1091-54T).

2.0 QUALITATIVE DETECTION OF PHOSPHORUS.

2.1 OUTLINE OF METHOD.

2.1.1 Phosphates react with molybdates to form salts of phosphomolybdic acid, which in turn may be used to oxidize benzidine, the products of the reaction being benzidine blue and molybdenum blue. Silicates also give this reaction, but their effect is eliminated either by removing as insoluble silica or by complexing with tartaric acid.

2.2 REAGENTS.

2.2.1 Ammonium molybdate solution. Dissolve 5 grams of the salt in 100 milliliters of water, and pour into 35 milliliters of HNO_3 (sp. gr. 1.42).

2.2.2 Benzidine solution, (0.5 percent in glacial acetic acid).

2.2.3 Sodium acetate solution, (saturated aqueous).

2.2.4 Ammonium hydroxide, (sp. gr. 0.90), reagent grade.

2.2.5 Tartrate-ammonium molybdate solution. Dissolve 15 grams of reagent grade tartaric acid in the ammonium molybdate solution (2.2.1).

2.3 PROCEDURE.

2.3.1 Removal of Organic Material. Burn off organic material in the manner described in Method 12, Paragraphs 5.0 through 5.4. It is not necessary to employ a sample larger than about one gram of oil or grease for the detection of phosphorus.

2.3.2 Procedure in the Absence of Silicates. Place one drop of the combined acidified filtrates (2.3.1) (from which silica has been removed by digestion with HCl) on a square of quantitative filter paper, followed by a drop of ammonium molybdate solution and a drop of benzidine solution. Pour a few drops of ammonium hydroxide onto a watch glass, and hold the paper in the fumes of ammonia. If phosphates are present, a blue stain will appear. If there is doubt as to whether the spot could have been caused by silicon, repeat the test as given in Paragraph 2.3.3 below.

2.3.3 Procedure in the Presence of Silicates. Place one drop of the combined acidified filtrates (2.3.1) on a square of quantitative filter paper, followed by a drop of tartrate-ammonium molybdate solution. Place the paper in an oven at 110°C., or hold over a heating plate for a moment, to increase the reaction rate. Now place a drop of benzidine reagent on the original spot. Pour a few drops of ammonium hydroxide onto a watch glass, and hold the paper in the fumes of ammonia. If phosphates are present, a blue stain will appear; if the first spot (2.3.2) was caused only by silicates, no spot will appear, and the absence of phosphates is confirmed.

3.0 QUANTITATIVE DETERMINATION OF PHOSPHORUS.

3.1 OUTLINE OF METHOD.

3.1.1 After oxidation of organic material in the sample and quantitative conversion of phosphorus to phosphate ion, the phosphate ion is separated from interfering metals by precipitation as ammonium molybdiphosphate in nitric acid solution. After an ammoniacal solution of the phosphate ion is obtained, the phosphorus is precipitated as magnesium ammonium phosphate, ignited, and weighed as magnesium pyrophosphate.

3.2 APPARATUS.

3.2.1 Digestion Flasks. Kjeldahl flasks, 300-milliliter, ground-glass stoppered.

3.2.2 Digestion Rack. A digestion rack to hold one or more 300-milliliter Kjeldahl flasks at an angle of approximately 45°, in such a fashion that direct heat is applied only to the bottom of the flask and such that the body and neck of the flask are insulated from the source of heat. Approximately three-fourths of the neck of the flask should be cooled by air at atmospheric temperature, preferably by directing an air stream against the neck of the flask. A Bunsen flame or high-capacity electric heater are suitable heat sources.

3.2.3 Muffle furnace. The furnace shall be capable of operating over a variable temperature range of 200 to 1100°C. and of maintaining a temperature of 1050±50°C.

3.2.4 Analytical balance, capable of weighing to 0.1 milligram.

3.3 REAGENTS.

3.3.1 Unless otherwise indicated, it is intended that all reagents shall conform to the specifications on analytical reagents established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. References to water shall be understood to mean distilled water.

3.3.2 Hydrogen peroxide (30 percent), containing no more than 0.00002 percent phosphorus.

3.3.3 Nitric acid (sp. gr. 1.42).

3.3.4 Sulfuric acid (sp. gr. 1.84).

3.3.5 White oil, phosphorus-free, or a pure dibasic acid ester, such as dioctyl sebacate.

3.3.6 Ammonium hydroxide (sp. gr. 0.90).

3.3.7 Ammonium hydroxide (3:5, v/v). Mix 3 volumes of NH_4OH (sp. gr. 0.90) with 5 volumes of water.

3.3.8 Ammonium hydroxide (1:24, v/v). Mix 1 volume of NH_4OH (sp. gr. 0.90) with 24 volumes of water.

3.3.9 Ammonium nitrate, crystals.

3.3.10 Ammonium nitrate solution. Dissolve 50 grams of NH_4NO_3 in water and dilute to 1 liter.

3.3.11 Hydrochloric acid (sp. gr. 1.19).

3.3.12 Magnesia mixture. Dissolve 50 grams of $MgCl_2 \cdot 6H_2O$ and 100 grams of NH_4Cl in 500 milliliters of water, add a slight excess of NH_4OH, and allow to stand overnight. Filter, make the solution just acid with HCl, and dilute to 1 liter.

3.3.13 Molybdate reagent. Dissolve 100 grams of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 400 milliliters of water. Add 80 milliliters of NH_4OH (sp. gr. 0.90) and filter if a precipitate appears. Mix 400 milliliters of HNO_3 (sp. gr. 1.42) with 600 milliliters of water. Prepare the ammonium molybdate reagent from these solutions immediately before use by slowly mixing one volume of the ammonium molybdate solution with two volumes of the diluted HNO_3, while stirring rapidly.

3.3.14 Nitric acid (1:1, v/v). Mix equal volumes of HNO_3 (sp. gr. 1.42) and water.

3.3.15 Methyl red indicator. Rub 100 mg. of the indicator in an agate mortar with 7.5 milliliters of 1/20 N NaOH. When dissolved, add sufficient water to make 100 milliliters.

4.0 PROCEDURE.

4.1 OXIDATION OF ORGANIC MATTER.

4.1.1 Weigh out a portion of the material to be analyzed, in accordance with Table III below, into a 300-milliliter Kjeldahl flask. Any convenient method of transferring the sample may be used as long as care is taken to avoid getting the sample on the neck of the flask (Note 1). Add 10 milliliters of H_2SO_4 and a 6-millimeter glass bead (Note 2), and swirl the flask to mix the contents.

TABLE III. Sample Size for the Determination of Phosphorus

Phosphorus Content Percent	Approximate Weight of Sample (grams)	Precision of Weighing, Plus or Minus (grams)
2 to 5	2	0.004
5 to 10	1	0.003
10 to 15	0.7	0.002
15 to 25	0.4	0.001

Place the flask on the digestion rack under a hood and warm gently with a micro burner until the sample is charred, while cooling the neck of the flask, preferably by use of an air stream (Note 3). Continue heating until dense white fumes appear (Note 4). While boiling, continuously add 1 milliliter of HNO_3 dropwise to oxidize the organic material. If the HNO_3 is not added dropwise, it may force excessive amounts of vapor from the flask and lead to loss of phosphorus-containing fumes. When the HNO_3 has boiled off and dense white fumes reappear, repeat the treatment with an additional 1 milliliter of HNO_3. In order to minimize the loss of H_2SO_4 in the dissolution process, it is advisable not to carry the digestion mixture to dense fumes between the additions of HNO_3. Continue the addition of HNO_3 in 1 milliliter increments until the digestion mixture is no darker than straw color, indicating that almost all the organic matter has been oxidized.

Note 1. In order to obtain satisfactory accuracy with the small amounts of phosphorus involved, it is necessary to take extensive precautions in handling. The usual precautions of cleanliness, careful manipulation, and avoidance of contamination should be scrupulously observed; all glassware should be cleaned before use, with cleaning acid or by some procedure that avoids the use of commercial detergents. These compounds often contain alkali phosphates which are strongly adsorbed by glass surfaces and are not removed by ordinary rinsing. It is desirable to segregate a special stock of glassware for use only in the determination of phosphorus.

Note 2. The volume occupied by the glass bead (0.1 milliliter) may be ignored for ordinary work. Excessive bumping is encountered occasionally in the digestion of some organic phosphorus compounds. This bumping may be minimized by using the glass bead.

Note 3. The amount of air used to cool the neck of the flask will at times have to be reduced or even shut off to allow vapors and fumes to leave the flask and to allow the sample to come to dense white fumes. However, this should not be done until the sample is in a well-decomposed state; the air stream should be turned on again each time before the addition of the HNO_3 or H_2O_2 .

Note 4. Excessive evaporation of H_2SO_4 should be avoided to minimize any loss of phosphorus that may occur. Care should be exercised to avoid heating above the liquid level. Since there is some indication that with samples containing inorganic compounds (that is, barium or lead salts) there may be losses of phosphorus due to sintering or fusion of the phosphate and sulfate to the glass; it is well to examine the dried vessel after use to detect any opaque film of fused material.

4.1.2 Cool the flask slightly and add 10 drops (0.5 milliliter) of H_2O_2 . Heat until dense white fumes appear, and while boiling cautiously add 1 milliliter of HNO_3 dropwise. When the HNO_3 has boiled off and dense white fumes reappear, repeat the treatment with H_2O_2 and HNO_3 until the digestion mixture is colorless, at which time the organic material will be completely oxidized. Four treatments will usually suffice. The total amount of H_2O_2 used should be noted, and the same amount used for each sample and the blank. When oxidation is complete, allow the flask to cool, wash down the mouth and neck with a minimum amount of water (5 milliliters), and mix the contents. Return the flask to the digestion rack and continue heating to the appearance of dense white fumes. Repeat the process of the addition of water and heating to dense fumes several times. This will remove all traces of H_2O_2 .

4.2 PROCEDURE FOR SAMPLES CONTAINING NO METALS OTHER THAN ALKALI METALS

4.2.1 Cool the Kjeldahl flask (4.1.2), transfer the solution to a 400-milliliter beaker, and wash the flask with small portions of water

until the volume of solution is approximately 100 milliliters. Boil the solution for 5 to 10 minutes, cool to near room temperature, and add NH_4OH (sp. gr. 0.90) until the solution is neutral to methyl red. Make the solution acid with HCl (sp. gr. 1.19) and add 1 milliliter in excess. Add 20 milliliters of magnesia mixture, slowly and while stirring, and cool the solution to below room temperature in an ice bath. Add NH_4OH (sp. gr. 0.90) slowly and while stirring constantly until the solution is basic. Continue stirring until most of the precipitate has formed (Note 5); then add 5 milliliters of NH_4OH (sp. gr. 0.90) in excess. Allow the precipitate to stand overnight. Filter through a weighed porcelain filter crucible of fine porosity, wash with NH_4OH (1:24), and dry in an oven. Place in a cold furnace, gradually raise the temperature to red heat, and ignite at 1050±50°C. for 30 to 40 minutes. Repeat the ignition for similar periods until constant weight is reached.

Note 5. For work of highest accuracy, it is generally necessary to test the precipitation technique on known inorganic samples. Reprecipitation sometimes aids in obtaining more accurate values.

4.3 PROCEDURE FOR SAMPLES CONTAINING METALS OTHER THAN ALKALI METALS.

4.3.1 Cool the Kjeldahl flask (4.1.2), add 40 to 50 milliliters of water, cool to room temperature, and filter the solution through a medium-texture, ashless paper. Collect the filtrate in a 500-milliliter wide-mouth, glass-stoppered Erlenmeyer flask, and wash the Kjeldahl flask and filter paper thoroughly with water; discard the paper. Boil the solution for several minutes and cool to near room temperature. Add NH_4OH (sp. gr. 0.90) until the solution is neutral to methyl red; then add HNO_3 (1:1) until the color just changes to red. Concentrate or dilute the solution to approximately 150 milliliters.

4.3.2 Add 15 grams of NH_4NO_3 crystals and swirl until dissolved. Adjust the temperature to 35° to 40°C. and add 240 milliliters of freshly prepared molybdate reagent. Stopper the flask, shake vigorously for 4 to 6 minutes, and allow to stand for at least 2 hours, or preferably overnight. Filter the solution through a medium-texture, ashless paper. Wash the precipitate with NH_4NO_3 solution. Do not attempt to transfer all of the precipitate from the flask to the paper; reserve the flask for later treatment. Wash the precipitate several times with the wash so-

lution but do not allow the stream of wash solution to strike the funnel above the edge of the paper as the precipitate has a tendency to creep.

4.3.3 Place a clean 400-milliliter beaker under the funnel and dissolve the precipitate through the paper into the beaker with NH_4OH (3:5). Use a little of the NH_4OH to dissolve any precipitate that remained in the flask set aside in Paragraph 4.3.2 and pour this solution through the paper. Wash the flask, funnel, and paper four times with hot water, once with NH_4OH (3:5), and once again with water. Discard any residue remaining on the paper. Evaporate the solution to a volume of 90 to 100 milliliters, make the solution acid with HCl, and add 1 milliliter in excess. Disregard any molybdiphosphate precipitate that may appear at this point. Add 10 milliliters of magnesia mixture slowly while stirring, and cool the solution below room temperature in an ice bath. Add NH_4OH (sp. gr. 0.90) slowly, while stirring constantly, until the solution is basic. Continue stirring until most of the precipitate has formed, then add 5 milliliters of NH_4OH (sp. gr. 0.90) in excess. Allow the precipitate to stand overnight. Filter through a weighed porcelain filter crucible (fine porosity), wash with NH_4OH (1:24), and dry in an oven. Place in a cold furnace, gradually raise the temperature to red heat, and ignite at 1050°±50°C. for 30 to 40 minutes. Repeat the ignition until constant weight is achieved.

4.4 CALCULATION. Calculate the percentage of phosphorus as follows:

$$\text{Phosphorus (percent)} = \frac{P \times 27.84}{W}$$

where: P=weight of magnesium pyrophosphate.
W=weight of sample in grams.

PRELIMINARY QUALITATIVE CLASSIFICATION OF SYNTHETIC GREASES

1.0 SCOPE

1.1 These methods permit qualitative classification of a synthetic grease by breaking the grease down into its major groups of components. These groups are base-oils, gelling agents (organic and inorganic), and thickeners (alkali and alkaline-earth soaps and urea-type thickeners). The components in each group are identified by the tests given (Note 1).

Note 1. Additives which are present in amounts less than about 1 percent, such as antioxidants, viscosity improvers, and corrosion preventive compounds, etc., are not detected by these methods. Most of these additives will be found in the base-oil group, and methods for their detection and determination will be found under the name of the specific compounds.

2.0 OUTLINE OF METHOD

2.1 The outline for this classification scheme is given in Figure 1. Quantitative methods for each of the possible components of synthetic greases are based on this outline; details for these quantitative methods may be found in the Table of Contents under the name of the specific compound or type of compound.

2.2 Several different samples of the grease will be required in carrying out this procedure, because the methods for isolating individual components from synthetic greases vary considerably, and the chemical treatment employed for isolating one component might change or destroy other components.

3.0 SAMPLE

3.1 The size of the samples employed for these procedures shall be about 5 to 10 grams and shall be estimated, since this is a qualitative method. Three samples are required to carry out the tests, a small sample to distinguish between Groups I and II, a small sample for the Group I analysis, and a larger sample for the Group II analysis. The grease shall be stirred or mixed until uniform, if it is not too hard. If working with a hard grease, scrape off surface layers with a spatula, and use the freshly exposed material for analysis.

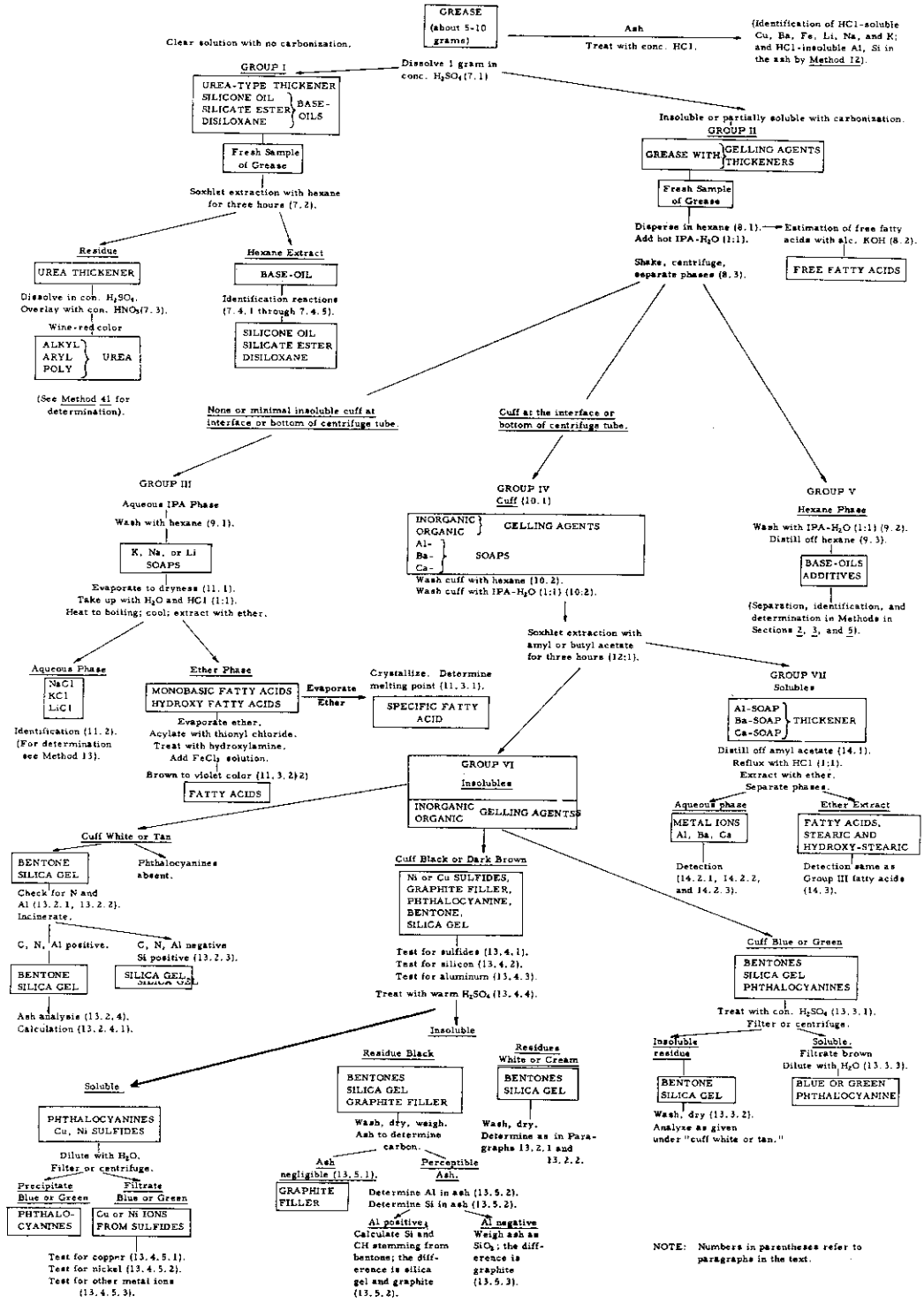

Figure 1. Qualitative Classification of Synthetic Greases.

4.0 APPARATUS

4.1 Centrifuge. A centrifuge is required which is equipped with head, trunnion carriers, and rubber cushions, which is capable of holding 100-milliliter capacity centrifuge tubes (such as the A.S.T.M. pear-shaped oil tubes) and which can be controlled to give rotational speeds up to at least 1800 r.p.m.

4.2 Suction apparatus. This simple apparatus (Figure 2) provides a fast, convenient method for separating and transferring various liquid layers by use of low vacuum from one container to another for further treatment. The tubing shall be capillary type with a 1 millimeter diameter bore, and the suction tip shall be drawn out to a length of about 4 inches to provide a minimum of glass surface. The 4 inch tip shall be about 1 millimeter in outside diameter. Equip a 125-milliliter separatory funnel with a two-hole rubber stopper which contains two sections of capillary tubing, as shown in Figure 2. Water aspirator vacuum is applied through the funnel to draw liquid from the oil tube (Note 2). Only low vacuum is needed, and a trap is provided in the vacuum line. The capillary-bore three-way stopcock, opening to the air, provides a means for controlling rate of flow through the tubing.

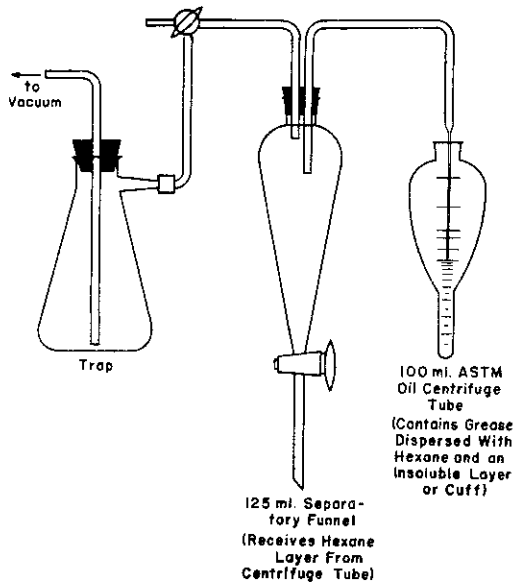

Figure 2. Schematic Diagram of Suction Apparatus For Separation of Gelling Agents From Base-Oils.

Note 2. A standard A. S. T. M. pear-shaped 100-milliliter oil tube is the best type of centrifuge tube for these methods, although this is not essential to the performance of the separations. Any type of centrifuge tube of about 100 milliliter capacity which can be used with the available centrifuge facilities will be adequate.

4.3 Soxhlet extraction apparatus. Standard laboratory Soxhlet apparatus with boiling flask, extraction chamber (preferably with a stopcock takeoff at the bottom of the chamber for withdrawing samples of solvent), reflux Allihn condenser, and cellulose extraction thimbles (double weight thimbles are recommended) which fit loosely in the extraction chamber. Standard taper glassware is preferable. A hot plate shall be used for heating, or a heating mantle with a variable voltage transformer.

4.4 Claisen distillation apparatus. Standard laboratory distillation apparatus with Claisen type distillation flask, West-type condenser, receiving tube 105° adapter, and receiving flask. Standard taper glassware is preferable, because of its ease of assembly, interchangeability, and elimination of rubber stopper fittings.

4.5 Melting point apparatus. Apparatus in which the temperature rise may be controlled to within one degree Centigrade per minute.

4.6 Drying oven, capable of maintaining 110°C.

4.7 Muffle furnace. Furnace capable of maintaining 1000°C., and equipped with a variable control device to adjust the temperature to ± 25°C.

4.8 Ultra-violet Lamp. A Blak-Ray Model XX-4 long wave ultra-violet lamp (Ultra-Violet Products, Inc., South Pasadena, California) has proven satisfactory for illuminating samples of oil and paper chromatograms.

5.0 REAGENTS

5.1 Sulfuric acid (sp. gr. 1.84), reagent grade.

5.2 Hexane. Technical grade hexane shall be distilled slowly from sodium hydroxide or anhydrous sodium carbonate in a distillation column, and the fraction boiling from 63°C. to 69°C. shall be collected for use in this method.

5.3 Nitric acid (sp. gr. 1.42), reagent grade.

5.4 Sodium peroxide, reagent grade.

5.5 Sodium carbonate, anhydrous, reagent grade.

5.6 Ammonium molybdate solution (15 percent aqueous).

5.7 Benzidine solution (0.5 percent in glacial acetic acid).

5.8 Ammonium hydroxide (15 N), reagent grade.

5.9 Sodium tetraborate, $Na_2B_4O_7 \cdot 10H_2O$ crystals.

5.10 Potassium dichromate solution (2 percent aqueous).

5.11 Aluminum chloride, anhydrous, reagent grade.

5.12 N,N,N',N',-Tetramethyl-4,4'-diaminobenzophenone[1] (2 percent in benzene).

5.13 Isopropyl alcohol, 99.8 percent, reagent grade.

5.14 Isopropyl alcohol-water solution (1:1, v/v). Mix thoroughly equal volumes of IPA[2] and distilled water.

5.15 Potassium hydroxide solution (alcoholic, 0.1 N). Add 6 grams of chemically pure KOH to 1 liter of 99.8 percent reagent grade isopropyl alcohol, contained in a 2-liter Erlenmeyer flask. Boil the mixture gently for 10 to 15 minutes, stirring to prevent the solids from

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[1] Obtainable from Eastman Kodak Company, Catalog No. 243.

[2] IPA = isopropyl alcohol.

forming a cake on the bottom. Add at least 2 grams of chemically pure $Ba(OH)_2$ and again boil gently for 5 to 10 minutes. Cool to room temperature, stopper the flask, and allow to stand for several hours; filter the supernatant liquid through a sintered-glass or porcelain filtering funnel (fine porosity). Avoid unnecessary exposure to CO_2 during the filtration. Store the solution in a chemically resistant bottle. Dispense in such a manner that it does not come in contact with cork, rubber, or saponifiable stopcock lubricant. Standardize frequently enough to detect normality changes of 0.0005 N, by titration against 0.16 gram (weighed to the nearest 0.1 milligram) of analytical reagent grade potassium acid phthalate dissolved in 125 milliliters of CO_2-free distilled water, using phenolphthalein indicator.

5.16 Potassium acid phthalate, reagent grade, primary standard.

5.17 Hydrochloric acid (1:1, v/v). Pour one volume of concentrated reagent grade HCl (sp. gr. 1.19) into an equal volume of distilled water.

5.18 Diethyl ether, anhydrous, reagent grade.

5.19 Methanol, anhydrous, reagent grade.

5.20 Sodium hydroxide, reagent grade, pellets.

5.21 Sodium hydroxide solution. Dissolve 12.5 grams of NaOH in 100 milliliters of absolute methanol.

5.22 Hydroxylamine hydrochloride solution. Dissolve 5.0 grams of $NH_2OH \cdot HCl$ in 100 milliliters of absolute methanol.

5.23 Ferric chloride solution (1 percent aqueous).

5.24 Amyl acetate, purified, boiling range 141° to 143°C. (Butyl acetate, purified, boiling range 124-126°C. may be substituted.)

5.25 Sodium metal, reagent grade.

5.26 Acetic acid (5 percent aqueous).

5.27 Lead acetate solution (4 percent aqueous).

5.28 Potassium fluoride solution (5 percent aqueous).

5.29 Ferrous sulfate solution (0.5 N). Dissolve 8 grams of $FeSO_4 \cdot 7H_2O$ in 100 milliliters of distilled water with a few drops of concentrated H_2SO_4.

5.30 Sulfuric acid solution (5 percent).

5.31 Morin indicator solution (saturated, in methanol).

5.32 Potassium hydroxide solution (2 N).

5.33 Acetic acid solutions (1 N, 2 N).

5.34 Alizarin S (Na alizarin sulfonate) solution (0.1 percent aqueous).

5.35 Sodium azide solution. Dissolve 3 grams of sodium azide in 100 milliliters of 0.1 N iodine solution.

5.36 Iodine solution (0.1 N).

5.37 Lead acetate solution (5 percent).

5.38 Benzoin oxime solution (5 percent, alcoholic).

5.39 Rochelle salt solution (Na K tartrate) (10 percent).

5.40 Dimethylglyoxime solution (1 percent in ethanol).

5.41 Sodium rhodizonate (0.2 percent aqueous).

5.42 Hydrochloric acid solution (1:20, v/v).

5.43 Ammonium ferrocyanide solution (saturated, aqueous).

5.44 Ethanol, absolute, purified grade.

5.45 Thionyl chloride, reagent grade.

6.0 ASH

6.1 Place a 1 to 2-gram sample of the grease in a porcelain crucible, burn the combustible matter off slowly in a muffle furnace starting cold, and ignite the residue until the ash is free of carbonaceous matter. After cooling to room temperature in a desiccator, inspect the ash as described below:

6.2 QUALITATIVE EXAMINATION OF THE ASH.

6.2.1 An easily fusible ash, dissolving completely in water to give a strongly alkaline solution, indicates a grease containing lithium, sodium, or potassium. A white infusible ash, practically insoluble in water, but imparting to it an alkaline reaction, may indicate calcium or barium, with or without aluminum. Silica is shown by its insolubility in acids, and by its ability to dissolve in warm alkaline solutions. A large volume of ash, which usually does not become white even with prolonged heating because of entrapped carbon, usually results from the ashing of silicone oils and some other silicon-containing base-oils. If the initial sample of grease yields a black or dark brown ash which does not turn white on prolonged heating, this indicates the presence of nickel, molybdenum, or copper sulfide gelling agents. Qualitative tests will confirm these metals in the acid-soluble portion of the ash. Further evidence of sulfides may be obtained by noting the hydrogen sulfide odor when burning a small sample of grease on a platinum wire or spatula.

6.2.2 Dissolve the ash in HCl (1:1), and confirm the presence of the several possible metals by suitable chemical tests, as outlined in Method 12. If only a portion of the ash is soluble in acid, filter the insoluble portion, wash with water, dry at 110°C. for one hour, cool and place in a platinum crucible. Fuse the residue with 10 times its weight of anhydrous Na_2CO_3, cool, dissolve the fused mass in hot water, and test for silicon and aluminum by the procedures described in Paragraphs 7.4.1 and 13.2.2.

7.0 DETECTION OF GROUP I GREASES (Figure 1).

7.1 Place about 1 gram of grease in a large test tube. Add concentrated H_2SO_4 dropwise to the tube, watching for any signs of chemical reaction. Shake the test tube continuously during addition of acid. If there is immediate carbonization, evolution of gas, or other evidence of rapid breakdown of the grease, stop adding acid. Ready breakdown

of the grease in H_2SO_4 indicates the presence of Group II to Group VII greases. If there is no evidence of carbonization, continue the slow addition of acid until the entire grease sample is submerged. If the grease slowly goes into solution, producing an almost clear water-white to pale yellow solution or thin gel, the grease belongs to Group I, containing either silicate ester, disiloxane, or silicone base-oil, thickened with a substituted-urea compound.

7.2 SEPARATION OF UREA THICKENER FROM BASE-OIL. If a Group I grease has been indicated by its solubility in concentrated H_2SO_4 (7.1), place a fresh 1 gram sample of the original grease in a Soxhlet extraction thimble, breaking the grease into as many pieces as practicable. Fill the boiling flask (usually 250-milliliter capacity) about half full with hexane or 1,1-dichlorethane, place the thimble in the chamber, and extract the grease for about three hours or overnight, maintaining a rapid rate of reflux. After about two hours withdraw a few drops of solvent through the stopcock at the bottom of the extraction chamber onto a clean watch glass, evaporate to dryness, and examine any residue. Traces of oil indicate incomplete extraction, and the process should be continued until the solvent shows no trace of oil on a watch glass. If necessary, add solvent through the top of the condenser to maintain at least 125 milliliters of solvent in the boiling flask. When extraction is complete, cool to room temperature and remove the boiling flask. Evaporate the solvent from the flask with a stream of warm air, while at the same time heating the flask on a steam bath. Place the wet extraction thimble on a watch glass and dry in an oven at 70°C. for about 30 minutes. Reserve the hexane-insoluble residue in the thimble to test for urea-type thickeners (7.3), and the extracted base-oil to test for its composition (7.4).

7.3 DETECTION OF UREA-TYPE THICKENERS. Transfer the dried residue from the extraction thimble (7.2) to a large test tube, and slowly add concentrated H_2SO_4. Use a minimum amount of acid to dissolve the residue, and shake the test tube continuously during the addition. When all of the residue is dissolved, incline the tube to a 45° angle and very carefully add concentrated HNO_3, allowing the acid to slide down the side of the tube and overlay the H_2SO_4. A total of about 1 milliliter of concentrated HNO_3 should be added in this manner. A dark wine-red ring at the interface between the two acid layers indicates a urea-type compound. If the concentration of urea thickener is low, several minutes will be required for this ring to appear. If no red ring

appears, or if the hexane-insoluble residue does not dissolve in concentrated H_2SO_4, test the residue for the presence of silica (7.4.1).

7.4 IDENTIFICATION OF SILICATE ESTER, DISILOXANE, AND SILICONE BASE-OILS. The following series of tests will identify the presence of silicon and will distinguish between silicate ester, disiloxane, and silicone base-oils:

7.4.1 Peroxide Fusion Method for Detection of Silicon. Mix 0.1 gram of anhydrous Na_2CO_3, 0.1 gram of Na_2O_2, and 3 drops of the hexane-soluble oil (7.2) or a few particles of the hexane-insoluble residue (7.3), into a smooth paste with a spatula in a spot plate depression. Make a 1/8 inch diameter loop in the end of a platinum wire, and clean the wire thoroughly by alternately dipping in dilute HCl and heating to redness in a Bunsen burner flame until no color is imparted to the flame by the wire. Dip the loop into the reaction paste and heat in the flame until all reaction has ceased (Note 3). Repeat this procedure until a 1/16 inch thick bead is formed. Heat for several minutes until it becomes water-white. Cool, unwind the wire, and drop the bead into a small platinum crucible containing 2 to 3 milliliters of distilled water. Warm over a burner until the bead has completely dissolved. Cut a 1 inch square piece of ashless filter paper and moisten the paper with the solution. Place a drop of ammonium molybdate solution on the paper, and warm over a burner or in an oven to evaporate excess moisture. With the paper still damp, place a small drop of benzidine solution over the ammonium molybdate spot. Wait one minute, then hold the paper over a watch glass containing a few drops of concentrated NH_4OH. The appearance of a blue spot indicates silicon in the oil.

Note 3. If a large quantity of dense black smoke is evolved during fusion, an aromatic compound such as a phenyl silicone oil is indicated.

7.4.2 Sodium Borate Reaction. Place several small crystals of $Na_2B_4O_7 \cdot 10H_2O$ in a 3 inch test tube, and add 5 drops of the hexane-soluble oil (7.2) and 5 drops of concentrated H_2SO_4. Place the tube in a boiling water bath for 15 minutes, observing the reaction from time to time. The appearance of a red to maroon deposit on the crystals indicates either silicate ester or disiloxane base-oils in the sample. Silicone base-oils do not give this reaction.

7.4.3 Potassium Dichromate Reaction. In a large test tube mix 1/2 milliliter each of the hexane-soluble oil (7.2), $K_2Cr_2O_7$ solution, and concentrated HNO_3. Shake well, heat slowly almost to the boiling point, and maintain this temperature for about 2 minutes. Silicate esters and disiloxanes oxidize under these conditions, indicated by a color change of the aqueous layer from orange to light blue or green (Note 4). Silicone oils do not react.

Note 4. Any oxidizable material in the base-oil will cause this color change, including dibasic acid esters, petroleum oils, and most of the organic additives used in synthetic lubricants; therefore interpretation of the results of this test should be made with reservation, and should be supplemented with data from Paragraphs 7.4.2 and 7.4.4 before definite conclusions are drawn.

7.4.4 Substituted Benzophenone Reaction. Heat 1/2 to 1 milliliter of the hexane-soluble oil (7.2) with approximately 0.1 gram of anhydrous $AlCl_3$ in a small test tube over a micro-burner until the reaction becomes self-sustaining. When the reaction has stopped, cool the tube and add 2 milliliters of N, N, N'N'-tetramethyl-4, 4'-diaminobenzophenone solution. Silicate esters, disiloxanes, and dibasic acid esters immediately produce a wine-red solution; alkyl and chlorinated silicone oils give a bright orange precipitate; and aryl silicones develop this precipitate after about 15 to 30 minutes. After waiting 30 minutes, add 5 milliliters of distilled water to the reaction mixture, shake well, and observe the color. Chlorinated silicone oils give a lime-green precipitate, aryl silicone oils give a royal-blue ether-insoluble solution, and alkyl silicone oils, silicate esters, disiloxanes, and dibasic acid esters give light colored precipitates ranging from tan to orange in color.

7.4.5 Acetic Acid Hydrolysis. If the preceding color reactions have established that the oil contains either silicate esters or disiloxanes, distinguish between these two classes of compound by placing 1 milliliter of the oil in a large test tube with about 5 milliliters of glacial acetic acid. Place a finger condenser in the test tube and heat the mixture with reflux, maintaining the original volume of liquid by adding acid, if necessary. If there is deposition of white silica particles, silicate esters are present in the oil; if there is formation of a water-white gel, disiloxanes are present. Formation of this gel usually requires a minimum of 1 hour and a maximum of 3 hours' heating.

8.0 SEPARATION OF GROUP II GREASES (Figure 1)

8.1 DISPERSION OF THE GREASE. If a Group II grease has been indicated by its susceptibility to attack by concentrated H_2SO_4 (7.1), place a fresh 3 to 5 gram sample of the grease in a 100-milliliter A.S.T.M. pear-shaped oil centrifuge tube. Break the grease into as many small pieces as practicable. Add 50 to 60 milliliters of hexane, stopper the tube with a cork or polyethylene stopper, and shake vigorously until the grease has been dispersed. Some greases are difficult to disperse, but can eventually be broken down by heating to the boiling point by immersion in a steam or water bath (Note 5), followed by vigorous shaking or continuous stirring with a small laboratory stirrer.

> Note 5. Caution should be exercised at all times when working with hexane and other volatile, flammable solvents. Under no conditions should the hexane be heated in the vicinity of open flames. Always use a water bath to heat hexane in the centrifuge tube.

8.2 DETERMINATION OF FREE FATTY ACIDS

8.2.1 Procedure. If it is desired to know approximately the free acid content of the grease, which is usually expressed in terms of free fatty acid, the grease sample (8.1) should be weighed to the nearest 0.1 gram in the centrifuge tube and a known volume of hexane maintained in the tube. After the grease is dispersed, centrifuge at 1800 r.p.m. (or at the speed designated for the type of tube being employed) for 10 minutes or until all insoluble material has been thrown down from the hexane. Withdraw an aliquot from the tube, transfer to an Erlenmeyer flask, and titrate with standardized alcoholic KOH with phenolphthalein indicator to a permanent pink color, shaking well after each addition of base.

8.2.2 Calculation. Calculate the approximate percentage of free fatty acids (as stearic acid) in the grease as follows:

$$\text{Free fatty acid (percent) (as stearic acid)} = \frac{B \times C \times 0.285 \times 100}{W}$$

where: B = milliliters of KOH solution required for titration.
C = normality of KOH solution used for titration.
W = weight of sample in grams.

8.3 SEPARATION OF BASE-OIL FROM ALKALI SOAP THICKENER. Take the hexane solution of the grease (8.1) or the remainder of the hexane solution after removing the aliquot for free acid titration (8.2.1), add about 50 milliliters of hot IPA-water (1:1) solution*, stopper the tube with a cork or polyethylene stopper, and shake vigorously for several minutes. As the solution cools, it should be reheated by immersion in a steam or boiling water bath, followed by further shaking. Centrifuge the tube at 1800 r.p.m. for 5 to 10 minutes, or until clear phases are obtained. If the grease contains only alkali soap thickeners, there should be little or no insoluble material at the interface between the phases, alkali soaps being soluble in the alcohol-water phase. If the grease contains aluminum or alkaline-earth soap thickeners, or inorganic or organic gelling agents, all of which are insoluble in both liquid phases, they will appear at the interface as an insoluble "cuff". Separate the phases using the suction apparatus illustrated in Figure 2. Draw the hexane phase, which contains base-oils and soluble additives, into a separatory funnel to be washed and retained for further analysis by paper and column chromatography (Method 16 and Section 5). The first 30 or 40 milliliters may be withdrawn rapidly, taking care to immerse the tip of the suction tube only a few millimeters below the surface of the hexane. The last portions of liquid should be withdrawn very slowly to prevent removal of any of the lower phase.

9.0 SEPARATION OF GROUP III COMPOUNDS (Figure 1).

9.1 WASHING THE ALCOHOL-WATER PHASE. If there is a minimum of insoluble material at the interface, the grease belongs to Group III (Figure 1). After separating the hexane phase by suction (8.3), leave the IPA-water phase in the centrifuge tube, add 25 milliliters of hexane, heat to the boiling point of hexane as before, stopper, and shake for a few moments to remove residual oils from the IPA-water phase. Centrifuge and withdraw the hexane into the separatory funnel which contains the original hexane extract. Repeat the washing with 15 milliliters of hexane, adding the washings to the previous hexane extracts. Place a few milliliters of hexane in a beaker and draw this hexane into the separatory funnel to rinse the suction tube. Allow the suction to continue for a moment to air-dry the tube.

*IPA= isopropyl alcohol.

9.2 WASHING THE HEXANE PHASE. Wash the combined hexane extracts in the separatory funnel by shaking with 15 milliliters of hot IPA-water solution. Allow the phases to separate by standing for several minutes, and withdraw the IPA-water, adding it to the original IPA-water extract. Repeat this washing. The combined extracts shall be reserved for the determination of alkali soap content (11.0).

9.3 Transfer the combined hexane extract and washings to a 250-milliliter round-bottom distillation flask and distill most of the hexane from the base-oil and additives, using a glass heating mantle. When the volume of the solution is about 10 milliliters, cool and remove the distillation flask, place it on a water bath, and evaporate the remainder of the hexane with a slow stream of air from a glass tube inserted through the neck of the flask. Reserve the oil for analysis by paper and column chromatography (Method 16 and Section 5).

10.0 SEPARATION OF GROUP IV COMPOUNDS (Figure 1).

10.1 If there is an insoluble cuff at the interface between the two liquid phases (8.3), the grease belongs to Group IV (Figure 1), and the cuff contains either aluminum or alkaline-earth soap thickeners, inorganic or organic gelling agents, or combinations of these materials. Separate the hexane phase by suction as described in Paragraph 8.3 and replace the funnel containing hexane with a clean 125-milliliter separatory funnel to receive the IPA-water phase. Place the centrifuge tube containing the cuff and IPA-water phase under the suction tube and, with no suction being applied, move the tip of the tube through the cuff into the IPA-water. Apply suction and slowly withdraw the IPA-water solution from below the cuff, taking care that none of the cuff is drawn into the tube. When only a few milliliters of IPA-water remain, turn off the vacuum by opening the stopcock above the trap. Withdraw the capillary tip to a point a small distance above the cuff and with a wash bottle, pipette, or medicine dropper wash off the tip of the suction tube with a few milliliters of IPA-water solution. Rinse out the suction tube by drawing several milliliters of hot IPA-water through the tube into the separatory funnel.

10.2 WASHING THE CUFF. Add 25 milliliters each of hexane and IPA-water solution to the centrifuge tube containing the cuff, heat

to boiling in a steam bath, shake for several moments to dissolve residual oils or possible alkali soaps, and centrifuge until both liquid layers are clear and the cuff is well defined between them. Withdraw the hexane phase first, adding the hexane to the first hexane extract (10.1). Next slowly withdraw the IPA-water phase as described previously, and add this to the first IPA-water extract (10.1). It is advisable to wash the cuff a third time with 15 milliliters each of hexane and IPA-water solution to remove further traces of base-oils and alkali soaps which could interfere with identification of specific compounds later in the procedure. Reserve the cuff for detection of soaps and gelling agents (13.0 and 14.0).

10.3 Wash the combined IPA-water extracts (10.2) once with about 20 milliliters of hexane, heating, shaking, centrifuging, and separating as described previously (9.1). Add the hexane to the hexane washings (10.2). Wash the combined hexane extracts once with about 20 milliliters of hot IPA-water solution, separate by suction, and add the washings to the combined IPA-water extracts (10.2).

11.0 ANALYSIS FOR ALKALI SOAP THICKENERS (Group III and IV Greases).

11.1 HYDROLYSIS OF THE ALKALI SOAP. Transfer the combined IPA-water extracts (9.1 or 10.2) to a large glass crystallization or porcelain evaporating dish or, if it is desired to recover some of the isopropyl alcohol, to a 250-milliliter round-bottom distillation flask. Distill off two-thirds of the alcohol and transfer the remaining solution to the crystallization or evaporating dish. Place the dish on a steam or water bath and evaporate the solution to dryness, using a stream of air across the surface of the solution. The residue consists of alkali metal soaps. After cooling, take up the residue with a few milliliters of water, add 25 milliliters of HCl solution (1:1), and heat to boiling for several minutes. Allow the solution to cool, and transfer to a 125 or 250-milliliter separatory funnel. Add 50 milliliters of diethyl ether, close the funnel, and shake vigorously for several minutes. Set the funnel aside in a vertical position, and allow the aqueous and ether phases to separate completely until both are almost clear. Remove the stopper and slowly drain the aqueous phase into a second separatory funnel, leaving the ether phase in the first funnel. Add another 50 milliliters of diethyl ether to the aqueous phase in the second funnel, close, and shake as before. Again separate the phases, receiving the

aqueous phase in a 250-milliliter beaker, and add the ether to the first ether solution. The aqueous phase now contains chloride salts of the alkali metal(s) from the hydrolyzed soap, and the ether phase contains fatty acid(s) from the soap.

11.2 IDENTIFICATION OF ALKALI SOAP METAL(S). Alkali metals from the hydrolyzed soap (11.1) can usually be identified by flame tests. Clean a platinum wire by repeated heating in a Bunsen burner flame, followed by immersion in dilute HCl. The wire is clean when it imparts no color to the flame when glowing red hot (sodium salts are the usual source of impurity on the wire, giving a bright orange-yellow color). When the wire is clean, dip it in the aqueous solution from the acid hydrolysis, hold the wire in the flame, and observe any color imparted to the flame. If sodium is present, an orange-yellow color will be seen, but the colors from lithium or potassium will be masked. If potassium is present without sodium, a violet flame occurs; when sodium is present, the potassium color may be seen through a cobalt glass. Lithium gives a carmine-red flame which tends to mask the violet potassium flame. This lithium color may also be observed through a cobalt glass. If there is doubt about interpretation of the flame tests, the aqueous solution may be concentrated and the tests repeated. If there still is doubt, a number of sensitive spot reactions may be employed, or the tests described in Method 12 may be utilized. It is likely, however, that these alkali metals will appear only singly in a given oil or grease, and that the flame tests will therefore be clear and easily interpreted.

11.3 IDENTIFICATION OF FATTY ACID(S) FROM ALKALI SOAP. The fatty acid(s) from the hydrolyzed soap (11.1) can usually be identified by (a) determination of melting point, (b) formation of the hydroxamate, or (c) by formation of a complex compound with urea. Both of the latter compounds have characteristic melting points.

11.3.1 Determination of Melting Point. Transfer the ether solution from hydrolysis of the alkali soap (11.1) to a beaker or crystallizing dish, and evaporate the ether on a water bath. Add about 10 milliliters of absolute ethanol to the residue, and boil for a few minutes. Filter the supernatant liquid while hot through a coarse filter paper into a clean Erlenmeyer flask, using a stemless funnel. Bring the filtered solution to a boil, cool to room temperature or below without disturbing the flask. Small crystals of fatty acid will form during cooling. When

cold, filter the mother liquor and crystals through a coarse filter paper by suction. Wash the crystals once with cold distilled water, then once with a small quantity of cold absolute alcohol. Remove the funnel and invert it over a clean, dry piece of filter paper, and tap the sides, if necessary, to dislodge the paper and to remove any adhering crystals. Press the crystals against the dry paper with a clean spatula. Finally press successive pieces of clean dry filter paper down on the crystals. Collect the crystals and store in a desiccator. Determine the melting point in any suitable apparatus in which the temperature rise may be controlled to within a degree Centigrade per minute (Note 6). The melting point of stearic acid is 69°C. and that of 10-hydroxystearic acid is 81°C. These fatty acids are employed most frequently in synthetic grease soaps.

Note 6. A preliminary determination, employing a rapid rate of temperature rise to obtain a rough order-of-magnitude melting point, usually saves time.

11.3.2 Formation of Acid Hydroxamates. Transfer a few milliliters of the ether solution of the fatty acids (11.1), or several of the fatty acid crystals from Paragraph 11.3.1 to a microcrucible. Evaporate the ether, add 2 drops of thionyl chloride, and evaporate almost to dryness. Add 2 drops of alcoholic $NH_2OH \cdot HCl$ solution, mix, and add dropwise with gentle mixing alcoholic NaOH solution until the mixture is slightly alkaline to indicator test paper. Heat nearly to boiling and keep hot for 5 minutes. Cool and acidify with 4 or 5 drops of 0.5 N HCl solution, testing for acidity with indicator test paper. Add dropwise dilute $FeCl_3$ or $Fe(ClO_4)_3$ solution. Stearic and 10-hydroxystearic acids will form a dark brown-violet color with ferric ion. This test is sensitive to small quantities of fatty acids.

11.3.3 Compound Formation With Urea. Fatty acids form easily identifiable complex compounds with urea. However, the two tests discussed above (11.3.1 and 11.3.2) should be sufficient for positive identification of fatty acids from alkali soaps.

12.0 SEPARATION OF GROUP VI AND GROUP VII COMPOUNDS (Figure 1).

12.1 Transfer with a clean spatula the washed cuff (10.2), which contains gelling agents or aluminum or alkaline-earth soap thickeners,

from the centrifuge tube to a Soxhlet extraction thimble. A double weight thimble is preferred because of the small particle sizes encountered in most gelling agents and thickeners. Dry the thimble at 110°C. for about twenty minutes, or until the cuff is dry. Place the dried thimble in a standard Soxhlet extraction assembly, which has a stopcock at the bottom of the extraction chamber for withdrawal of solvent. Fill a 250-milliliter flat bottom standard taper boiling flask about half full of pure amyl or butyl acetate, and extract the cuff overnight. Check on the completeness of extraction by withdrawing two or three drops of liquid through the stopcock onto a small clean watch glass and evaporating to dryness. When no residue is apparent on the watch glass, the extraction is complete.

Allow the assembly to cool to room temperature, and carefully lift the thimble from the chamber with tweezers or forceps, draining solvent from the thimble into the chamber. Place the wet thimble on a large watch glass and dry at 105-110°C. for at least one hour. If a vacuum oven is available, dry the thimble for a short preliminary period at 110°C. in the air oven, followed by drying in vacuum at 50°C. The thimble contains inorganic and organic gelling agents, such as bentones, silica gel, phthalocyanines, metal sulfides, and graphite filler. The boiling flask contains an ester solution of aluminum or alkaline-earth soap thickeners. Reserve the thimble for detection of gelling agents (13.0) and the boiling flask for detection of soap thickeners (14.0).

13.0 DETECTION OF GROUP VI COMPOUNDS (Figure 1).

13.1 COLOR CLASSIFICATION OF GROUP VI COMPOUNDS.

Remove the extraction thimble containing organic and inorganic gelling agents (12.1) from the air- or vacuum-oven, and observe the color of the dried residue. If it is white or tan colored, the residue contains bentones and/or silica gel without phthalocyanines, metal sulfides, or graphite filler; if the residue is bright blue or blue-green, phthalocyanines are present, possibly with bentones and/or silica gel, but without metal sulfides or graphite filler; if the residue is black or very dark brown, metal sulfides and/or graphite fillers are present, possibly (but not likely) with phthalocyanines and/or bentones or silica gel. The analyst must determine the proper analytical procedure to follow, based on the color of the residue.

13.2 DETECTION OF BENTONES AND/OR SILICA GEL. If the residue is white or tan, bentones and/or silica gel are present. Bentones are detected by the presence of nitrogen, carbon, and aluminum in the residue. Silica gel without bentone is indicated by the absence of nitrogen, carbon, and aluminum. Quantitative ash analysis is necessary to detect a mixture of silica gel with bentones.

13.2.1 Detection of Nitrogen and Carbon. Place a small (about 1/8 inch diameter) piece of clean, dry, metallic sodium in a dry 2-inch test tube which is suspended by its lip in a small hole in an asbestos board or wire screen. Add a few particles of the residue (12.1), and heat the tube with a small flame until the sodium melts and its vapors form a layer 1/2 inch up the test tube. Drop about 0.05 gram of the residue directly into the sodium vapor (avoid standing over the test tube, as some compounds react violently, sending a jet of flame out of the tube). Continue heating the mixture to oxidize residual sodium and to remove decomposition products. Remove the flame and with forceps quickly lift the hot tube from the board or screen and lower it into a small beaker containing 10 milliliters of water. Take special care during this operation not to stand over the beaker. Touch the bottom of the hot tube to the water to crack the glass, then wait a moment for the glass to cool. Tap the cracked tube against the side of the beaker to open the reaction mixture to the air. When all of the pieces of glass are in the water, bring the water to boiling with stirring to break up solid particles, and filter through a coarse paper. The filtrate should be colorless; otherwise, repeat the decomposition. Test for alkalinity with litmus or indicator test paper. The solution should be strongly alkaline. To about 5 milliliters of the alkaline filtrate add 5 or 6 drops of $FeSO_4$ solution and 2 drops of $FeCl_3$ solution. Heat to boiling for a minute or two, cool, and acidify by the dropwise addition of dilute H_2SO_4 with shaking. Stop the addition of acid when the solution becomes acidic and the hydroxide precipitate dissolves. A brilliant blue color (actually a precipitate) will appear immediately if nitrogen is present. If the concentration of nitrogen is low (as it is in bentones), the blue color may be faint and may require several moments to appear. After ten minutes, filter the solution through a fine-texture paper; the Prussian blue precipitate should be visible against the white paper background. If no color appears, bentones are absent; the light-colored cuff may be assumed to be silica gel.

13.2.2 Detection of Aluminum. If the above test for nitrogen and carbon (13.2.1) is questionable, or if further corroboration of the test is desired, the presence of bentones may be established by detecting aluminum (which is present in bentones but not in silica gel). Place a small part (0.01 gram) of the residue (12.1) in a platinum microcrucible, and break up lumps into a fine powder. Add about 0.05 gram dry Na_2O_2 and 0.1 gram dry Na_2CO_3, and mix these thoroughly with the sample, adding a thin layer of Na_2CO_3 on top of the fusion mixture. Fuse slowly over a low flame until the mixture is molten. Increase the heat and continue heating for several minutes until the mixture appears clear. Remove the heat and cool to room temperature. If the solidified melt removes easily from the crucible, transfer it to a small beaker and dissolve in a minimum amount of dilute HCl; otherwise, place the entire crucible in the beaker and dissolve out the melt with dilute HCl. Divide the solution, reserving one half for detection of aluminum and the other half for detection of silicon (13.2.3) (Note 7). Transfer one of the portions of the fusion mixture solution to a small beaker, make alkaline to indicator paper with 2 N KOH, heat to boiling for a few minutes, cool, and filter to remove insoluble hydroxides. Reserve the filtrate for the aluminum spot tests (13.2.2.1 or 13.2.2.2).

Note 7. There are a number of sensitive color reactions for aluminum ion, employing such organic reagents as morin, alizarin sulfonic acid, aluminon, quinalizarin, etc. (see Method 12). The alumina in bentones must be fused with Na_2O_2 and Na_2CO_3 to obtain aluminum in water-soluble form.

13.2.2.1 Detection of aluminum with morin. Place a drop of the filtrate on a black spot plate, acidify with 2 N acetic acid, and add a drop of a saturated alcoholic solution of morin. In the presence of aluminum an intense green fluorescent spot will appear both in daylight and under ultraviolet light. If the test is questionable, a blank should be run for comparison. The presence of aluminum identifies bentones in the residue (12.1).

13.2.2.2 Detection of aluminum with alizarin sulfonic acid (alizarin S). Place a drop of the alkaline filtered solution of the fusion mixture (13.2.2) in the depression of a white spot plate, and add a drop of 0.1% alizarin S solution in water. Add dropwise 1 N acetic acid until the violet color disappears, and then a further drop of acetic acid. In the presence of aluminum, a red precipitate or color appears. Wait at least five minutes for this color to appear, as low concentrations of aluminum cause the color to form very slowly. A blank should be run

if the test is questionable. The presence of aluminum identifies the presence of bentones in the residue (12.1).

13.2.3 Detection of Silicon. Even though bentones are absent in the residue (12.1), it is necessary to demonstrate the presence of silica gel by testing for silicon. This is done by the method already described (7.4.1), using the solution of fusion mixture set aside for this purpose (13.2.2). A positive test for silicon indicates silica gel; a negative test indicates other insoluble compounds which do not contain silicon. Further testing to establish the identity of these materials could be employed, using standard methods of qualitative analysis, although it is unlikely that many such compounds would be found.

13.2.4 Detection of Silica Gel in the Presence of Bentones. In the event that bentone has been detected in the residue (12.1), it is impossible to determine directly whether silica gel has been added to the grease in addition to bentone. The only possibility is to determine quantitatively the amounts of silicon, aluminum, and organic matter present in the bentone-silica gel mixture, and subtract from the total silica the amount attributable to bentone, as calculated from the aluminum content of the ash.

13.2.4.1 Procedure. Weigh the remainder of the insoluble residue (12.1) to the nearest 0.1 milligram in a clean dry platinum crucible. Ash the sample over a Meker burner, using low heat to burn off organic matter, and increase the heat to dull redness for about 15 minutes. Remove the burner, cool the crucible in a desiccator, and weigh. Re-ignite until constant weight is achieved. Calculate the amount of volatile matter which was driven off during ashing. Determine the silicon and aluminum contents of the ash by the procedures described in Method 13. To determine whether there is silica gel in addition to bentone in the residue, calculate the amounts as follows:

13.2.4.2 Calculation of bentone and silica gel. The amount of silica derived from bentone is found through its constant relationship with the alumina content in the ash of the mixture (determined in Method 13):

$$\%SiO_2 \text{ from Bentone} = \%Al_2O_3 \text{ in ash} \times 3.194$$

The amount of silica in the mixture which does not stem from bentone is then obtained by difference:

$\%SiO_2$ Added = $\%SiO_2$ Total in ash - $\%SiO_2$ From Bentone

If the SiO_2 added value is less than 1/2 percent, it is unlikely that silica gel was added as such to the grease; if the value is above 1/2 percent, it is probable silica gel was added to the grease.

13.3 DETECTION AND SEPARATION OF PHTHALOCYANINES. If the color of the residue (12.1) is bright blue or blue-green, phthalocyanines are present, either with or without bentones and silica gel. Phthalocyanines may be separated from the latter compounds by dissolving the phthalocyanine in concentrated H_2SO_4. If there is an H_2SO_4-insoluble portion, this is bentone and/or silica gel, and shall be verified by the methods given in the previous paragraphs (13.2.1-13.2.4.1).

13.3.1 Separation of Phthalocyanines From Other Gelling Agents. Transfer the dried residue (12.1) to a small test tube and fill the tube half full with concentrated H_2SO_4. Shake carefully to avoid spilling the acid. If the residue is pure phthalocyanine, the blue color will be discharged, the acid will become a clear brown color, and there will be no insoluble material. In this case there is no further need for silica gel and/or bentone tests. However, if there is an appreciable quantity of insoluble material, it is likely that silica gel and/or bentones are present. Pour the acid into a small fritted glass funnel (medium frit), mounted in suction flask with a small test tube positioned inside the flask in such a way that it will receive all of the filtrate (Note 8). Apply aspirator vacuum until all of the acid has been filtered. Remove the small test tube containing the filtrate, and set the test tube aside to test for phthalocyanines (13.3.3). Replace the funnel in the flask to wash the acid-insoluble material (13.3.2).

Note 8. If it is desired, the insoluble residue may be removed from the filtrate by centrifugation, removing the supernatant filtrate with a medicine dropper to a second test tube. Washing may be done in the same way, placing the wash liquid in the test tube, shaking, centrifuging, and removing the supernatant liquid. This technique results in lower loss of insolubles than occurs in transferring the residue from the glass frit in the filtration method.

13.3.2 Detection of Bentones and/or Silica Gel. Wash the H_2SO_4-insoluble residue (13.3.1) with several successive 3 milliliter portions of concentrated H_2SO_4 to remove all traces of phthalocyanine, either

centrifuging or using aspirator vacuum to remove the wash acid. Wash three times with 5 milliliters of distilled water, twice with 5 milliliters of ethyl alcohol, and once with 5 milliliters of diethyl ether, removing the liquid after each washing. Remove the funnel and dry in an oven at 110°C. for one-half hour. Remove from the oven, cool, and carefully brush the residue into a small beaker to avoid breaking the frit or introducing glass into the residue, and test for bentone and/or silica gel, using the methods described in Paragraphs 13.2.1 through 13.2.4.1.

13.3.3 Detection of Phthalocyanines. Pour the acid filtrate (13.3.1) slowly into a 100-milliliter beaker containing 20 milliliters of distilled water. Immediate precipitation of bright blue phthalocyanine is proof of its presence. If it is desired to test this precipitate for the presence of copper, nickel, or nitrogen, filter through a fine filter paper, washing several times with water and drying at 110°C. Techniques for destruction of the difficultly decomposed phthalocyanines are available in analytical texts, and tests for nitrogen (13.2.1), copper (13.4.5.1) and nickel (13.4.5.2) may be found in this Method as cited.

13.4 DETECTION AND SEPARATION OF NICKEL OR COPPER SULFIDES AND GRAPHITE FILLER. If the color of the residue (12.1) is black or very dark brown, it is likely that nickel or copper sulfide gelling agents or graphite filler are present, either with or without phthalocyanines, silica gel, and bentone. By the following series of tests the presence of these compounds in the grease can be established. Sulfides are detected by reacting a small portion of the residue with sodium azide solution to evolve nitrogen. Fusion of a second small part of the residue with Na_2O_2 and Na_2CO_3 is employed to detect aluminum and silicon which would stem from bentones and silica gel. Solution of a small part of the residue in concentrated H_2SO_4, followed by precipitation with water, is used to detect the presence of phthalocyanines. The type of sulfide is established by analysis of the filtrate from the diluted H_2SO_4 solution, the phthalocyanine being precipitated, and the metal ions from the sulfide going into solution. Bentones, silica gel, and graphite are insoluble in concentrated H_2SO_4 and can therefore be separated; these separated insolubles must be washed, dried, and weighed for subsequent determination of each of the compounds. The presence of graphite is indicated by the

black color of the residue. Ashing of the weighed residue indicates whether pure graphite (ash negligible) or a mixture of compounds is present. In the event of a mixture of these compounds, aluminum must be determined quantitatively in order to find the proportionate amount of carbon-hydrogen and silica which stem from bentone in the residue. Having determined the total amount of silica present, silica gel added to the grease is determined by difference; graphite added is also determined by difference.

13.4.1 Test For Metal Sulfides

13.4.1.1 Sodium azide reaction. Place a drop of sodium azide-iodine test solution either in a closed end capillary tube or in a conical-shaped microcentrifuge tube. Introduce the solution with a fine glass capillary medicine dropper in such a way that the closed end of the tube is completely filled with the solution and no air bubbles may be seen in the solution or clinging to the walls of the glass tube. Clean a platinum wire with HCl in a flame (as described in detail in Paragraph 11.2), bend a small loop in the end of the wire about 1/32" in diameter to hold the sample, and bend the wire into a 45° angle at a distance from the end of the wire far enough to permit immersion of the loop under the surface of the liquid in the capillary of microcentrifuge tube. Press the platinum wire into the insoluble residue (12.1) to hold the sample in the loop, invert the glass tube (capillary action will hold the liquid in the upper end of the tube), and introduce the sample into the liquid. In the presence of metal sulfides nitrogen is generated immediately in the form of minute bubbles which collect in the closed upper end of the inverted tube. If there is any doubt about the presence of these gas bubbles, inspection with a magnifying glass is helpful in observing their formation on the sample.

13.4.1.2 Hydrogen sulfide reaction. Place a small quantity of the insoluble residue (12.1) in a microcrucible and cover with a drop of dilute acid, either HCl or H_2SO_4. Cover the crucible with a watch glass to the under side of which is attached a moistened piece of filter paper which has been dipped in dilute lead acetate solution. Wait about two minutes; if a black coloration on the paper has not appeared within this time, warm the crucible gently, but do not boil the contents. If no discoloration has occurred within 5 minutes, the test may be taken as negative.

13.4.2 Test for Silicon. Test for the presence of silicon in the residue (12.1) by the Na_2O_2 fusion method (7.4.1). A positive reaction indicates the presence of silica gel and/or bentones.

13.4.3 Test for Aluminum. Test for the presence of aluminum in the residue (12.1) by the Na_2O_2 fusion method (13.2.2), followed by qualitative detection reactions for aluminum ion (13.2.2.1 and 13.2.2.2). If the aluminum test is positive, bentones are present in the residue.

13.4.4 Test For Phthalocyanines. Transfer the remaining residue (12.1) to a small test tube, crush into a fine powder, and fill the tube half full with concentrated H_2SO_4. Agitate the tube to mix the residue throughout the acid. Note any odor which might be evolved; if the test for sulfides was positive (13.4.1.1 or 13.4.1.2), a distinct odor of hydrogen sulfide should be noticed. If all of the residue does not go into solution, or if it is known that silicon and/or aluminum are present, warm the acid to about 50-60°C. and agitate again. Filter through a fritted glass funnel (medium porosity), using a suction flask with a test tube at the outlet of the funnel to catch the filtrate. Continue as described in Paragraphs 13.3.1 and 13.3.2 . Dry the residue for the detection of graphite, silica gel, and bentones (13.5.1). Reserve the phthalocyanine-containing diluted acid for the detection of metal ions from hydrolysis of sulfide gelling agents (13.4.5).

13.4.5 Detection of Metal Ions From Sulfide Gelling Agents. Filter the dilute acid solution containing precipitated phthalocyanines (13.4.4) through a medium filter paper into a clean small beaker. If the filtrate is distinctly blue, copper is present; if the filtrate is green, nickel is present. Color of the filtrate, however, should not be taken as proof of the presence of these metals; the filtrate should be reserved and checked with the following color reactions:

13.4.5.1 Detection of copper. Place a few milliliters of the filtrate (13.4.5) in a small test tube and add NH_4OH (sp. gr. 0.90) dropwise. A precipitate will appear when the solution becomes slightly alkaline, but if copper is present the precipitate will re-dissolve with the appearance of a dark blue-violet color, due to a $Cu(NH_3)_4{}^{++}$ complex. If nickel is present, a light blue complex, $Ni(NH_3)_6{}^{++}$, will form. If both ions are present, the copper complex will mask the nickel complex.

Centrifuge the solution to permit clear inspection of the filtrate. If there is doubt about the presence of copper, the benzoin oxime test may be applied: Impregnate a piece of filter paper with alcoholic benzoin oxime solution by dipping in the solution and drying. Lower the acidity of a few milliliters of the filtrate (13.4.5) with concentrated NH_4OH to a pH of 5 or 6, using indicator test paper. Place a drop of the filtrate on the impregnated paper and hold the paper over a watch glass containing a few drops of concentrated NH_4OH. Appearance of a green coloration indicates the presence of copper. If nickel is suspected, repeat the test using untreated filter paper: place a drop of filtrate on the paper, add a drop of Rochelle salt solution and a drop of benzoin oxime solution on the filtrate spot. A green coloration due to copper will appear, and nickel will not interfere.

13.4.5.2 Detection of nickel. If copper has not been detected in the filtrate (13.4.5.1), use the following test for nickel: lower the acidity of a few milliliters of the filtrate (13.4.5) with concentrated NH_4OH to a pH of 5 or 6, using indicator test paper. Place a drop of the neutralized filtrate on a piece of dry, clean filter paper. Add a drop of alcoholic dimethylglyoxime solution to the first spot, and hold the paper over a watch glass containing a few drops of concentrated NH_4OH. A red circle or coloration on the paper indicates the presence of nickel. If the test is questionable, impregnated paper may be employed to increase the sensitivity of the method, using a warm saturated solution of the dimethylglyoxime reagent in acetone to impregnate the paper, followed by drying. The test with impregnated paper is carried out by placing a drop of the filtrate on the paper, and holding the paper over NH_3. If copper has been detected in the filtrate, the test must be modified in the following way: place a drop of the filtrate on filter paper impregnated with dimethylglyoxime. Wait a moment, then immerse it in a Petri dish or large watch glass containing about 20 milliliters of 5 percent NH_4OH, keeping the paper in constant motion to wash out the copper dimethylglyoxime compound. The red nickel dimethylglyoxime compound will remain on the paper.

13.4.5.3 Tests for other metals. Most metal sulfides will react with warm concentrated H_2SO_4, the metals going into solution as in the case of nickel and copper sulfides. If it is suspected that other metal sulfides are present in the grease, or if it is desired to analyze the filtrate (13.4.5) thoroughly for other metals, standard analytical schemes may be employed, either on a semi-micro or micro scale.

13.5 DETECTION OF GRAPHITE FILLER, SILICA GEL, AND/OR BENTONES

13.5.1 Detection of Graphite Carbon. If the insoluble residue from the H_2SO_4 treatment for phthalocyanines (13.4.4) is black, weigh the total residue in a small platinum crucible to 0.1 milligram. Ignite over a Meker burner or in a muffle furnace, starting at a low temperature until most of the carbon is burned off, and increasing the heat to dull redness for about 15 minutes. Remove the crucible from the heat, place in a desiccator to cool, and weigh. Re-ignite until constant weight is achieved. Record the weight loss of the insoluble residue. If the weight of ash remaining is very small, or negligible, it may be assumed that there is only graphite filler in the grease with no silica gel or bentone (the aluminum and silicon tests (13.4.2 and 13.4.3) should have verified this finding). If there is a perceptible ash content, and if the silicon test was positive and the aluminum test negative, the ash may be assumed to be silica gel, and this part of the qualitative analysis is complete. However, if aluminum was found in the residue, it is necessary to determine quantitatively the amounts of aluminum and silicon in the residue after ashing in order to find whether the silica and carbon present stemmed entirely from bentone or from bentone plus silica gel and/or graphite. Reserve the weighed residue for the determination of aluminum, and silicon (13.5.2).

13.5.2 Determination and Calculation of Aluminum, Silicon, and Graphite. Use the quantitative techniques employed in Method 13 to determine silica and alumina in the ash after burning off graphite (13.5.1). Calculate the amounts of silica gel, bentone, and graphite present in the acid-insoluble residue by the following methods:

$$\%SiO_2\ \text{Bentone} = \%Al_2O_3 \text{ in ash} \times 3.194$$

$$\text{Silica Gel Added (\%)} = \%SiO_2\ \text{(Total)} - \%SiO_2\ \text{Bentone}$$

If the percent silica from bentone as calculated from the alumina value is close to the total silica found in the ash, then it may be assumed that all of the silica found in the ash stems from bentone, and that no silica gel was added to the grease. The amount of graphite found in the H_2SO_4-insolubles from the grease may be found in a similar manner.

$$\%\text{Volatiles in Bentone}^1 = \%Al_2O_3 \times 2.51.$$

%Graphite = %Weight Lost in Ashing - %Volatiles From Bentone

If the weight loss in ashing approximates the percent volatile matter from the bentone, it may be assumed that no graphite filler is present in the grease.

The percent bentone in the H_2SO_4-insolubles may be obtained by the following calculation:

$$\%\text{Bentone in } H_2SO_4\text{-insolubles} = \%Al_2O_3 \times 6.93.$$

The total percentages of silica gel, bentone, and graphite should total 100 percent of the H_2SO_4-insolubles. In the event that the results do not total 100 percent, it is possible that other types of bentones than Bentone-34, containing different amounts of carbon-hydrogen, have been employed. In this case, reference may be made to WADC TR 54-464, Part 1, pp. 10-41, for more extensive calculations based on different Q-salt (quaternary ammonium base) contents in the bentone.

13.5.3 Determination of Bentone and/or Silica Gel in Absence of Graphite. If the insoluble residue from the H_2SO_4 treatment for phthalocyanines (13.4.4) is white or cream-colored, graphite is absent and the mixture could consist of bentone and/or silica gel. If the preliminary tests for silicon and aluminum (13.4.2 and 13.4.3) showed silicon to be present and aluminum absent, then the residue could only be silica gel. If the silicon and aluminum tests are both positive, the possible presence of both types of gelling agent is indicated. Analysis for the mixture shall be carried out as indicated in Paragraph 13.2.4 of this method and in Method 13, and the calculations are identical with those given in Paragraph 13.2.4.1.

14.0 DETECTION OF GROUP VII COMPOUNDS (Figure 1).

14.1 HYDROLYSIS OF ALUMINUM AND ALKALINE-EARTH SOAPS. Attach the 250-milliliter boiling flask containing the ester solution of aluminum or alkaline-earth soap thickeners (12.1) to a Claisen distillation apparatus and distill off the bulk of the butyl or amyl acetate at a slow distillation rate of about one drop per second to avoid overheating the flask. When the bulk of the solvent has been removed, place

[1] Assuming Bentone-34 (see Method 44).

the flask on a steam bath and evaporate the remainder with a stream of dry air. (CAUTION: always evaporate solvents in a fume hood or well-ventilated area!) When all of the solvent has been removed, as indicated by the absence of the typical ester odor in the flask, add 100 milliliters of HCl solution (1:1) and reflux one-half hour, or until the particles of soap have dissolved and the solution is fairly clear. Allow the flask and contents to cool and transfer the liquid to a 250-milliliter separatory funnel. When the solution is cold, add 50 milliliters of diethyl ether, stopper the funnel, and shake vigorously. Allow the funnel to stand until there is distinct separation of the two phases. Remove the stopper and slowly drain the aqueous layer into a second 250-milliliter separatory funnel, leaving the ether phase in the first funnel. Repeat the extraction with 50 milliliters of ether, drawing off the aqueous layer into a 250-milliliter beaker and adding the ether to the first ether extract. The aqueous phase contains aluminum and alkaline-earth metal ions, and the ether extract contains fatty acids from hydrolysis of the soaps. Reserve the aqueous phase for detection of the metal ions (14.2), and the ether extract for identification of the fatty acids (14.3).

14.2 IDENTIFICATION OF ALUMINUM AND ALKALINE-EARTH METALS. Tests for aluminum and alkaline-earth metals in the aqueous phase from hydrolysis of the soaps (14.1) are as follows:

14.2.1 Test for Barium and Strontium. Barium in the acid hydrolyzate may be detected by flame test. Clean a platinum wire (as described in Paragraph 11.2) thoroughly until there is no color imparted to the flame by the wire. Dip the wire in the aqueous solution (14.1) and then into a Bunsen burner flame. A yellow-green coloration, even though of short duration, is evidence of the presence of barium. If this flame test is not conclusive, the following test will prove the presence of barium, and may also prove the presence of possible strontium in the hydrolyzate: evaporate the aqueous phase down to about 20 milliliters, and transfer a few milliliters to a small test tube. Neutralize the solution to pH 5 or 6 by adding dilute HCl dropwise, using indicator test paper. Place a drop of the solution and a drop of 0.2 percent aqueous sodium rhodizonate solution on a piece of clean, dry filter paper. If barium and/or strontium are present, a dark red-brown spot is formed. Now place a drop of dilute HCl (1:20) on the red-brown spot. If the spot turns a brilliant red, barium is present; if the spot disappears, only strontium is present. Calcium and aluminum do not interfere with this test.

14.2.2 Test for Aluminum. Aluminum in the hydrolyzate (14.1) can be detected with morin, the procedure being described in Paragraph 13.2.2.1. The Alizarin S test for aluminum (Paragraph 13.2.2.2) is not definitive in the presence of large amounts of alkaline-earth ions. If barium and calcium are not present in the hydrolyzate, then the Alizarin S test for aluminum may be employed (if there is doubt about the results of the morin test).

14.2.3 Test for Calcium. In the event that no barium, strontium, or aluminum have been detected in the hydrolyzate (14.1), a flame test will identify the presence of calcium. Clean a platinum wire as before, and dip it into the concentrated hydrolyzate solution. A brick-red color in the flame is due to calcium. This flame color is masked by the colors of barium and strontium. If the flame test cannot be performed, or if it is inconclusive, the following reaction can be carried out: place a drop of the hydrolyzate in a small test tube with a few drops of saturated aqueous ammonium ferrocyanide and a drop of absolute alcohol. A crystalline precipitate or cloudiness indicates calcium. The tube should be observed against a black background, because it is difficult to see the faint cloudiness when only small amounts of calcium are present.

14.3 DETECTION OF FATTY ACIDS FROM HYDROLYZED SOAPS. The ether solution of the fatty acids from the hydrolysis of aluminum and alkaline-earth soaps (14.1) shall be treated in the same manner as the ether solution from the hydrolysis of alkali soaps (Paragraphs 11.3 and following) to identify the acid portion of the soap(s).

15.0 SUMMARY AND CONCLUSIONS. Having carried out all of the analytical procedures given in Method 15, the analyst should know qualitatively the gelling agents and thickeners present in the sample of grease. With this information he may quantitatively determine these compounds according to the procedures outlined in Section 4 of this manual. The analysis of base-oils present in the grease shall be carried out according to the procedures outlined in Section 5 of this manual.

PRELIMINARY ADSORPTION ANALYSIS OF SYNTHETIC LUBRICANTS AND BASE-OILS FROM GREASES

1.0 SCOPE

1.1 This method describes procedures for qualitative adsorption analysis of synthetic lubricants and the base-oil (hexane-soluble) fraction from synthetic greases. The method provides a qualitative means for rapid identification of certain types of compounds, such as antioxidants, in synthetic lubricants, and in some cases provides a semi-quantitative measure of the compounds present (Note 1). This is primarily a comparison technique, in which the appearance of the adsorbed oil on a column of silica gel and its performance upon elution may be compared to that of known lubricants.

Note 1. In addition the technique allows the more strongly adsorbed compounds to be concentrated in a small, oil-free fraction, thereby permitting more accurate quantitative determination of these materials than would otherwise be possible.

2.0 OUTLINE OF METHOD

2.1 A sample of synthetic lubricant or the base-oil fraction from a grease is charged to a silica gel adsorption column. When the sample is adsorbed, the general appearance of the column is noted and compared with columns of known lubricants. The least polar materials are eluted from the column with hexane, followed by elution of more polar compounds in order with benzene, ethanol, water, and dilute NH_4OH. Each of the fractions is collected and tested for the presence of antioxidants and other compounds of interest. Evaporation of solvents and weighing the eluted compounds gives about 95 percent recovery (Note 2).

Note 2. It is not always possible to obtain chemically pure fractions, due to overlapping of adsorbed zones of compounds both in the column and during elution.

3.0 SAMPLE

3.1 This method may be employed only with liquids or solutions, i.e., synthetic lubricants themselves or the base-oil (hexane-soluble) fraction from synthetic greases after removal of gelling agents and thick-

eners. The oil does not require treatment prior to the adsorption analysis: in fact, it is not necessary to remove all of the hexane after the extraction of base-oils from greases, before placing the solvent-containing oil in the column.

4.0 APPARATUS

4.1 Chromatography tube, Pyrex glass. Several types of chromatographic tube may be employed for this analysis. A convenient tube is Corning Glass Catalog No. 38460, having a 10 millimeter o.d. by 300 millimeter length, with a 10/18 or 14/35 standard taper joint in the middle of the tube. A coarse porosity fritted disc is sealed into the inner member of the joint. This joint facilitates removal of adsorbent or extrusion of the adsorbent column, if this is desired. The ground joint is supplied with hooks and springs to permit application of higher pressures; however, pressure is usually not employed in a column of this size, vacuum being used instead. Aspirator vacuum is sufficient, and a trap should be supplied in the vacuum line.

4.2 Suction flask, Erlenmeyer-shape, Pyrex glass, heavy wall, 250-milliliter capacity. This flask is equipped with a one-hole rubber stopper into which the bottom section of the chromatography tube is placed. The tube should extend about 1/2 inch through the stopper.

4.3 Test tubes, Pyrex glass with rim, 10-milliliter capacity, 15 millimeter o.d. by 85 millimeter length. These tubes should fit inside the suction flask (4.2).

4.4 Wire rack. This wire rack is designed to facilitate placing and removing test tubes (4.3) in the suction flask (4.2). A stiff 1/16 inch o.d. wire should be bent to form a series of three loops into which a test tube can be placed, be held firmly, and not fall through. A vertical projection of wire on one side, extending above the rim of the test tube, provides a handle which is used to raise and lower the test tube into the flask. This projection should provide clearance when the stopper is in position in the suction flask. The rack should position the test tube in the center of the flask. The chromatography tube should be positioned in the stopper so that the tip extends about 1/8 inch inside the test tube. Figure 3 (on following page) presents a schematic drawing of the assembled apparatus. Design of the wire rack is arbitrary, but should include those features discussed above.

4.5 Drying oven, capable of maintaining a temperature of 110°C.

4.6 Analytical balance, capable of weighing to 0.1 milligram.

5.0 REAGENTS

5.1 Hexane, purified grade. Technical grade hexane is purified by distilling from sodium hydroxide or anhydrous sodium carbonate in a good distillation column, and the fraction boiling from 63 to 69°C. is collected for use in this method.

5.2 Ether, anhydrous, reagent grade, alcohol-free.

5.3 Benzene, reagent grade.

5.4 Ethanol, absolute, reagent grade.

5.5 Ammonium hydroxide solution (4 percent).

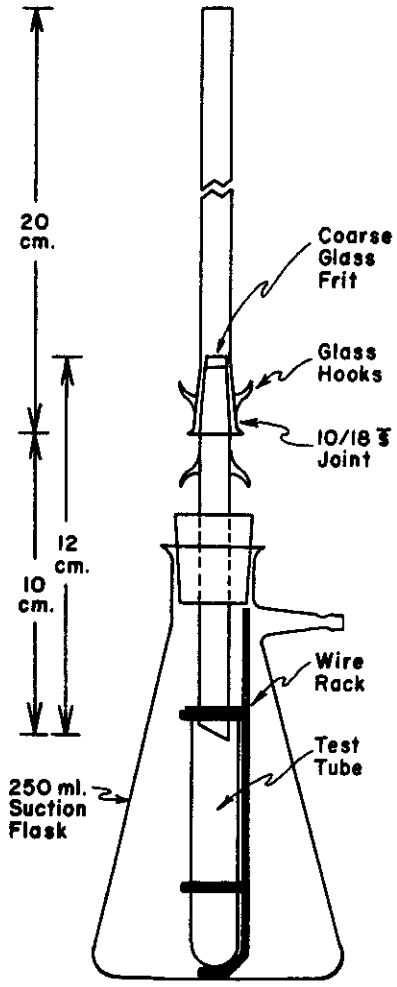


Figure 3. Adsorption Chromatography Apparatus.

5.6 Silica gel, through 200 mesh, chromatographic grade. Davison silica gel No. 22-08-09-216, through 200 mesh, has been found satisfactory for these separations (Davison Chemical Corporation, Baltimore 3, Maryland).

5.7 Filter paper, coarse fiber, qualitative grade.

6.0 PROCEDURE

6.1 PREPARATION OF THE SILICA GEL COLUMN. Mount the chromatographic tube in the one-hole stopper as described in Paragraph 4.4, insert a test tube in the wire rack, place the tube and rack in the suction flask, and position the chromatographic tube in the flask. Be sure the tip of the chromatographic tube extends far enough below the stopper that it reaches about 1/8 inch into the test tube, so that the eluate will be caught in the test tube. Cut a small circle of coarse qualitative grade filter paper to fit on top of the fritted disc. A close fit is required to prevent the pores from becoming clogged with silica gel. Weigh about 5 grams of silica gel in a weighing bottle (keep the bottle stoppered to prevent adsorption of moisture). Using a paper or glass funnel, quickly pour the gel into the tube. Tap the sides of the tube sharply for several minutes to settle the gel. When there is no further settling, the column is ready for use. The gel makes a column 9 millimeters in diameter and about 120 millimeters long, leaving the upper 60 millimeters of the tube as a reservoir.

6.2 APPLICATION OF THE OIL TO THE COLUMN. Weigh a small weighing tube to the nearest 0.01 gram and add about 2 grams of sample oil. Weigh the oil and tube to the nearest 0.1 milligram. Pour the oil directly onto the column of silica gel (Note 3). It is often convenient to mount the weighing tube over the column to drain. Avoid letting the oil strike the sides while pouring onto the column. Re-weigh the weighing tube to the nearest 0.1 milligram to obtain by difference the weight of oil added to the column. Turn on the water aspirator and draw the oil slowly into the column. Low vacuum should be employed, and the movement of the oil front in the column should be relatively slow, at a rate of about 1 centimeter per minute. Application of vacuum may be controlled through a pinchclamp on the vacuum line. Continue the aspirator vacuum until there is no further movement of the front. This quantity of oil (2 grams) should not reach the bottom of the column. Note carefully the appearance of the column in both visible and ultra-violet light and record such data as color, width and number of bands on the column, color of the oil front, etc.

Note 3. This analysis may also be carried out by saturating the column with hexane before adding the oil. The oil may be dissolved in a small quantity of hexane, and added to the column when the wash hexane level has reached the surface of the gel.

6.3 COMPARISON COLUMNS. If a rapid analysis is being made and it is desired to compare the unknown oil with oils of known compositions, prepare further columns as described in Paragraphs 6.1 and 6.2, apply the known oils to these columns, and draw the oil into the gel. Compare the appearance of the columns containing known oils with that of the unknown oil. If the unknown oil column has the same appearance as one of the known columns both in visible and in ultra-violet light, it is possible that the composition of the two oils is similar, if not identical. As will be seen in the descriptions of columns given below (7.0), the performance of each antioxidant during adsorption and elution is different, which permits well-founded conclusions to be drawn concerning the antioxidant content of the oil. If one of the columns of known oil appears similar to the unknown oil, it is recommended that both of the columns be carried through the remaining procedures together to provide further evidence of their similarity or dissimilarity.

6.4 ELUTING THE OIL FROM THE COLUMN

6.4.1 Hexane Elution. Pour a total of 100 milliliters of hexane into the column in small increments, keeping the reservoir above the gel about half full. The liquid column should not be broken by allowing the level of the liquid to sink below the surface of the gel. Use sufficient vacuum to maintain a flow of about 1 drop per second from the column. At the end of the hexane elution, continue the application of vacuum until no further liquid emerges. Collect the eluate in successive labelled test tubes, recording the volume of eluate in each tube as it is collected. Set the tubes in a rack, inspect them in ultra-violet light, and note fluorescence or other characteristics of the solutions (of both the known and unknown oils). Place a cork lightly in each tube, and reserve each solution to test for antioxidants (6.5).

6.4.2 Benzene Elution or Ether-Benzene Elution. The second eluting solvent is usually benzene, particularly for the first analysis of an unknown oil. If closer scrutiny of the oil is desired, precede the benzene elution by ether elution, using 100 milliliters of ether in the same manner as described in Paragraph 6.4.1. Next elute with 100 milliliters of benzene. Collect the fractions in test tubes, note their appearance, and reserve for further testing.

6.4.3 Ethanol Elution. Elute with absolute ethanol as described in Paragraph 6.4.1. If colored zones at the top of the column are eluted by the ethanol, it is unnecessary to use more than 20 milliliters. If zones still remain after 20 milliliters have passed through the column, they will be eluted by NH_4OH solution (6.4.4), so that it is rarely necessary to use more than 50 milliliters of ethanol. Collect the fractions in test tubes, note their appearance, and reserve for further testing.

6.4.4 Ammonium Hydroxide Elution. Elute with 4 percent NH_4OH solution as described in Paragraph 6.4.1, until the column of silica gel is white and all zones have been removed. Wash silica gel from the chromatographic tube by a jet of water placed near the surface of the gel. Fresh dry gel must be used for each run. Collect the fractions in test tubes, note their appearance, and reserve for further testing.

6.5 TESTING THE ELUENT FRACTIONS FOR ANTIOXIDANTS

6.5.1 Having collected the eluent fractions and noted their physical characteristics (such as color, fluorescence in ultra-violet light) and elution performance (eluents which caused zones to move, test tubes in which specific zones were caught, etc.), the individual fractions should be tested for antioxidants or other compounds. Withdraw single drops of solvent from the test tube, place on spot test paper, and test by appropriate color reactions (for antioxidants see Methods 22 through 27). In addition, these fractions may be studied by withdrawing with a micropipet a 2.5 to 5 lambda sample to be run by paper chromatography to establish the R_f-value of antioxidants. Use the paper chromatographic technique on a sample of the first hexane fraction to test for the presence and type of dibasic acid esters in the oil (most base-oils are eluted in the first eluent) (Method 53). Test the first few test tubes of hexane for the presence of silicon-containing compounds, usually base-oils of the silicate ester, disiloxane, or silicone type (Method 15). Corrosion preventive compounds, such as barium sulfonate, and certain other additives, such as tricresyl phosphate, are eluted in the first eluent, and appropriate elemental tests may be applied to detect their presence qualitatively (Method 12).

6.5.2 The techniques employed to detect various compounds in the eluent fractions are described in appropriate sections of this manual. The analyst must decide which tests should be made, and the order in which to perform these tests. A standard sequence of tests is not recommended, as this would be time-consuming. Instead, the analyst should be familiar

with the various types of compounds encountered in synthetic lubricants so that he knows how they behave during an adsorption analysis, how to compare known and unknown oils in columns, and what tests are necessary to establish the presence of certain compounds.

6.5.3 The analyst should be aware that the concentration of compounds in the eluent fractions is low, and that it may not be possible to obtain a positive test for a compound at these dilutions. Evaporation of the solvent to concentrate the compounds for weighing is described below (6.6); the fractions may then be diluted slightly with an appropriate solvent and re-tested. Performance of the known oil should serve as a guide as to whether the tests are sensitive enough to detect the compounds in the unknown oil; a test for a given anti-oxidant on the known oil should be performed the same way as with the unknown oil. If the two oils do not react in identical manners, the analyst can assume that the oils are different in composition.

6.6 WEIGHING OF THE ELUTED COMPOUNDS

6.6.1 Place all of the test tubes with corks removed in a drying oven or ovens, set at temperatures appropriate to remove the particular solvent. Hexane and benzene fractions will evaporate overnight in an oven set at 60°C., but the water and NH_4OH-containing tubes should be dried at a temperature of 95°C. (Note 4). When the solvents have evaporated, inspect the test tubes for the location of compounds, note any other pertinent information (such as whether all of the base-oil is in the first few hexane fractions, whether some base-oils are in the benzene fractions, where the anti-oxidants are found, etc.), and record these observations. To have a semi-quantitative measure of the weight of each fraction from the lubricant, rinse the test tubes out individually with small portions of the same solvent which eluted the fraction, and transfer the washings to a weighed Petri dish. Three washings are usually sufficient to achieve quantitative transfer. Evaporate the solvent from the Petri dish on a steam bath with dry air blowing over the surface of the liquid. When all of the solvent has been removed, dry at 110°C. for about 15 minutes, cool in a desiccator, and weigh.

Note 4. A second technique for removing solvent is to pour all of the fractions of one solvent from the test tubes into an evaporating dish or distillation flask, and evaporate or distill off the solvent; this technique has the disadvantage that when a given solvent elutes two different compounds from a column at different times during the elution operation, the two compounds are re-combined,

and the advantage of the adsorption separation is lost. (This case occurs when quinizarin is present in the oil: the antioxidant remains adsorbed during hexane elution, but moves slowly down the column during benzene elution, and is eluted in the latter half of the benzene fractions. Any compounds eluted in the first portions of the benzene elution would be re-combined with the quinizarin, and the identity of each compound would be partially lost).

6.6.2 Calculation. Calculate the percent of the original weight of oil eluted in each fraction as follows:

$$\text{Fraction (percent)} = \frac{A \times 100}{W}$$

where: A = weight of the compounds in the fraction.

W = weight of oil sample charged to the column.

Usually 95 percent or more of the sample weight can be recovered by the technique described, depending on the amount of each fraction withdrawn for testing. If closer quantitative results are desired, the run should be repeated, withdrawing no test samples.

7.0 PERFORMANCE OF SPECIFIC OILS IN ADSORPTION COLUMNS. Table IV, following, describes the appearance of certain specific lubricants when charged to silica gel adsorption columns in the manner described in Paragraphs 6.1 through 6.6.

TABLE IV

Appearance of WADC Lubricants When Adsorbed on Silica Gel Columns

Lubricant (WADC Designation)	Composition	Appearance of Column After Adsorption
MLO-53-361	90% Dioctyl sebacate 4% Polyester 5% Tricresyl phosphate 1% Phenothiazine	Upper 2 centimeters deep purple zone. Remainder of wetted column slightly yellow. Faint green fluorescence.
MLO-5277	89% Tetra(2-ethylbutoxy)-orthosilicate. 10% Silicone DC-200, 100,000 cs. 1% Phenyl-alpha-naphthylamine	Upper 15 millimeters bright red zone. Remainder of wetted column water-white. Bright blue fluorescence
MLO-53-360	94.5% Dioctyl sebacate 5.0% Barium sulfonate 0.5% 2,6-ditertiary-butyl 4-methylphenol.	Upper 2 centimeters yellow zone. Remainder of wetted column water-white. No fluorescence.
MLO-8200	93.2% Hexa(2-ethylbutyoxy)-disiloxane 4.8% Silicone DC-200, 100,000 cs. 2.0% Dioctyl-diphenyl-amine 0.02% Quinizarin.	Upper 10 millimeters brilliant orange-red zone. Remainder of wetted column water-white. Slight fluorescence
MLO-53-291	--* Silicate ester --* Acryloid --*Ester --*Dilauryl selenide	Upper 10 millimeters bright yellow zone. Next 15 millimeters pale yellow zone. Remainder of wetted column nearly water-white. Bright blue fluorescence.

*Quantities and specific compounds not given.

Table V gives the results of qualitative tests for specific antioxidants (performed as described in the appropriate methods in Section 2 of this manual):

TABLE V

Antioxidant Tests After Elution of WADC Lubricants From Columns With Various Eluents

Lubricant (WADC Designation)	Eluent			
	Hexane	Benzene	Ethanol	NH_4OH
MLO-53-361	PT Positive*	No Positive Tests.	No Positive Tests.	No Positive Tests.
MLO-5277	No Positive Tests.	PANA Positive*	No Positive Tests.	No Positive Tests.
MLO-53-360	No Positive Tests.	No Positive Tests.	No Positive Tests.	No Positive Tests.
MLO-8200	No Positive Tests.	DODPA Positive* Qz Positive in last fractions.	Qz Positive*	No Positive Tests.
MLO-53-291	No Positive Tests.	DLSe Positive*	No Positive Tests.	No Positive Tests.

*Abbreviations:

PT = Phenothiazine.
PANA = N-phenyl-alpha-naphthylamine.
DODPA = Dioctyl-diphenylamine.
Qz = Quinizarin.
DLSe = Dilauryl selenide.

It can be seen from this listing that one antioxidant (Qz), is isolated in the ethanol fraction, and that others (PANA, DLSe) are concentrated in the benzene fractions where their determination by appropriate analyses (described in Section 2) can be carried out with more accuracy than is possible in the original sample of oil. PT is isolated from other antioxidants, being eluted in the hexane fraction, but remains with the base-oil at the same time.

SECTION 2

DETECTION AND DETERMINATION OF ANTIOXIDANTS

PREPARATION OF ACETYLCELLULOSE PAPER FOR REVERSED PHASE CHROMATOGRAPHY

1.0 SCOPE

1.1 This method gives the procedure for preparation of acetylcellulose chromatographic paper for those Methods which require reversed phase paper chromatography for their execution (Note 1).

Note 1. Several techniques for the preparation of acetylcellulose paper are described in the literature, employing a variety of solvents with acetic anhydride or acetyl chloride in different ratios and for different reaction times. However, Method 21 has been verified a number of times and gives consistent results; therefore, since other techniques have not been investigated, it is suggested that this method be employed.

2.0 OUTLINE OF METHOD

2.1 The desired quantity of chromatographic grade filter paper is placed in a glass rack in a glass reaction vessel. The apparatus employed is diagrammed in Figure 4 and photographed in Figure 5. Acetic anhydride in benzene, with a trace of H_2SO_4 catalyst, is allowed to react with the paper for six hours at 70°C. At the end of this period, the reaction mixture is replaced with absolute methanol. After soaking over night the methanol is drained from the vessel, and the paper is washed, rinsed, air-dried, and oven-dried. This treatment provides a paper with about 23 percent acetylcellulose, a degree of acetylation sufficient to make the paper lipophilic and water-repellent; the acetyl content is uniform for the entire surface and the paper is wettable by most organic solvents. (Note 2).

Note 2. Large quantities of ketones should not be used because of the high solubility of acetylcellulose in ketones. This may destroy the capillary texture of the paper, thereby preventing its use for chromatography.

3.0 APPARATUS

3.1 Reaction vessel, Pyrex glass (Corning Catalog No. 6947), and consisting of a 3 liter resin kettle with ground glass top and lip or

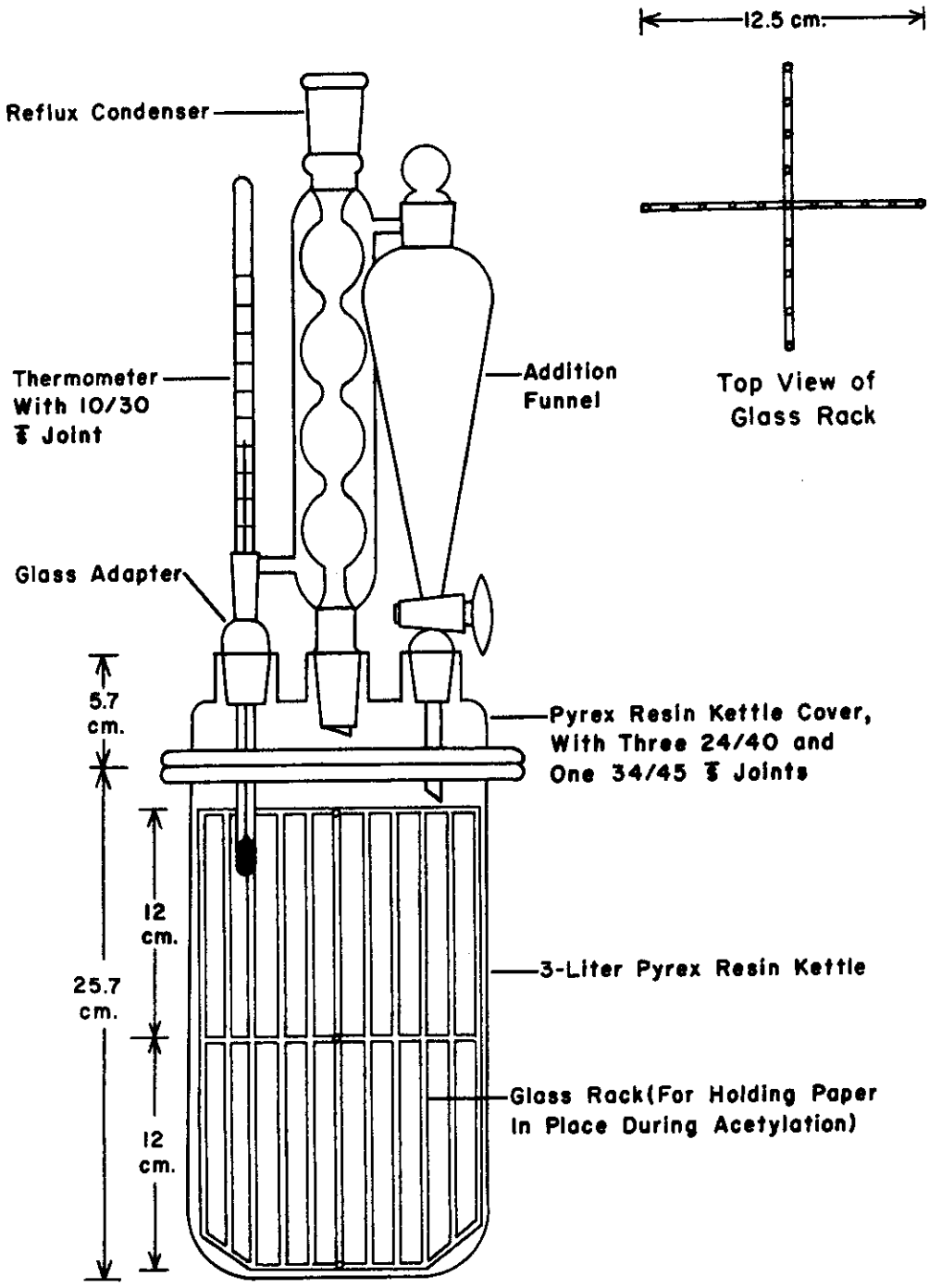


Figure 4. Acetylation Apparatus Used in Preparation of Lipophilic Chromatographic Paper.

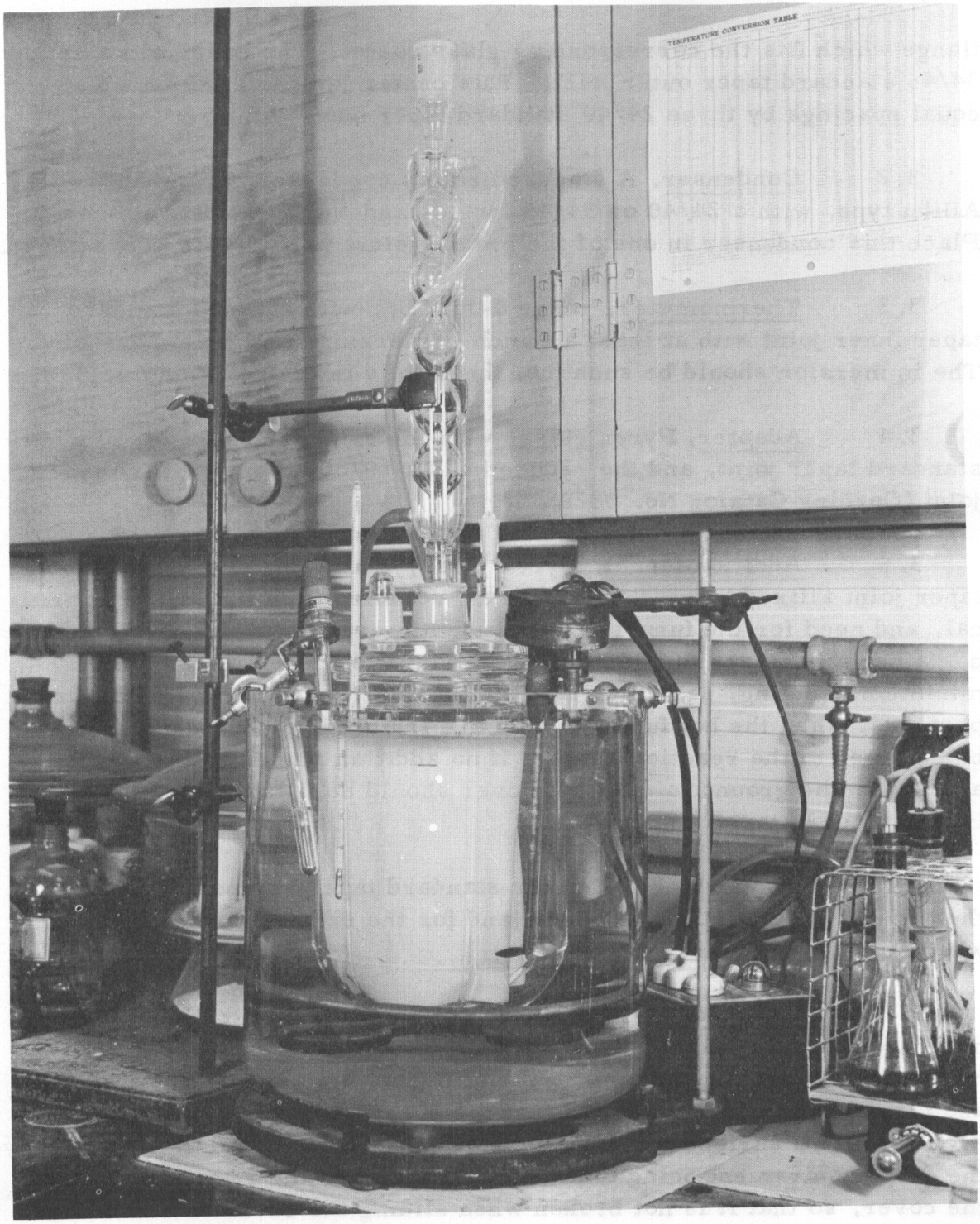


Figure 5. Paper Acetylation Apparatus in Constant Temperature Bath. (Addition Funnel Not Pictured in the Resin Kettle).

flange which fits the corresponding glass cover. The cover has a center 34/45 standard taper outer joint. This center joint is surrounded at equal spacings by three 24/40 standard taper outer joints.

3.2 Condenser. A standard reflux condenser, preferably of the Allihn type, with a 24/40 or 34/45 inner standard taper joint at one end. Place this condenser in one of the ground joints in the resin kettle cover.

3.3 Thermometer, range 0-110°C., with a 10/30 standard taper inner joint with at least a 5 inch immersion stem below the joint. The immersion should be such that the bulb is in the reaction mixture.

3.4 Adapter, Pyrex glass, with the enlarged end a 24/40 inner standard taper joint, and the reduced end a 10/30 outer standard taper joint (Corning Catalog No. 8820).

3.5 Addition funnel, Pyrex glass, with a 24/40 inner standard taper joint affixed below the stopcock. Volume of the funnel is not critical, and need for the funnel is not vital; it merely provides a convenient container and means to add reaction mixture to the resin kettle with minimum handling, particularly after the reaction mixture is up to temperature, when the hot fumes (which are irritating and poisonous) may be confined to the reaction kettle. If no addition funnel of this type is available, the ground joint in the cover should be filled with a 24/40 inner standard taper stopper.

3.6 Stoppers, 24/40 inner standard taper stoppers, for closing the third ground joint in the cover (and for the extra joint in the cover when no dropping funnel is available).

3.7 Glass rack. The glass rack must be constructed, since none are commercially available. This rack provides a convenient means for supporting the long strips of paper in a vertical position, and for separating the strips so that the reaction mixture can react evenly with all surfaces of the paper. Construction details are arbitrary, the only requirement being that the rack fit inside the resin kettle below the cover, so that it is not broken when sliding the cover on and off the kettle. Reference to the top and side views of the glass rack in Figure 4 shows that the rack consists of 17 vertical glass rods slightly shorter than the inside height of the kettle. These vertical members are connected with horizontal pieces of rod at the top, middle, and bottom in

the form of a symmetrical cross, as seen in the top view. The vertical and horizontal pieces are constructed with 3 millimeter diameter Pyrex rod, and the outer frame (top, bottom, and four edges) of the rack are strengthened by using 5 millimeter diameter Pyrex rod. The number of vertical pieces should be sufficient to separate the paper and hold it in a loose spiral; 17 vertical members, four in each arm and one in the center, have been found adequate. A minimum of glass-blowing ability is required to fabricate the rack.

3.8 Constant temperature bath. A constant temperature bath is required in which the resin kettle is immersed during the reaction period. This bath must be large enough to accommodate the kettle (immersed to one-half inch below the lip or flange), and consists of a large glass jar, heaters, thermoregulator capable of controlling the temperature to ±1/2°C. at 71.5°C., an electric stirrer, thermometer, a circuit through which the heaters are controlled by the thermoregulator, and a metal stand to support the assembly (see Figure 5 for picture of resin kettle in water bath). A Fisher Unitized Constant Temperature Bath (Catalog No. 15-445), or equivalent, is adequate for holding the acetylation assembly.

3.9 Stainless steel clips. Small stainless steel clips similar to those employed for holding photographic film are required to hold the individual sheets of acetylated paper while drying. About two dozen are required.

3.10 Drying oven, capable of maintaining 110°C., and preferably having an interior high enough to hang the strips of paper vertically without their touching the sides or bottom (about 30 inches).

4.0 MATERIALS AND REAGENTS

4.1 Benzene, reagent grade.

4.2 Acetic anhydride, reagent grade.

4.3 Sulfuric acid (sp. gr. 1.84), reagent grade.

4.4 Methanol, purified grade, absolute.

4.5 Diethyl ether, anhydrous, reagent or purified grade.

4.6 Chromatographic grade filter paper sheets (Note 3). Whatman No. 1 or No. 4 filter paper sheets are supplied in 100 sheet packages measuring 18-1/4 inches by 22-1/2 inches by H. Reeve Angel & Co. Ltd., 52 Duane Street, New York 7, New York, or by local chemical supply houses. Schleicher & Schuell No. 589 Blue Ribbon quantitative chromatographic filter paper is supplied in 100 sheet packages, the sheets measuring either 52 by 52 centimeters or 58 by 58 centimeters, by Carl Schleicher & Schuell Co., Keene, New Hampshire, or by local chemical supply houses. Whatman No. 1 paper may also be obtained in 600 foot rolls either 1 or 1-1/2 inches wide.

Note 3. Avoid handling the chromatographic paper as much as possible. Wash and dry the hands before handling to avoid leaving any traces of oil, salts, or other contaminating materials on the paper. Avoid creasing the paper during handling, as this causes uneven acetylation and inconsistent results.

5.0 PROCEDURE

5.1 PREPARATION FOR ACETYLATION. Having set the thermoregulator and checked the assembly of the apparatus, the paper shall be prepared for acetylation (Note 4). Place two large squares of the chromatographic paper on top of each other on a clean flat surface such as a glass square on a desk top. With a ruler divide the short edges of the paper into four equally spaced sections, marking the points lightly with a pencil. Using a clean metal straight edge and a sharp razor blade, cut the sheets parallel to the long dimension into four equal width strips, giving eight strips total. With Whatman No. 1 or 4 paper, the strips will have dimensions of 4-9/16 by 22-1/2 inches. Thread four of the strips into the lower half of the glass rack, and four strips into the upper half of the rack. Spiral the strips out from the center post, and distribute them in the rack in such a way that no more than four thicknesses of paper are touching at any point. If there are points where eight layers of paper are pressed together, the acetylation mixture will not penetrate evenly to give uniform acetylation. Place the rack in the clean resin kettle. Lubricate the outer half of the lip of the kettle lightly with a heavy stopcock lubricant. Place the cover on the kettle with the reflux condenser, addition funnel, thermometer with adapter, and stopper. It is not necessary to lubricate the standard taper joints heavily; a light coating will be sufficient.

Note 4. Since the acetylation reaction requires six hours, and heating the water bath and changing the acetylation mixture at the end of the run each require about one hour, it is well to make most of the preliminary preparations on the previous day. The thermoregulator on the water bath should be adjusted to maintain a temperature of 71.5°C. In addition, the water bath and acetylation apparatus should be assembled in a location close to a sink or laboratory drain, because the large volume of hot water in the bath must be drained quickly at the end of the run.

5.2 THE ACETYLATION REACTION. Mix thoroughly in a closed container of suitable size 2430 milliliters of benzene, 810 milliliters of acetic anhydride, and 3.25 milliliters of concentrated sulfuric acid. (CAUTION: Benzene is poisonous and acetic anhydride is a strong lachrymator; therefore perform this operation in a well ventilated area, such as a good hood!) When the reagents are mixed, remove a stopper from the resin kettle and pour just enough reaction mixture into the kettle to cover the paper. Replace the stopper and carefully lower the entire assembly into the heated constant temperature bath, clamping the condenser to a heavy ring-stand to prevent the kettle from rising in the water due to the low density of the reaction mixture. Adjust the level of the water in the bath so that it is about one-half inch below the lip of the kettle. Turn the water on in the condenser and adjust to a medium flow rate. When the temperature of the reaction mixture reaches 68°C., note the time and allow the reaction to continue for six hours. Add the remaining reaction mixture to the addition funnel and stopper the funnel; add small increments of mixture to the kettle whenever the level of the reaction liquid reaches the upper edges of the paper. Because of evaporation, occasionally check the water in the bath and renew when necessary to bring it up to the starting level.

5.3 WASHING THE PAPER. At the end of the reaction period, turn off the heat in the bath, and with a large diameter rubber hose (about 3/8 or 1/2 inch inside diameter) siphon most of the hot water from the bath into a sink or drain. Re-fill the bath with cold water from the tap, starting slowly at first to avoid cracking the glass kettle and bath jar. When the temperature of the reaction mixture has been lowered to about 35-40°C., remove the kettle and assembly from the bath, insert a glass tube to the bottom of the kettle through one of the joints, and either by suction or by siphoning remove half of the reaction mixture from the kettle. When the kettle is half full, remove the cover and pour the remaining liquid out into a large bottle (Note 5). (CAUTION:

Do not attempt to pour from the full kettle, both because of spillage and because of poisonous fumes generated by the warm reaction mixture). After the liquid has been drained, refill the kettle with absolute methanol and cover the paper completely. Replace the cover on the kettle, turn on the water in the condenser, and allow the kettle to remain overnight. In the morning insert a glass tube to the bottom of the kettle and remove half of the methanol either by suction or by siphoning. Remove the cover from the kettle and pour out the remaining methanol. Fill a sink, large glass jar, or photographic washing tank with cold tap water and place the rack containing the acetylated paper in the water. Under the water carefully unwind the strips of paper from the rack, allowing them to float free. The washing tank should be arranged to provide a continuous flow of fresh water with circulation to ensure complete washing of the paper. After a washing period of three hours, fill a liter beaker with distilled water. Spread absorbent paper drying towels on a clean flat surface, remove the strips from the wash tank, allow a moment for them to drain, and place them on the dry towel. Press the strips gently with a second dry towel to absorb as much water as possible, then place the strips in the beaker of distilled water. After all of the strips are in the distilled water, replace the wet towels with dry towels, and repeat the blotting procedure, again placing the strips in distilled water.

Note 5. The acetylation mixture may be stored for periods up to about one month and may be re-used for two more batches of paper.

5.4 DRYING THE PAPER. After the second wash in distilled water (5.3), remove the strips one at a time and permit them to drain. Attach a stainless steel photographic clip to each end of each strip, and suspend from a rack to air-dry with one end hanging free. Fasten small weights to the bottom film clip during the air- and oven-drying periods to prevent the paper from curling or wrinkling excessively. Dry in an oven at 110°C. for 10 minutes. Do not dry longer, as the paper will scorch. When dry, store the paper in a loosely wound spiral in a clean, dry, wide-mouth bottle with a screw cap.

5.5 ETHER RINSING THE PAPER. When the paper is dry (5.4), it may either be stored immediately or it may be washed with ether before placing in storage. In any event the paper must receive

this ether wash before being used for paper chromatography. Place about 200 milliliters of anhydrous diethyl ether in a shallow tray, such as a photographic print tray (in a well-ventilated hood, away from flames). Draw the paper strips back and forth in the ether, using the clips to hold the ends of the paper. When all the strips have been washed once, discard the used ether and replace with clean ether. Repeat the washing procedure twice more. Hang the strips to air dry for a few moments, then dry in an oven at 110°C. for 10 minutes. Do not dry longer, as the paper will scorch. When dry, store the paper in a loosely wound spiral in a clean, dry, wide-mouth bottle with a screw cap.

DETECTION AND DETERMINATION OF PHENOTHIAZINE

1.0 SCOPE

1.1 This method describes procedures for the qualitative detection and quantitative determination of the antioxidant phenothiazine (abbreviated PT) in synthetic lubricants and in the hexane-soluble fraction from synthetic greases. Commercial grade phenothiazine may also be analyzed with these techniques.

1.2 This method shall be employed for the detection and determination of PT in the eluent fractions from adsorption separations of synthetic lubricants (Method 16).

2.0 OUTLINE OF METHOD

2.1 PT is detected directly in the lubricant by diazotization with nitrous acid and sulfanilic acid on normal filter paper at room temperature. It is further identified and separated from other antioxidants by paper partition chromatography on acetylated cellulose (reversed-phase) paper, being identified by its color upon diazotization and by its R_f-value with the solvent combination employed. It is determined quantitatively by paper partition chromatography, the area of the unknown spot of antioxidant being compared to areas of spots containing known amounts of PT.

3.0 APPARATUS

3.1 Hydrometer cylinder, height 300 millimeters, diameter 50 millimeters, with expanded base. This cylinder is used for ascending paper chromatography. It is equipped with a #11 one-hole rubber stopper, through which a piece of wire with a hook at the end is placed. A glass rod which closely fits the hole in the stopper and which has four horizontal short glass rods at the lower end may be substituted for the wire. The wire or glass rod shall be held in place by friction in such a way that it can be raised to hold the paper strip or strips in the atmosphere above the solvent, and lowered to hold the paper with the lower edge in the solvent. This type of chromatographic cylinder is illustrated in Figure 6. Other types of cylinders with wide mouths may be substituted, providing the cylinder is made of glass and tall enough to hold the paper and supporting clip (3.4)

with about 2 inches of space for raising or lowering the paper.

3.2 Glass weights. Small glass weights, illustrated in Figure 6, are used to hold the paper straight in the chromatographic chamber (3.1), and to counteract any tendency of the paper to curl.

3.3 Micro-pipet, capable of delivering 2.5 lambdas of solution (1 lambda = 0.000001 liter). A variety of sizes of micro-pipets from 1 to 50 lambdas capacity is recommended. (Micro-pipets and other micro-equipment may usually be obtained from local chemical supply houses, or from microchemical equipment suppliers, such as Microchemical Specialties Co., 1834 University Ave., Berkeley 3, California.)

3.4 Stainless steel clips, small metal spring-loaded clips similar to photographic clips, but having a jaw about 1 inch long.

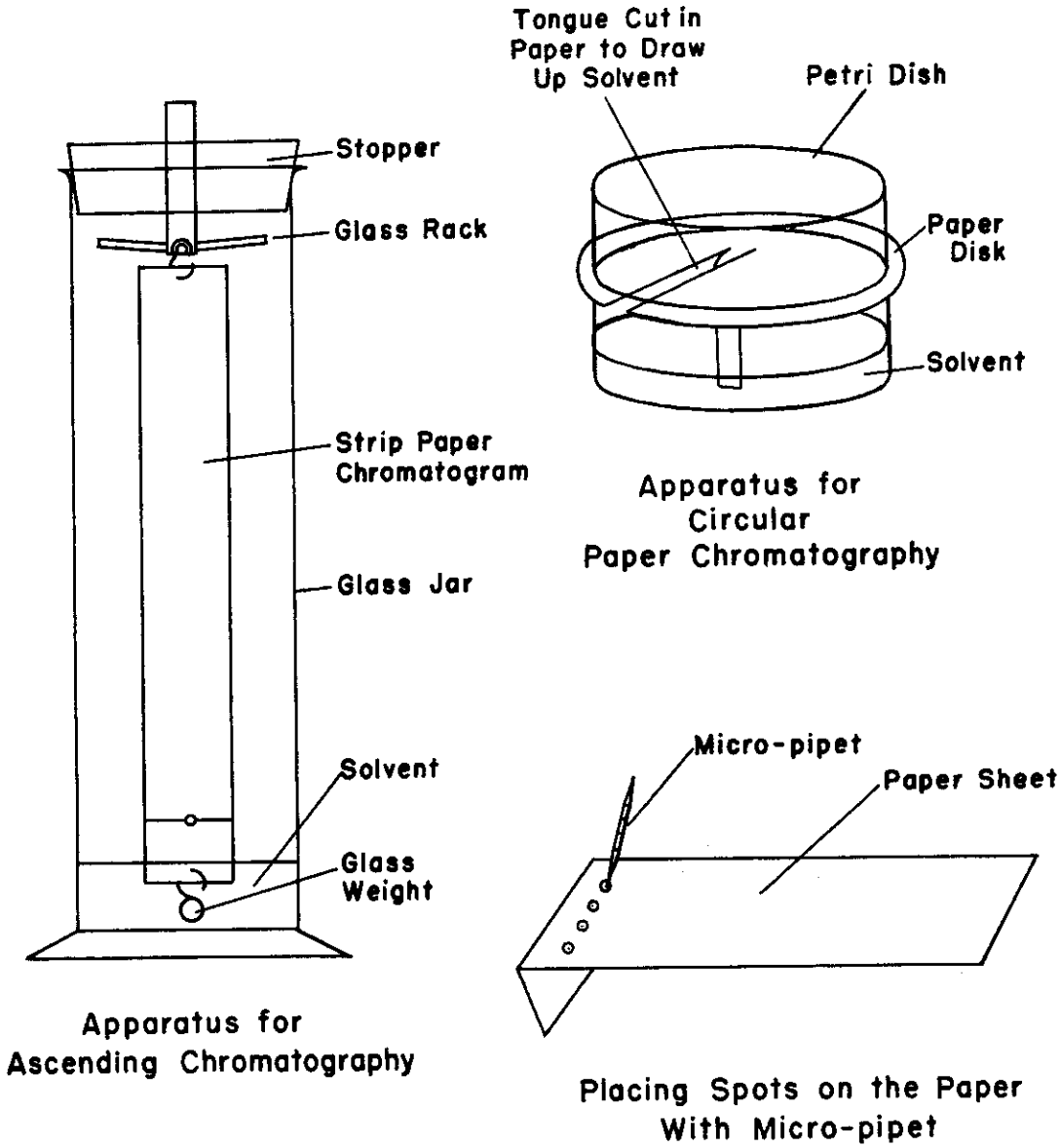
3.5 Descending paper chromatography assembly. This assembly is illustrated in Figure 7, and photographed in Figure 8. It consists of:

(1) Pyrex jar, 18 inches high by 12 inches outside diameter, with 3/8 inch walls and a ground upper edge to which is fitted a 12 inch diameter circular piece of 1/4 inch thick plate glass.

(2) Stainless steel rack which rests on the bottom of the chamber and supports the solvent racks and troughs near the top of the chamber. The height of this rack is adjustable with set screws at the upper four corners.

(3) Stainless steel solvent trough supports (2). These supports rest on the rack and hold the glass solvent troughs and glass anti-siphon rods over which the paper is suspended.

(4) Solvent troughs (2), consisting of a half-cylinder of glass, closed at each end, 8-1/2 inches long and 1-1/2 inches in diameter, cut parallel to the long dimension and with ground glass edges.

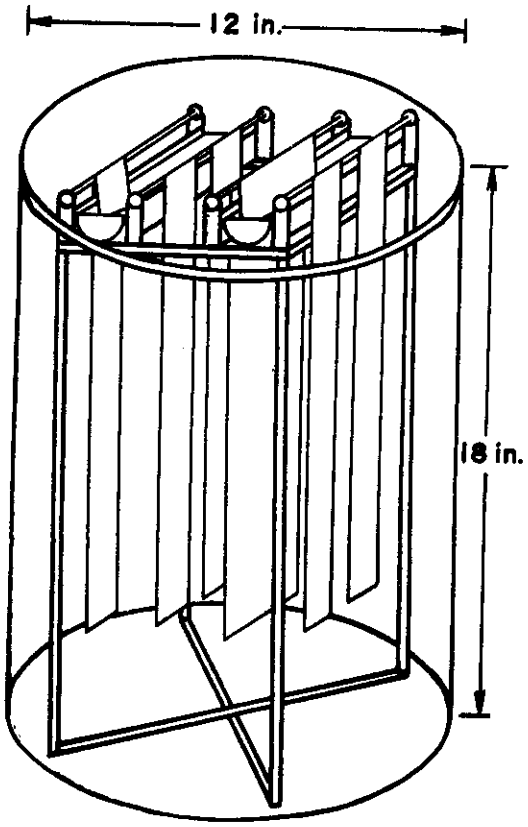


Apparatus for Circular Paper Chromatography

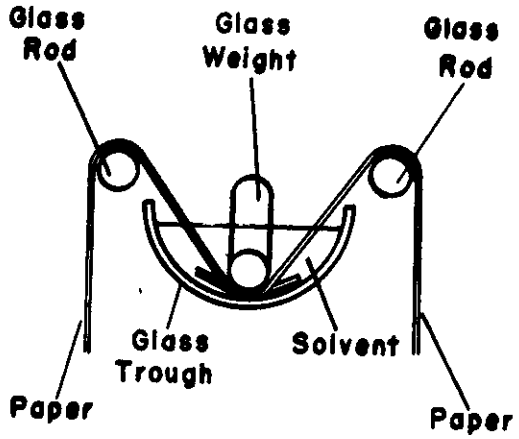
Apparatus for Ascending Chromatography

Placing Spots on the Paper With Micro-pipet

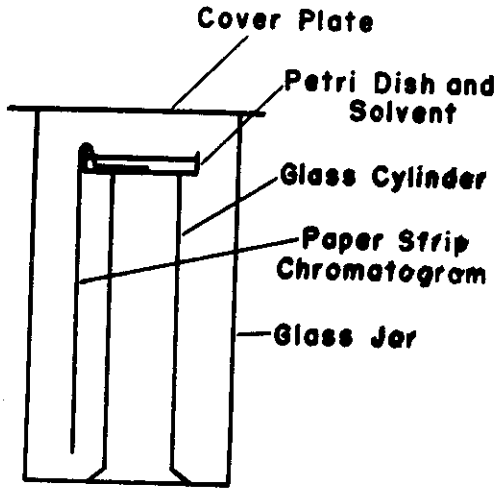
Figure 6. Apparatus For Partition Paper Chromatography.



Detail of Large Apparatus
for
Descending Chromatography
(Trough Supports and
Rack Are Stainless Steel.)



Cross-section of Small Trough
for
Descending Chromatography



Simplified Apparatus
for
Descending Chromatography

Figure 7. Apparatus For Descending Paper Chromatography.

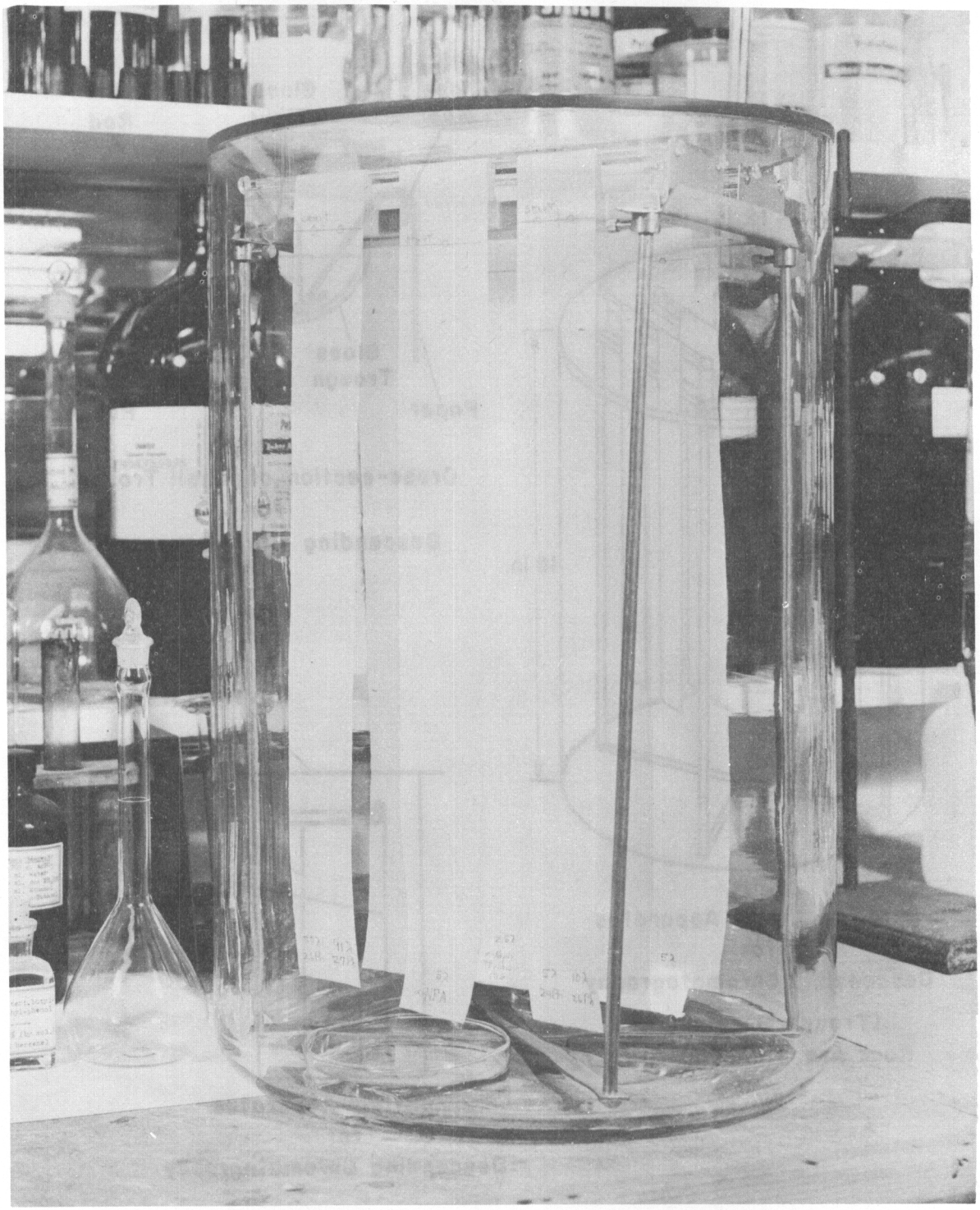


Figure 8. Apparatus For One-Dimensional Descending Partition Paper Chromatography.

(5) Anti-siphon rods (4), glass rods 3/16 inch in diameter and 9-1/4 inches long with the ends flattened to 5/16 inch in diameter to prevent their slipping from slots in the metal trough support.

(6) Glass weights (2), consisting of 5/16 inch diameter glass rod bent in a U-shape, the arms of the U being 1-1/4 inches long and the bottom of the U being 7 inches long. These weights fit inside the glass solvent troughs to hold the paper down in the solvent.

(7) Solvent cups (2), such as Petri dishes, crystallizing dishes, or other low, wide solvent receptacles, which are placed on the floor of the chamber to assist in saturating the atmosphere with the solvent combination.

This entire assembly can be obtained as a unit from laboratory supply houses.

3.6 Drying oven or low speed hot air fan, for evaporating solvents from paper strips.

3.7 Analytical balance, capable of weighing to 0.1 milligram.

3.8 Planimeter, a mechanical device employed for measuring areas.

4.0 REAGENTS

4.1 Butyl acetate-pyridine-water (6:30:60, v/v) solvent combination. Measure the volumes of each of the reagent grade solvents in separate graduated cylinders, and combine these in a glass-stoppered Erlenmeyer flask with shaking.

4.2 Sodium nitrite solution (1 percent), made with reagent grade crystals.

4.3 Hydrochloric acid (sp. gr. 1.19), reagent grade.

4.4 Sulfanilic acid solution (0.5 percent), made with reagent grade crystals.

4.5 Phosphomolybdic acid solution (5 percent in ethanol-water (1:1, v/v)). Mix equal volumes of ethanol and water to make 95 milliliters and dissolve 5 grams of reagent grade phosphomolybdic acid in this mixture.

4.6 Ammonium hydroxide (sp. gr. 0.90), reagent grade.

4.7 Phenothiazine solutions (1, 2, and 3 percent in benzene). Use reagent grade antioxidant and benzene.

4.8 Benzidine solution (1 percent in benzene). Use reagent grade benzid and benzene.

4.9 Acetylcellulose paper. See Method 21 for preparation of this paper.

4.10 Normal filter paper. Whatman No. 1 filter paper roll, either 1 inch or 1-1/2 inches wide by 600 feet long is recommended.

4.11 Blotting paper. Use any clean absorbent paper, such as brown paper towelling. Do not use tissue-weight paper.

5.0 QUALITATIVE DETECTION OF PHENOTHIAZINE

5.1 PROCEDURE

5.1.1 Diazotization Reaction. Place about 15 milliliters of sulfanilic acid solution in a clean Petri dish. To a second Petri dish add 15 milliliters of $NaNO_2$ solution, add 5 drops of HCl (sp. gr. 1.19), and stir. Place a small droplet of the oil to be tested on a 1 inch square piece of normal filter paper and allow the oil to diffuse through the paper for about 2 minutes. Dip the paper in the sulfanilic acid solution for about 5 seconds, remove, and blot excess reagent from the paper by pressing between sheets of absorbent paper (if acetylcellulose paper is employed, dip in the reagent for 20 seconds). Dip the paper in the acidified $NaNo_2$ solution for 5 seconds (20 seconds if acetylcellulose paper is being used), and again blot off excess liquid. Hang the paper with a stainless steel clip in a drying oven or in front of a hot air fan until dry. The appearance of a dark violet to red colored spot indicates the presence of PT. Other amine-type antioxidants react with this reagent, but do not give the intense dark color that is obtained with PT.

5.1.2 Phosphomolybdic Acid-Ammonia Reaction. Phosphomolybdic acid in the presence of ammonia reacts with amine-type antioxidants to give a dark blue spot on paper. Place 5 milliliters of phosphomolybdic acid solution in a Petri dish, and pour a few milliliters of NH_4OH (sp. gr. 0.90) onto a watch glass or into a small beaker. Place a small droplet of the oil to be tested on a 1 inch square of normal filter paper, and allow the oil to diffuse through the paper for about 2 minutes. Dip the paper in the phosphomolybdic acid solution for 5 seconds, remove, and blot by pressing between sheets of absorbent paper. Hold the paper in the ammonia vapor until the yellow color of the phosphomolybdic acid has been discharged. The immediate appearance of a dark blue spot shall be taken as evidence of the presence of amine-type antioxidants in the oil. PT cannot be distinguished from other amine-type antioxidants by this reaction, but must be identified by its color upon diazotization and by its R_f-value after running a paper chromatogram (Note 1).

Note 1. There are several color reagents for the detection of amine-type compounds in oils, such as glucose-phosphoric acid, chlorine, and phosphomolybdic acid-ammonia. However, none of these reagents distinguishes between the individual compounds conclusively.

6.0 QUALITATIVE SEPARATION AND IDENTIFICATION OF PHENOTHIAZINE BY PAPER CHROMATOGRAPHY.

6.1 PROCEDURE.

6.1.1 Preparation of the Paper Strip. Place a large piece of acetylated paper (see Method 21 for preparation of this paper) on a clean dry surface, like a glass plate, and mark the following dimensions:

(a) Total length = 9 inches.
(b) Width = 1 and 1/4 inches.
(c) Width of tail = 5/16 inch.
(d) Length of tail = 1 inch.
(e) Length of paper to the diagonal cut = 7 and 1/4 inches.
(f) Length of divided portion of tail = 1/2 inch.
(g) Width of paper removed to divide tail into two segments = about 1/8 inch.
(h) Location of starting spot = 1 and 1/4 inches above bottom of tail and centered.

Use a pencil to mark these dimensions. With a scissors or razor blade and metal straight edge, cut the paper in the same shape as that illustrated in Figure 9. Always handle the paper with clean hands on clean surfaces to avoid contamination and consequent misleading results.

6.1.2 Preparation of the Sample. The sample applied to the paper (in a 2.5 lambda spot) should have a concentration of about 1 percent PT; therefore the oil to be tested should be diluted (if necessary) to approximately this concentration; if the concentration of PT is too high, the spot will spread out and obscure other spots of antioxidants, and will lower the accuracy of the R_f-value determination. When working with an unknown oil, dilute with an equal volume of benzene or other volatile solvent to make the oil spread rapidly (and uniformly) after application. Several preliminary runs are usually necessary to establish the best conditions for a successful paper chromatographic run.

6.1.3 Application of Sample to the Paper. Place the prepared paper strip (6.1.1) on a small piece of clean plate glass in such a way that the starting point, marked lightly on the paper with pencil, is in the center of the glass. Dip the tip of a clean, dry 2.5-lambda micro-pipet into the sample solution (6.1.2), and allow capillary forces to fill the pipet completely. In the case of viscous solutions, even though diluted with benzene or hexane, this sometimes requires a minute or so (inclining the pipet will also help). When the pipet is full, remove the tip from the solution, and wipe the outside of the tip with a piece of dry, absorbent tissue in such a way that the tissue does not touch the opening at the tip of the pipet; otherwise some of the test solution would be absorbed into the paper. Place the tip on the starting point on the paper, holding the pipet vertical and applying slight pressure. The solution will not drain onto the paper until it establishes close contact; therefore it may be neces-

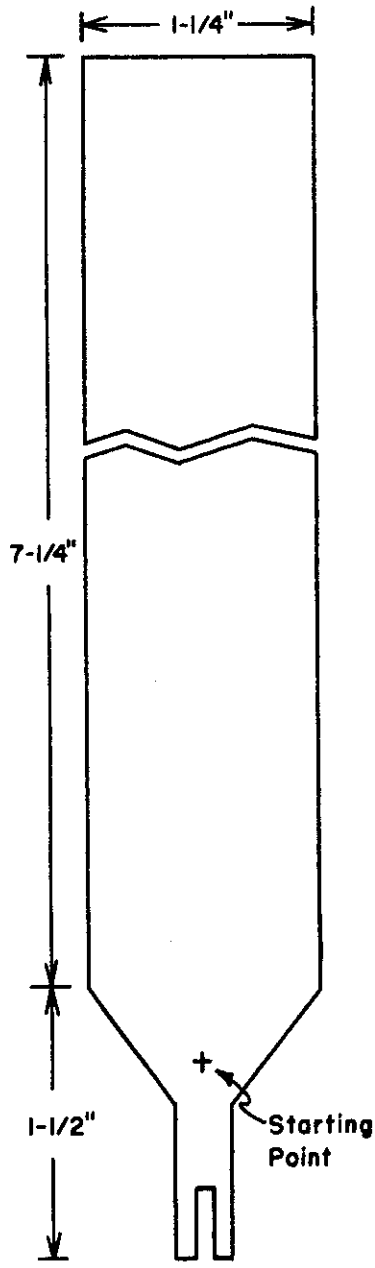


Figure 9. Paper Strip Used For Qualitative Identification of Antioxidants.

sary to rotate the upper end of the pipet slightly to establish this contact. Allow the pipet to drain into the paper, remove the pipet, and hang the paper in the air for a few moments to evaporate solvent. If an undiluted oil is applied to the paper, hang the paper for about one hour to permit diffusion of the oil. Clean the pipet by placing the tip in a suitable solvent, filling the capillary, and removing the solvent by touching the tip to tissue paper; repeat this procedure several times, and set the pipet aside to dry.

6.1.4 Developing the Chromatogram. Prepare the solvent combination by measuring 3 milliliters of butyl acetate in a graduated cylinder, 15 milliliters of pyridine in a second cylinder, and 30 milliliters of water in a third cylinder. Combine the three solvents in a stoppered Erlenmeyer flask, mix and pour about 20 milliliters of the solvent combination into the hydrometer cylinder. Attach a stainless steel clip to the top of the paper strip, and attach the clip to the glass or wire rack in the stopper of the hydrometer cylinder. Adjust the height of the wire or glass rack so that when the stopper is in place, the entire paper strip will be suspended above the solvent combination. Allow the atmosphere in the cylinder to saturate with vapors of the solvent combination for at least one hour (overnight is better, but not absolutely necessary). At the end of the saturation period, lower the wire or glass rack so that the tips of the paper dip 2 or 3 millimeters below the surface of the solvent combination. Be sure that the paper hangs free in the cylinder, not touching the sides at any point (Note 2). Allow the chromatogram to develop (usually about 2 hours at room temperature) until the solvent front has reached a point about one inch from the top of the paper. At this point, quickly remove the stopper and paper from the chamber, lay the paper flat on a clean glass surface, mark the exact location of the solvent front with a soft lead pencil, taking care not to tear the wet paper, and hang the strip in a drying oven at 110°C. for 5 or 6 minutes, or in front of a hot air fan until the paper is completely dry.

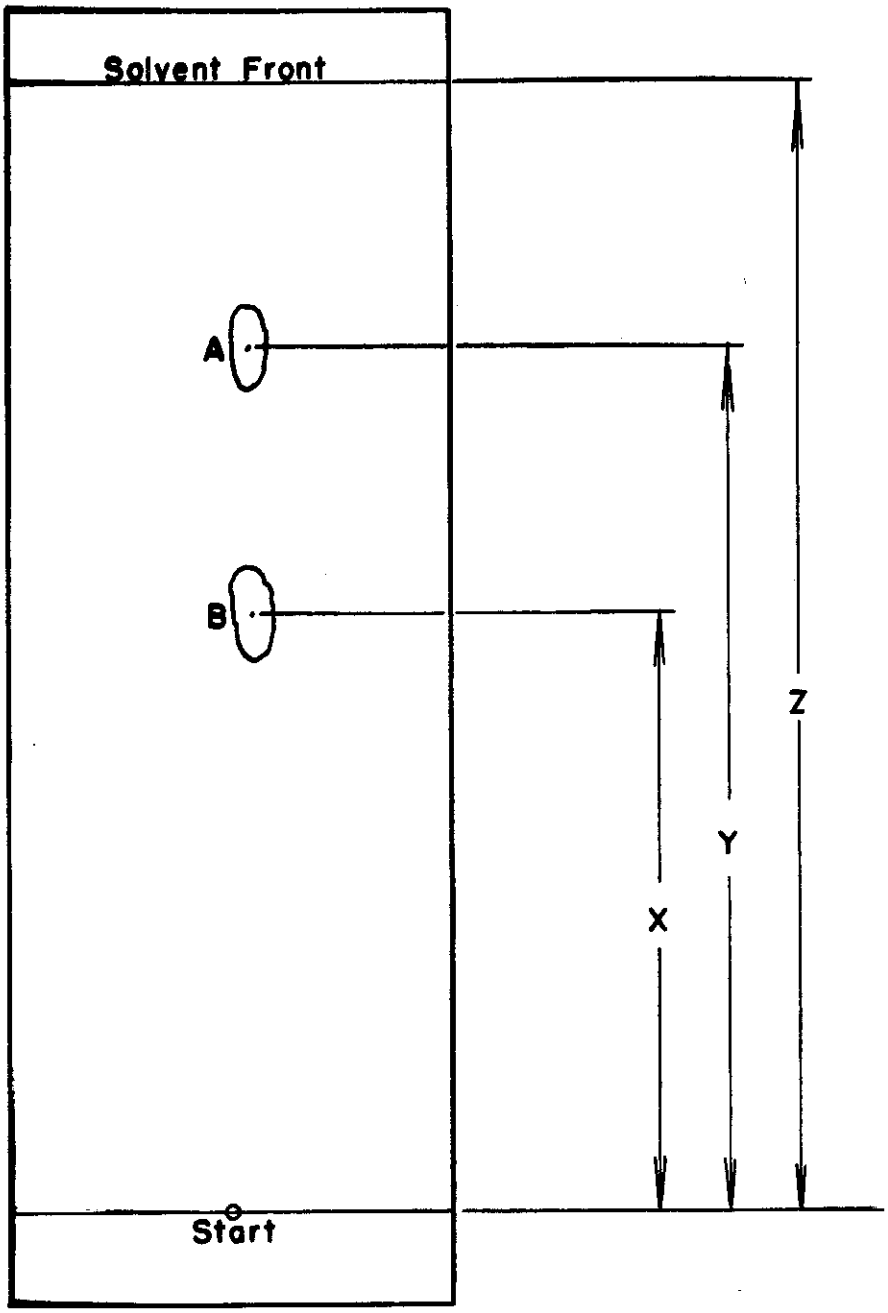
Note 2. If the acetylcellulose paper does not hang straight in the chamber, particularly after saturating the paper and atmosphere, it may be necessary to add glass weights to the paper, as illustrated in Figure 6. In this case cut the paper so that there is a bridge between the two narrow tails of the paper at the bottom on which a glass weight with hook may be hung. It is necessary to maintain the double tail to slow down the rate of rise of solvent combination through the paper.

6.1.5 Detecting the Spots. The spots on the dried paper strip are detected in the manner described in Paragraph 5.1.1 or 5.1.2. If diazotization is employed, the PT spot will appear violet, the depth of color depending on the amount of antioxidant present. If phosphomolybdic acid is employed, the spot will be blue, the depth of color increasing with increasing PT concentration. When detecting spots on a strip chromatogram, it is usually necessary to dip and re-dip the paper in the reagents several times, in order to bring the color to maximum intensity. When the spots have been developed, blot the paper, and outline the spots with a soft lead pencil on a glass surface, taking care not to tear the paper. After the paper is dry, the pencilled outline of the spots may be re-traced to darken the first pencil line.

6.2 DETERMINING THE R_f-VALUE. The R_f-value of a substance on a developed paper chromatogram is defined as the ratio of the distance the substance has traveled to the distance the solvent combination has traveled with a given solvent combination, both distances being measured from the starting point. The center of the spot is marked on the paper and used in determining the R_f-value as illustrated in Figure 10 for two spots on the same chromatogram. Measure the R_f-value of all spots appearing on the dried paper chromatogram (6.1.4 and 6.1.5). If a perceptible spot is found at R_f 0.22, it may be assumed that PT is present in the sample oil; this R_f-value may be used to verify the results of the qualitative tests for PT (5.1 or 5.2). The presence of other discrete spots on the chromatogram indicates other antioxidants than PT; their R_f-values should be checked against the known R_f-values of these antioxidants (Methods 23, 24, 25, 26, 27).

6.3 COMPARISON WITH STANDARD SUBSTANCES. It is usually necessary to prepare two types of standard materials to be used as comparison substances with the unknown chromatogram. These substances shall be chromatographed in exactly the same manner as the unknown sample on individual strips of acetylcellulose paper.

6.3.1 Phenothiazine Standard. Prepare a 1 percent solution of PT in benzene, and chromatograph a 2.5 lambda spot of this known substance as described in Paragraphs 6.1.1 through 6.1.5, measuring the R_f-value of the known material. This chromatogram may be run in the same chamber and at the same time as the unknown, provided that the two pieces of paper do not touch during development. Comparison of the known spot with the unknown sample assists in ascertaining the presence and identity of PT in the unknown.



$$R_{f(A)} = \frac{Y}{Z} \quad ; \quad R_{f(B)} = \frac{X}{Z}$$

Figure 10. Schematic Diagram of R_f-Value On a Paper Chromatogram.

6.3.2 Benzidine Standard. For very accurate determinations of the R_f-value, it is sometimes helpful to run an additional paper chromatogram containing a solution of a known concentration of a reference substance, such as benzidine in the case of amine-type anti-oxidants. The R_f-value of this substance is previously determined under carefully controlled conditions, using pure chemicals, controlled temperature, overnight saturation, etc. When the unknown sample and the known PT sample are run, a sample of benzidine is also run. The spots are developed and the R_f-values measured. The percent deviation which the benzidine spot exhibits from the value obtained under controlled conditions is applied as a correction factor on the measured PT R_f-values. For the purposes of this manual, however, it is not felt that such a reference correction is necessary. Use of a chromatogram containing a known spot of PT is usually satisfactory for comparison purposes.

7.0 QUANTITATIVE DETERMINATION OF PHENOTHIAZINE BY DESCENDING PAPER CHROMATOGRAPHY

7.1 PROCEDURE

7.1.1 Preparation of the Paper Strips. The descending chromatography apparatus described in Paragraph 3.5 and illustrated in Figures 7 and 8 will be employed for this determination. Place a large piece of acetylated paper (see Method 21 for preparation of this paper), or better, a long strip of 1-1/2 inch wide acetylated paper on a clean dry surface, like a glass plate, and mark on the sheet the following dimensions:

(a) Total length - about 33 inches (or two pieces about 17 inches long).

(b) Width - 1-1/2 inches.

(c) Width of narrow sections - 3/8 inch.

(d) Length of narrow sections - 1/2 inch.

(e) Length of tapered sections - 3/4 inch.

(f) Length of chromatograms - 13 inches.

(g) Length of middle section - 4 inches.

(h) Location of starting points - 3/16 inch from start of tapered sections, and centered in the paper.

Figure 11 illustrates the shape of the paper for this determination. Two 33 inch strips are required (four individual chromatograms). If 17 inch pieces of paper are used, it has been found best to staple these together in the middle, although the glass weight will usually prevent the unclipped paper from falling out of the solvent trough. It is important that the paper strips do not touch the bottom of the chamber when completely saturated with solvent. At least 1 inch clearance should be provided to allow for stretching of the paper.

7.1.2 Application of Sample to the Paper. For quantitative paper chromatography, PT in the unknown oil is compared to known concentrations of PT. It is usually necessary to run three different concentrations of PT, such as 1, 2, and 3 percent benzene solutions of the reagent. Place one 2.5 lambda spot of the 1 percent solution on the starting point of one of the strips (as described in Paragraph 6.1.3), dry the strip, and label the concentration applied with a pencil notation or code at the bottom end of the strip. Place spots of the 2 and 3 percent solutions on two more of the strips. Next place a 2.5 lambda spot of the diluted unknown oil (6.1.2) on the fourth paper strip, and dry the paper. Clean the pipet as described in Paragraph 6.1.3.

7.1.3 Development of the Chromatogram. Place two Petri dishes, or other low, wide glass con-

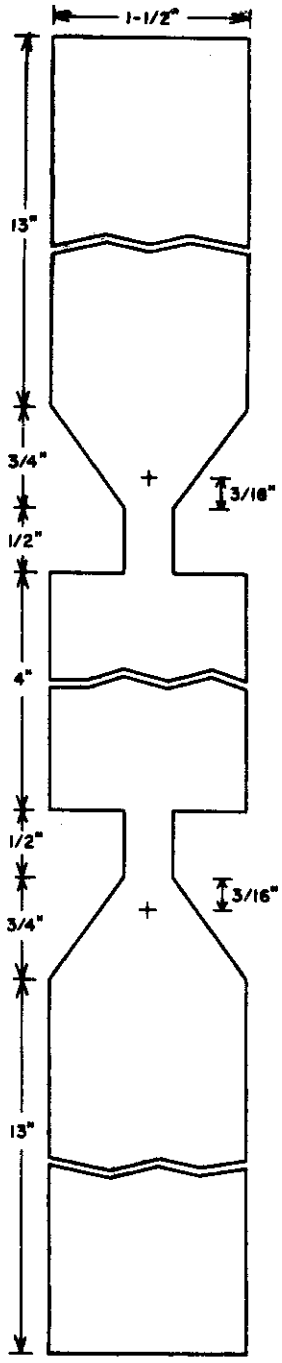


Figure 11. Paper Strip Used For Quantitative Determination of Antioxidants By Descending Chromatography.

tainers in the bottom of the chromatograph chamber and fill these dishes half full with solvent combination, which has been prepared as described in Paragraph 6.1.4. Fill the two solvent troughs in the racks half full with solvent combination. Grease the upper edge of the chamber to form a tight seal against the glass cover plate. Leave the glass weights outside of the chamber while the saturation process is taking place. Place the paper strips in the chamber to saturate overnight, hanging them over the anti-siphon rods in such a way that the papers cannot touch the solvent in the troughs, nor can the ends dip into the Petri dishes when the paper is completely saturated. Position the paper strips so that in the morning the glass weights may be placed in the solvent troughs quickly with equal lengths of paper hanging down on each side of the anti-siphon rods. In the morning, open the chamber for as brief a time as possible to avoid disturbing the saturated atmosphere, place the glass weights on the papers, pressing them into the solvent, and close the chamber. Allow the run to proceed until the solvent fronts are about 1 inch from the bottom edge of the paper strips. Open the chamber, remove the glass weights, place the papers on a clean glass surface, and mark the solvent fronts with a soft lead pencil, taking care not to tear the wet papers. Hang the strips in a drying oven at 110°C. for 5 or 6 minutes, or in front of a hot air fan until the papers are completely dry. When the papers are dry, the solvent fronts may be marked more clearly with the pencil.

7.1.4 Detecting the Spots. The spots on the dried paper strips are detected in the manner described in Paragraph 5.1.2. Since PT is known to be present in the oil, diazotization is not necessary. The phosphomolybdic spot usually has a more intense color than the diazotized spot, and therefore is recommended for detection of quantitative spots. Mark the center of each spot with a soft pencil, and determine the R_f-values as described in Paragraph 6.2. Outline the spots carefully with the pencil for the quantitative determination below.

7.2 QUANTITATIVE DETERMINATION OF PHENOTHIAZINE. Two simple techniques may be employed for quantitative comparison of the unknown sample with the three known concentrations of phenothiazine.

7.2.1 Spot Area Method. If a planimeter is available, measure the area of each spot five times, taking the average value for the area (use of the instrument is described in a pamphlet supplied by the manufacturer). Record the areas of all four spots. Using semi-logarithmic

paper, plot the areas of the three known spots as the abscissa and the concentration (expressed in weight per unit volume) as the ordinate. An approximately straight-line function will be obtained. Connect these three points with a straight-edge. Find the point on the curve corresponding to the area of the unknown oil, and on the ordinate read off the concentration of PT. Correct this reading for the dilution of the oil with hexane or benzene (6.1.2) to obtain the actual content of phenothiazine. If the PT concentration is too low, and gives a weak or diffuse spot, repeat the run using two or more superimposed 2.5 lambda spots of the diluted oil, drying each spot before application of the next spot. In this way the concentration of PT is brought up to a readable level; the value for the concentration must be corrected to allow for the increased volume of oil taken (Note 3).

7.2.2 Weighing Method. After outlining the four spots with pencil, each spot is cut out with scissors and weighed. Assuming uniform thickness of the paper, the area of the spot is proportional to the weight of paper in the spot. Plot on semi-logarithmic paper the concentration (expressed in weight per unit volume) as the ordinate, and the weight of paper in each spot as the abscissa. Plot the weight of the unknown spot, and determine the concentration of PT as described in Paragraph 7.2.1.

Note 3. Although Paragraphs 7.2.1 and 7.2.2 discuss non-instrumental techniques for quantitative paper chromatography, their accuracy is not high, and it is suggested that a photoelectric densitometer be employed whenever possible to scan each spot, plotting optical density versus length of spot. In this way the area under the optical density curves can be plotted versus concentration on semi-logarithmic paper, and greater accuracy is achieved.

DETECTION AND DETERMINATION OF N-PHENYL-ALPHA-NAPHTHYLAMINE

1.0 SCOPE

1.1 This method describes procedures for the qualitative detection and quantitative determination of the antioxidant N-phenyl-alpha-naphthylamine (abbreviated PANA) in synthetic lubricants and in the hexane-soluble fraction from synthetic greases. Commercial grade PANA may also be determined by these techniques.

1.2 This method shall be employed for detection and determination of PANA in the eluent fractions from adsorption separations of synthetic lubricants (Method 16).

2.0 OUTLINE OF METHOD

2.1 PANA is detected directly in the lubricant (1) by its brilliant blue fluorescence under UV-radiation, (2) by diazotization with nitrous acid and sulfanilic acid on normal filter paper at room temperature, and (3) by its reaction with phosphomolybdic acid and ammonia. It is further identified and separated from other antioxidants by paper partition chromatography on acetylated cellulose (reversed-phase) paper, being identified by its color upon diazotization, its fluorescence, and its R_f-value with the solvent combination employed. It is determined quantitatively by paper partition chromatography, the area of the unknown spot of antioxidant being compared to areas of spots containing known amounts of PANA.

3.0 APPARATUS

3.1 Black box, for viewing oil samples and paper chromatograms under UV-radiation. A simply constructed plywood box with the approximate dimensions 12 inches by 12 inches by 18 inches is adequate for this purpose. The front of the box is open and has a black cloth curtain along the front. Two holes on top of the box, 2 inches by 6 inches, permit entry of UV-light and allow an opening for viewing. A black cloth hood to cover the head and top of the box should be provided to exclude room light. The interior surfaces should be painted with a dull black finish.

3.2 UV-lamp. A Blak-Ray Model XX-4 long wave ultra-violet lamp (Ultra-Violet Products, Inc., South Pasadena, California) has proven satisfactory for illuminating samples of oil and paper chromatograms.

3.3 All other pieces of apparatus are identical with those described in Paragraphs 3.1 through 3.8, Method 22.

4.0 REAGENTS

4.1 All reagents are identical with those described in Paragraphs 4.1 through 4.11, Method 22.

5.0 QUALITATIVE DETECTION OF N-PHENYL-ALPHA-NAPHTHYLAMINE

5.1 PROCEDURE

5.1.1 UV-Radiation Fluorescence. Any oil containing even trace amounts of PANA exhibits a brilliant blue fluorescence when viewed in a black box under ultra-violet excitation. Few other compounds encountered in synthetic lubricants exhibit the intensity of fluorescence which PANA imparts; therefore, it is almost certain that PANA will be detected by the following chemical reactions if the oil exhibits this fluorescence.

5.1.2 Diazotization Reaction. Proceed as described in Paragraph 5.1.1, Method 22. A bright orange spot indicates the presence of PANA. Other amine-type antioxidants react with this reagent but do not give the intense orange color that is obtained with PANA.

5.1.3 Phosphomolybdic Acid Reaction. Proceed as described in Paragraph 5.1.2, Method 22. As with other amine-type antioxidants, PANA gives a dark blue spot, which is characteristic of amine-type antioxidants, but not of specific compounds.

6.0 QUALITATIVE SEPARATION AND IDENTIFICATION OF N-PHENYL-ALPHA-NAPHTHYLAMINE BY PAPER CHROMATOGRAPHY

6.1 PROCEDURE.

6.1.1 Preparation of the Paper Strip. Proceed as described in Paragraph 6.1.1, Method 22.

6.1.2 Preparation of the Sample. Proceed as described in Paragraph 6.1.2, Method 22.

6.1.3 Application of the Sample to the Paper. Proceed as described in Paragraph 6.1.3, Method 22.

6.1.4 Developing the Chromatogram. Proceed as described in Paragraph 6.1.4, Method 22.

6.1.5 Detecting the Spots. The spots on the dried paper strip are detected in the manner described in Paragraphs 5.1.1, 5.1.2, or 5.1.3. If the paper is viewed under UV-radiation, the spot should be outlined in the black box with a soft pencil. This fluorescence is not quenched by the diazotization or phosphomolybdic acid color reactions (5.1.2 and 5.1.3). PANA forms a bright orange spot with diazotization and a dark blue spot with phosphomolybdic acid. Proceed as described in Paragraph 6.1.5, Method 22.

6.2 DETERMINING THE R_f-VALUE. Proceed as described in Paragraph 6.2, Method 22. PANA has an R_f-value of 0.14; this value may be used to verify the results of the qualitative tests for PANA (5.1.1, 5.1.2, and 5.1.3). The presence of other discrete spots on the chromatogram indicates other antioxidants than PANA; their R_f-values should be checked against the known R_f-values of these antioxidants (Methods 22, 24, 25, 26 and 27).

6.3 COMPARISON WITH STANDARD SUBSTANCES. Proceed as described in Paragraphs 6.3.1 and 6.3.2, Method 22, using a 1 percent solution of PANA in benzene.

7.0 QUANTITATIVE DETERMINATION OF N-PHENYL-ALPHA-NAPHTHYLAMINE BY DESCENDING PAPER CHROMATOGRAPHY

7.1 PROCEDURE.

7.1.1 Preparation of the Paper Strips. Proceed as described in Paragraph 7.1.1, Method 22.

7.1.2 Application of Sample to the Paper. Proceed as described in Paragraph 7.1.2, Method 22, using 1, 2, and 3 percent solutions of PANA in benzene.

7.1.3 Development of the Chromatogram. Proceed as described in Paragraph 7.1.3, Method 22.

7.1.4 Detecting the Spots. The spots on the dried paper strips are first detected under UV-radiation in the black box, and are outlined with a soft pencil at this time. It is not necessary to perform the color reactions (5.1.2 or 5.1.3) to make the spots visible on the paper, although this may be done if desired. Repeated diazotization followed by the phosphomolybdic acid reaction will make the spots visible. Mark the center of each spot with a soft pencil, and determine the R_f-values of the spots (as described in Paragraph 6.2, Method 22).

7.2 QUANTITATIVE DETERMINATION OF N-PHENYL-ALPHA-NAPHTHYLAMINE. Proceed as described in Paragraphs 7.2.1 and 7.2.2, Method 22.

DETECTION OF p,p'-DIOCTYL-DIPHENYLAMINE

1.0 SCOPE

1.1 This method describes procedures for the qualitative detection of the antioxidant p,p'-dioctyl-diphenylamine (abbreviated DODPA) in synthetic lubricants and in the hexane-soluble fraction from synthetic greases (Note 1).

Note 1. Quantitative paper chromatographic determination of DODPA has not been investigated. Because of the unreactive nature of the compound, it seems unlikely that adequate color reactions for quantitative detection and determination of the compound can be developed. It is therefore suggested that the Kjeldahl nitrogen determination be employed to estimate the antioxidant in synthetic lubricants.

1.2 This method shall be employed for detection of DODPA in the eluent fractions from adsorption separations of synthetic lubricants (Method 16).

2.0 OUTLINE OF METHOD

2.1 DODPA is a relatively unreactive compound, and does not respond to the diazotization or glucose reactions but does react slowly with phosphomolybdic acid or chlorine. The latter two reactions are employed to detect DODPA in a lubricant. It is further identified by its R_f-value on a paper chromatogram and separated from other antioxidants on acetylcellulose (reversed phase) paper.

3.0 APPARATUS

3.1 The same apparatus listed in Paragraph 3.0, Method 22, shall be employed in this method. The descending chromatography apparatus and the planimeter are not required because of lack of a quantitative paper chromatographic technique for DODPA.

4.0 REAGENTS

4.1 Butyl acetate-pyridine-water (6:30:60, v/v) solvent combination. Measure the volumes of each of the reagent grade solvents in

separate graduated cylinders, and combine these in a glass-stoppered Erlenmeyer flask with shaking.

4.2 Phosphomolybdic acid solution (5 percent in ethanol-water (1:1, v/v)). Mix equal volumes of ethanol and water to make about 95 milliliters, and dissolve 5 grams of reagent grade phosphomolybdic acid in this mixture.

4.3 Ammonium hydroxide (sp. gr. 0.90), reagent grade.

4.4 p,p'-Dioctyl-diphenylamine solution (1 percent in benzene). Use reagent grade antioxidant and benzene.

4.5 Hydrochloric acid solution (alcoholic, 1:1, v/v). Mix equal volumes of HCl (sp. gr. 1.19) and ethanol.

4.6 Hydrochloric acid solution (4:1, v/v). Pour 4 volumes of HCl (sp. gr. 1.19) into 1 volume of distilled water.

4.7 Potassium permanganate, purified crystals.

4.8 Acetylcellulose paper. See Method 21 for preparation of this paper.

4.9 Normal Filter Paper. Whatman No. 1 filter paper roll, either 1 or 1-1/2 inches wide by 600 feet long is recommended.

4.10 Blotting Paper. Use any clean absorbent paper, such as brown paper towelling. Do not use tissue-weight paper.

5.0 QUALITATIVE DETECTION OF p,p'-DIOCTYL-DIPHENYLAMINE.

5.1 PROCEDURE.

5.1.1 Phosphomolybdic Acid Reaction. Proceed as described in Paragraph 5.1.2, Method 22. The reaction with DODPA is not immediate; the blue color appears gradually in about 15 minutes while the paper air-drys (do not dry the paper with heat after removing from the reagent solutions). This reaction does not distinguish individual compounds, only the group of amine-type antioxidants. Determination of the R_f-value of DODPA identifies the actual antioxidant.

5.1.2 Chlorine Reaction. Place a small droplet of the oil on a 1 inch square piece of normal filter paper, and allow the oil to diffuse through the paper for about 2 minutes. Dip the paper in an alcoholic solution of HCl (1:1, v/v), contained in a Petri dish. Blot excess moisture from the paper. Cover the bottom of a 50-milliliter beaker with $KMnO_4$ crystals, and add HCl solution (4:1) in small dropwise increments to generate chlorine gas. Hold the paper over, or place it on, the beaker. Chlorine reacts with amine-type antioxidants giving a red-brown spot with DODPA, a bright yellow spot with phenothiazine (PT), and a yellow-orange spot with N-phenyl-alpha-naphthylamine (PANA). Diphenylamine gives a purple-blue spot. This reaction is strong enough to allow identification of DODPA on the paper.

6.0 QUALITATIVE SEPARATION AND IDENTIFICATION OF p,p'-DIOCTYL-DIPHENYLAMINE BY PAPER CHROMATOGRAPHY

6.1 PROCEDURE.

6.1.1 Preparation of the Paper Strip. Proceed as described in Paragraph 6.1.1, Method 22.

6.1.2 Preparation of the Sample. Proceed as described in Paragraph 6.1.2, Method 22.

6.1.3 Application of Sample to the Paper. Proceed as described in Paragraph 6.1.3, Method 22.

6.1.4 Developing the Chromatogram. Proceed as described in Paragraph 6.1.4, Method 22.

6.1.5 Detecting the Spots. The spots on the dried paper strip are detected by immersion in phosphomolybdic acid solution in a Petri dish for about 5 seconds. Blot the paper by pressing between sheets of absorbent paper, and allow the phosphomolybdic acid to react for 1 minute. Place a few milliliters of NH_4OH (sp. gr. 0.90) on a watch glass or in a small beaker, and hold the chromatogram in the ammonia vapors until the yellow color of the phosphomolybdic acid has been discharged. Repeat the acid and ammonia treatment in sequence twice. Hang the moist paper to air dry for ten minutes before drying in the oven or in front of the hot air fan (do not dry immediately). A blue spot will appear at the starting point if DODPA is present in the oil.

If and when a spot does appear, outline it with a soft lead pencil on a glass surface, taking care not to tear the paper. After the paper is dried, the pencilled outline of the spot may be re-traced to darken the first pencil line.

6.2 DETERMINING THE R_f-VALUE. Proceed as described in Paragraph 6.2, Method 22. The R_f-value of DODPA in this solvent combination is 0.01, indicating that the antioxidant does not travel from the starting point, while all other antioxidants travel to R_f-values of 0.11 and above. The appearance of a blue spot at this location on the chromatogram verifies the results of the qualitative tests for DODPA (5.1.1 and 5.1.2). The presence of other discrete spots on the chromatogram indicates antioxidants other than DODPA; their R_f-values should be checked against the know R_f-values of these antioxidants (Methods 22, 23, 25, 26, and 27).

6.3 COMPARISON WITH STANDARD SUBSTANCES. Proceed as described in Paragraphs 6.2.1 and 6.2.2, Method 22, using a 1 percent solution of DODPA in benzene.

7.0 QUANTITATIVE DETERMINATION OF p,p'-DIOCTYLDIPHENYLAMINE

7.1 Since quantitative paper chromatographic methods for the determination of DODPA have not been developed, it is suggested that the analyst employ the standard Kjeldahl nitrogen determination, either macro or micro, to obtain the nitrogen content of the oil. The analyst must determine by Method 15 and other pertinent analyses whether other nitrogen-containing compounds are present in the oil. If so, these compounds must either be separated out, or determined quantitatively so that the nitrogen content can be corrected by subtracting the nitrogen contents of these known compounds, the remainder being attributed to DODPA. Multiplication of this value by 28.1 gives the content of DODPA in the sample oil.

DETECTION OF QUINIZARIN

1.0 SCOPE

1.1 This method describes the procedure for qualitative detection of the antioxidant quinizarin (abbreviated Qz) in synthetic lubricants and in the hexane-soluble fraction from synthetic greases (Note 1). Amine-type antioxidants and the hindered phenol antioxidants do not interfere with the test.

1.2 This method shall be employed for detection of Qz in the eluent fractions from adsorption separations of synthetic lubricants (Method 16.)

Note 1. Quantitative paper chromatographic determination of Qz has not been investigated.

2.0 OUTLINE OF METHOD

2.1 Qz forms a complex compound with thorium nitrate and other metal salts, as well as with ammonia, most of these compounds having a bright pink color. The test involves preparation of filter paper impregnated with thorium nitrate, followed by application of the sample oil. In the presence of Qz, a bright pink color develops slowly. Other antioxidants do not interfere. This technique will detect as little as 0.01 percent Qz in a synthetic lubricant.

3.0 APPARATUS

3.1 The same apparatus listed in Paragraph 3.0, Method 22, shall be employed in this method. The descending chromatography apparatus and the planimeter are not required because of lack of a quantitative paper chromatographic technique for Qz.

4.0 REAGENTS

4.1 Butyl acetate-pyridine-water (6:30:42, v/v) solvent combination. Measure the volumes of each of the reagent grade solvents in separate graduated cylinders, and combine these in a glass-stoppered Erlenmeyer flask with shaking.

4.2 Thorium nitrate, $Th(NO_3)_4 \cdot 4H_2O$, solution (5 percent). Use reagent grade crystals.

4.3 Ammonium hydroxide (sp. gr. 0.90), reagent grade.

4.4 Quinizarin solution (0.02 percent in benzene).

4.5 Acetylcellulose paper. See Method 21 for preparation of this paper.

4.6 Normal filter paper. Whatman No. 1 filter paper roll, either 1 or 1-1/2 inches wide by 600 feet long is recommended.

4.7 Blotting Paper. Use any clean absorbent paper, such as brown paper towelling. Do not use tissue-weight paper.

5.0 QUALITATIVE DETECTION OF QUINIZARIN

5.1 PROCEDURE

5.1.1 Thorium Nitrate Reaction. Dip a 1 inch square piece of normal filter paper in a 5 percent solution of thorium nitrate contained in a Petri dish. Blot the paper by pressing between sheets of clean, dry absorbent paper. Hang the impregnated paper to air-dry. Place a droplet of the sample oil on the dry paper, and set aside for several minutes. The appearance of a bright pink spot indicates the presence of Qz. A comparison spot of 0.02 percent Qz in benzene should be run on a second piece of thorium nitrate paper. Frequently development of the colored spot is rather slow, so at least 10 minutes should be allowed before drawing conclusions about the test.

5.1.2 Ammonia Reaction. Frequently Qz can be detected simply by placing a droplet of sample oil on a 1 inch square of normal filter paper, allowing the oil to diffuse into the paper, and holding over a watch glass containing a few milliliters of NH_4OH (sp. gr. 0.90). A pink spot will form, but will disappear almost immediately upon removal from the ammonia atmosphere.

6.0 QUALITATIVE SEPARATION AND IDENTIFICATION OF QUINIZARIN BY PAPER CHROMATOGRAPHY.

6.1 PROCEDURE.

6.1.1 Preparation of the Paper Strip. Proceed as described in Paragraph 6.1.1, Method 22.

6.1.2 Preparation of the Sample. Proceed as described in Paragraph 6.1.2, Method 22.

6.1.3 Application of Sample to the Paper. Proceed as described in Paragraph 6.1.3, Method 22.

6.1.4 Developing the Chromatrogram. Proceed as described in Paragraph 6.1.4, Method 22, using the solvent combination butyl acetate-pyridine-water (6:30:42, v/v). Do not dry the paper strip after removal from the chamber and after marking the solvent front. Instead proceed immediately with Paragraph 6.1.5.

6.1.5 DETECTING THE SPOTS.

6.1.5.1 The spot of Qz may be distinguished immediately upon removal from the chromatography cylinder after marking the solvent front and blotting the paper to remove excess solvent combination. Place a few milliliters of NH_4OH (sp. gr. 0.90) in a hydrometer cylinder, stopper, and shake to saturate the atmosphere with ammonia. Remove the stopper and hold the entire paper strip in the cylinder, but do not let the paper touch the NH_4OH on the walls or in the bottom of the cylinder. A faint pink spot indicates the presence of Qz in the sample oil. Remove the paper quickly from the cylinder, and mark the outline and center of the spot before it disappears with a soft lead pencil, taking care not to tear the paper.

6.1.5.2 If a test for phenol-type or amine-type antioxidants is to be performed on the sample of oil, the same paper strip which has just been tested for Qz may be employed. Perform the phosphomolybdic acid-ammonia reaction on the still-damp strip as described in Paragraph 6.1.5, Method 24, to detect any phenol or amine antioxidants which might be present.

6.2 DETERMINING THE R_f-VALUE. Proceed as described in Paragraph 6.2, Method 22. In this solvent combination Qz has an R_f-value of 0.33. Other antioxidants do not interfere in this test because Qz is detected before the others, and they do not react with the reagents employed for detection of Qz.

DETECTION AND DETERMINATION OF 2,4-DIMETHYL-6-TERTIARYBUTYLPHENOL

1.0 SCOPE

1.1 This method describes procedures for the qualitative detection and quantitative determination of the antioxidant 2,4-dimethyl-6-tertiarybutylphenol (abbreviated 24Ph) when contained in solution in inert solvents such as benzene, hexane, etc. The tests do not apply to detection of the phenol in synthetic lubricants or greases. No tests or methods of separation of this phenol from lubricants and greases have been found. This method is included to provide information on the determination of this hindered phenol in commercial products.

2.0 OUTLINE OF METHOD

2.1 24Ph is detected by its reaction with phosphomolybdic acid and ammonia, forming a blue spot on a paper square. The compound may be separated from other hindered phenols by ascending paper chromatography and identified on the paper by its R_f-value. Because of its high volatility the compound must be run either at reduced temperatures on normal paper or at room temperature on acetylcellulose paper (Note 1). Quantitative determinations are made on acetylcellulose paper, using the descending chromatographic technique and phosphomolybdic acid-ammonia to detect the spots. Comparison with spots of known concentration establishes the amount of hindered phenol in the solution being tested.

Note 1. The acetylcellulose chromatogram requires about 1/4 the development time of the normal paper chromatogram. Hence the effect of volatility is reduced sharply by using the reversed phase technique.

3.0 APPARATUS

3.1 The same apparatus listed in Paragraph 3.0, Method 22, shall be employed in this method.

4.0 REAGENTS

4.1 Butyl acetate-pyridine-water (6:30:42, v/v) solvent combination. Measure the volumes of each of the reagent grade solvents in

separate graduated cylinders, and combine these in a glass-stoppered Erlenmeyer flask with shaking.

4.2 Phosphomolybdic acid solution (5 percent in ethanol-water (1:1, v/v)). Mix equal volumes of ethanol and water to make about 95 milliliters, and dissolve 5 grams of reagent grade phosphomolybdic acid in this mixture.

4.3 Ammonium hydroxide (sp. gr. 0.90), reagent grade.

4.4 2,4-Dimethyl-6-tertiarybutylphenol solutions (0.50, 0.75, 1.00, 1.50, 2.00, and 2.50 percent in benzene). Use reagent grade or recrystallized phenol and reagent grade benzene.

4.5 Acetylcellulose paper. See Method 21 for preparation of this paper.

4.6 Blotting paper. Use any clean absorbent paper, such as brown paper towelling. Do not use tissue-weight paper.

5.0 QUALITATIVE DETECTION OF 2,4-DIMETHYL-6-TERTIARYBUTYLPHENOL

5.1 PROCEDURE.

5.1.1 Phosphomolybdic Acid-Ammonia Reaction. Place a droplet of the solution to be tested on a 1 inch square of acetylcellulose paper. Allow the volatile solvent to evaporate in the air (do not dry in the oven or in front of the hot air fan). Dip the paper in a Petri dish containing alcoholic phosphomolybdic acid solution for about 10 seconds. Blot the paper by pressing between sheets of absorbent paper. Place a few drops of NH_4OH (sp. gr. 0.90) on a watch glass or in a small beaker, and hold the paper in the ammonia fumes until all of the yellow color of the phosphomolybdic acid has been discharged. The appearance of a blue spot is an indication of the presence of an antioxidant. This test is not definitive for 24Ph, but only indicates the presence of phenol and amine antioxidants in the solution. Positive identification must be obtained by the R_f-value of the substance on a qualitative paper chromatogram (6.0).

6.0 QUALITATIVE SEPARATION AND IDENTIFICATION OF 2,4-DIMETHYL-6-TERTIARYBUTYLPHENOL BY PAPER CHROMATOGRAPHY

6.1 PROCEDURE

6.1.1 Preparation of the Paper Strip. Proceed as described in Paragraph 6.1.1, Method 22.

6.1.2 Preparation of the Sample. The sample applied to the paper (in a 2.5 lambda spot) should have a concentration of about 1 percent 24Ph; therefore adjust the solution to be tested approximately to this concentration; if the concentration of 24Ph is too high, the spot will spread out and obscure other spots of antioxidants, and will lower the accuracy of the R_f-value determination. Several preliminary runs are usually necessary to establish the best conditions for detecting 24Ph.

6.1.3 Application of the Sample to the Paper. Proceed as described in Paragraph 6.1.3, Method 22.

6.1.4 Developing the Chromatogram. Proceed as described in Paragraph 6.1.4, Method 22, but do not saturate the paper overnight because the phenol will volatilize, and do not dry the paper after removing it from the cylinder and marking the solvent front. Proceed with detection of the spots immediately.

6.1.5 Detecting the Spots on the Paper.

6.1.5.1 Blot the wet paper chromatogram by pressing between sheets of absorbent paper. Draw the entire paper strip through the alcoholic phosphomolybdic acid solution contained in a Petri dish, covering both sides of the paper with the reagent. Place the strip between sheets of absorbent paper to absorb excess moisture, and allow the reagent to react for about one minute. Place a few milliliters of NH_4OH (sp. gr. 0.90) in a hydrometer cylinder, stopper, and shake to saturate the atmosphere with ammonia. Remove the stopper and hold the entire paper strip in the cylinder, but do not let the paper touch the NH_4OH on the walls or in the bottom of the cylinder. Hold the paper in the ammonia until the yellow color of the phosphomolybdic acid has been discharged. Spots of both phenol and amine antioxidants will appear blue on the white paper. Remove the paper from the cylinder, and on a clean glass plate outline and mark the centers of all spots appearing on the paper with a soft lead pencil, taking care to avoid tearing the paper. Place the chromatogram in a drying oven at 110°C. for ten minutes or in front of a hot air fan until dry.

6.1.5.2 Detection of Quinizarin. If it is desired to test for the presence of quinizarin in the solution, it is necessary that this be done before performing the above reaction for hindered phenols. Proceed as described in Paragraph 6.1.5.1, Method 25, to detect quinizarin, and then proceed as described above (6.1.5.1) to detect hindered phenols.

6.2 DETERMINING THE R_f-VALUE. Proceed as described in Paragraph 6.2, Method 22. The R_f-value of the 24Ph is 0.42. With this solvent combination, the R_f-values of other antioxidants are as follows:

Phenothiazine = 0.35
N-Phenyl-alpha-naphthylamine = 0.28
p,p'-Dioctyl-diphenylamine = 0.02
Quinizarin = 0.33
2,6-Ditertiarybutyl-4-methylphenol = 0.31

It can be seen that any spots formed by the above antioxidants will not fall at the same R_f-value as 24Ph. 24Ph can therefore be identified by its R_f-value. If other spots appear on the chromatogram, they should be labelled and identified by the above list of R_f-values and by further paper chromatographic runs with other solvent combinations (Methods 22, 23, 24, 25 and 27).

7.0 QUANTITATIVE DETERMINATION OF 2,4-DIMETHYL-6-TERTIARYBUTYLPHENOL BY DESCENDING PAPER CHROMATOGRAPHY

7.1 PROCEDURE.

7.1.1 Preparation of the Paper Strips. Proceed as described in Paragraph 7.1.1, Method 22. Additional strips containing spots of known concentrations of 24Ph may be run at the same time if close comparisons with the unknown are desired. It is suggested that 6 strips be run containing 24Ph concentrations of 0.50, 1.00, 1.50, 2.00, and 2.50 percent in benzene, and one spot of the unknown solution. Adjust the concentration of the unknown solution by the use of preliminary runs to fall within the percent limits of the known concentrations.

7.1.2 Application of the Sample to the Paper. Proceed as described in Paragraph 7.1.2, Method 22, using the strips and concentrations suggested in Paragraph 7.1.1 above, and the unknown solution.

Because of the volatility of 24Ph, the spots should not be placed on the paper until one hour before starting the run; saturate the atmosphere and paper overnight, remove the paper from the chamber and quickly place the spots on the paper; replace the paper and start the run in one hour.

7.1.3 Development of the Chromatograms. Proceed as described in Paragraph 7.1.3, Method 22.

7.1.4 Detecting the Spots. Detect the spots as described in Paragraph 6.1.5.1 above.

7.1.5 Quantitative Determination of 2,4-Dimethyl-6-Tertiary-Butylphenol. Proceed as described in Paragraphs 7.2.1 and 7.2.2, Method 22.

DETECTION AND DETERMINATION OF 2,6-DITERTIARYBUTYL-4-METHYLPHENOL

1.0 SCOPE

1.1 This method describes procedures for the qualitative detection and quantitative determination of the antioxidant 2,6-ditertiarybutyl-4-methylphenol (abbreviated 26Ph) when contained in solution in inert solvents such as benzene, hexane, etc. The tests do not apply to detection of the phenol in synthetic lubricants or greases. No tests or methods of separation of this phenol from lubricants and greases have been found. This method is included to provide information on the determination of this hindered phenol in commercial products.

2.0 OUTLINE OF METHOD

2.1 26Ph is detected by its reaction with phosphomolybdic acid and ammonia, forming a blue spot on a paper square. The compound may be separated from other hindered phenols by ascending paper chromatography and identified on the paper by its R_f-value. Because of its high volatility the compound must be run either at reduced temperatures on normal paper or at room temperature on acetylcellulose paper (Note 1). Quantitative determinations are made on acetylcellulose paper, using the descending chromatographic technique and phosphomolybdic acid-ammonia to detect the spots. Comparison with spots of known concentration establishes the exact amount of hindered phenol in the solution being tested.

Note 1. Because the reversed phase acetylcellulose chromatogram develops in about 1/4 the time required for a normal paper chromatogram, the effect of volatility is reduced to an extent that reduced temperatures are not required.

3.0 APPARATUS

3.1 The same apparatus listed in Paragraph 3.0, Method 22, shall be employed in this method.

4.0 REAGENTS

4.1 Butyl acetate-pyridine-water (6:30:42, v/v) solvent combination. Measure the volumes of each of the reagent grade solvents in separate graduated cylinders, and combine these in a glass-stoppered Erlenmeyer flask with shaking.

4.2 Phosphomolybdic acid solution (5 percent in ethanol-water (1:1, v/v)). Mix equal volumes of ethanol and water to make about 95 milliliters, and dissolve 5 grams of reagent grade phosphomolybdic acid in this mixture.

4.3 Ammonium hydroxide (sp. gr. 0.90), reagent grade.

4.4 2,4-Dimethyl-6-tertiarybutylphenol solutions (0.50, 0.75, 1.00, 1.50, 2.00 and 2.50 percent in benzene). Use reagent grade or recrystallized phenol and reagent grade benzene.

4.5 Acetylcellulose paper. See Method 21 for preparation of this paper.

4.6 Blotting paper. Use any clean absorbent paper, such as brown paper towelling. Do not use tissue-weight paper.

5.0 QUALITATIVE DETECTION OF 2,6-DITERTIARYBUTYL-4-METHYLPHENOL

5.1 PROCEDURE.

5.1.1 Phosphomolybdic Acid-Ammonia Reaction. Place a droplet of the solution to be tested on a 1 inch square of acetylcellulose paper. Allow the volatile solvent to evaporate in the air (do not dry in the oven or in front of the hot air fan). Dip the paper in a Petri dish containing alcoholic phosphomolybdic acid solution for about 10 seconds. Blot the paper by pressing between sheets of absorbent paper. Place a few drops of NH_4OH (sp. gr. 0.90) on a watch glass or in a small beaker, and hold the paper in the ammonia fumes until all of the yellow color of the phosphomolybdic acid has been discharged. The appearance of a blue spot is an indication of the presence of an antioxidant. This test is not definitive for 26Ph, but only indicates the presence of phenol and amine antioxidants in the solution. Positive identification must be obtained by the R_f-value of the substance on a qualitative paper chromatogram (6.0).

6.0 QUALITATIVE SEPARATION AND IDENTIFICATION OF 2,6-DITERTIARYBUTYL-4-METHYLPHENOL BY PAPER CHROMATOGRAPHY

6.1 PROCEDURE

6.1.1 Preparation of the Paper Strip. Proceed as described in Paragraph 6.1.1, Method 22.

6.1.2 Preparation of the Sample. The sample applied to the paper (in a 2.5 lambda spot) should have a concentration of about 1 percent 26Ph; therefore adjust the solution to be tested approximately to this concentration; if the concentration of 26Ph is too high, the spot will spread out and obscure other spots of antioxidants, and will lower the accuracy of the R_f-value determination. Several preliminary runs are usually necessary to establish the best conditions for detecting 26Ph.

6.1.3 Application of the Sample to the Paper. Proceed as described in Paragraph 6.1.3, Method 22.

6.1.4 Developing the Chromatogram. Proceed as described in Paragraph 6.1.4, Method 22, but do not saturate the paper overnight because the phenol will volatize, and do not dry the paper after removing it from the cylinder and marking the solvent front. Proceed with detection of the spots immediately.

6.1.5 Detecting the Spots on the Paper.

6.1.5.1 Blot the wet paper chromatogram by pressing between sheets of absorbent paper. Draw the entire paper strip through the alcoholic phosphomolybdic acid solution contained in a Petri dish, covering both sides of the paper with the reagent. Place the strip between sheets of absorbent paper to absorb excess moisture, and allow the reagent to react for about one minute. Place a few milliliters of NH_4OH (sp. gr. 0.90) in a hydrometer cylinder, stopper, and shake to saturate the atmosphere with ammonia. Remove the stopper and hold the entire paper strip in the cylinder, but do not let the paper touch the NH_4OH on the walls or in the bottom of the cylinder. Hold the paper in the ammonia until the yellow color of the phosphomolybdic acid has been discharged. Spots of both phenol and amine antioxidants will appear blue on the white paper. Remove the paper from the cylinder, and on a clean glass plate outline and

mark the centers of all spots appearing on the paper with a soft lead pencil, taking care to avoid tearing the paper. Place the chromatogram in a drying oven at 110°C. for 10 minutes or in front of a hot air fan until dry.

6.1.5.2 Detection of Quinizarin. If it is desired to test for the presence of quinizarin in the solution, it is necessary that this be done before performing the above reaction for hindered phenols. Proceed as described in Paragraph 6.1.5.1, Method 25 to detect quinizarin, and then proceed as described above (6.1.5.1) to detect hindered phenols.

6.2 DETERMINING THE R_f-VALUE. Proceed as described in Paragraph 6.2, Method 22. The R_f-value of 26Ph is 0.31. With this solvent combination, the R_f-values of other antioxidants are as follows:

Phenothiazine = 0.35
N-Phenyl-alpha-naphthylamine = 0.28
p,p'-Dioctyl-diphenylamine = 0.02
Quinizarin = 0.33
2,4-Dimethyl-6-Tertiarybutylphenol = 0.42

It can be seen that any spots formed by the above antioxidants will not fall at the same R_f-value as 26Ph. 26Ph can therefore be identified by its R_f-value. If other spots appear on the chromatogram, they should be labelled and identified by the above list of R_f-values and by further paper chromatographic runs with other solvent combinations (Methods 22, 23, 24, 25, and 27).

7.0 QUANTITATIVE DETERMINATION OF 2,6-DITERTIARY-BUTYL-4-METHYLPHENOL

7.1 PROCEDURE

7.1.1 Preparation of the Paper Strips. Proceed as described in Paragraph 7.1.1, Method 22. Additional strips containing spots of known concentrations of 26Ph may be run at the same time if close comparisons with the unknown are desired. It is suggested that 6 strips be run containing known 26Ph concentrations of 0.50, 1.00, 1.50, 2.00, and 2.50 percent in benzene, and one spot of the unknown solution. Adjust the concentration of the unknown solution by the use of preliminary runs to fall within the percent limits of the known concentrations.

7.1.2 Application of the Sample to the Paper. Proceed as described in Paragraph 7.1.2, Method 22, using the strips and concentrations suggested in Paragraph 7.1.1 above, and an unknown solution. Because of the volatility of 26Ph, the spots should not be placed on the paper until one hour before starting the run; saturate the atmosphere and paper overnight, remove the paper from the chamber and quickly place the spots on the paper; replace the paper and start the determination in one hour.

7.1.3 Development of the Chromatograms. Proceed as described in Paragraph 7.1.3, Method 22.

7.1.4 Detecting the Spots. Detect the spots as described in Paragraph 6.1.5.1 above.

7.1.5 Quantitative Determination of 2,6-Ditertiarybutyl-4-Methylphenol. Proceed as described in Paragraphs 7.2.1 and 7.2.2, Method 22.

DETECTION AND DETERMINATION OF DILAURYL SELENIDE

1.0 SCOPE

1.1 This method describes the procedure for detection and determination of selenium in synthetic lubricants and greases. The method is not restricted by the type of selenium compound present, because selenium compounds are oxidized quantitatively to selenic acid during the analysis. Selenium antioxidants employed in synthetic lubricants are usually divalent selenium compounds with two alkyl substituents. They do not react directly with the usual detection reagents; it is therefore necessary to destroy the organic matter in the compound and to convert the divalent selenium into selenic acid, which can be detected and determined directly. Other metals or compounds encountered in synthetic lubricants or greases do not interfere with this color reaction for selenium.

2.0 QUALITATIVE DETECTION OF SELENIUM.

2.1 OUTLINE OF METHOD.

2.1.1 The organic components in the lubricant or grease are oxidized by sodium peroxide and sodium carbonate in a platinum wire loop, converting selenium to selenate ion. The resulting melt is dissolved in dilute hydrochloric acid, and a drop of the solution is treated with asymmetric diphenylhydrazine in the presence of glacial acetic acid to form a bright red-violet color.

3.0 REAGENTS

3.1 Asymmetric diphenylhydrazine (1 percent in glacial acetic acid).

3.2 Acetic acid, glacial, reagent grade.

3.3 Hydrochloric acid (2N).

3.4 Sodium peroxide, anhydrous, reagent grade.

3.5 Sodium carbonate, anhydrous, reagent grade.

3.6 Hydrochloric acid solution (1:1, v/v). Pour one volume of HCl (sp. gr. 1.19) into an equal volume of distilled water.

4.0 PROCEDURE.

4.1 REMOVAL OF ORGANIC MATTER.

4.1.1 Mix 0.1 gram of anhydrous Na_2CO_3, 0.1 gram Na_2O_2, and three drops of the synthetic lubricant or an equivalent quantity of grease into a smooth paste with a spatula in a spot plate depression. Make a 1/8" diameter loop in the end of a platinum wire, and clean the wire thoroughly by alternately dipping into HCl (1:1) and heating to redness in a Bunsen burner flame until no color is imparted to the flame by the wire. Dip the loop into the reaction paste and heat in the flame until all reaction has ceased. Re-dip the loop into the reaction paste and fuse. Repeat this procedure several times until a 1/16" thick bead is formed. Heat for several minutes until the bead becomes water-white. Cool, unwind the wire, and dissolve the bead in 2 to 3 milliliters of distilled water in a small beaker. Add 2 or 3 milliliters of HCl (1:1), heat to boiling, and cool (Note 1).

Note 1. This reduces selenic acid to selenious acid, H_2SeO_3, which can be detected by any one of several sensitive color reactions.

4.2 ASYMMETRIC DIPHENYLHYDRAZINE REACTION FOR SELENIUM.

4.2.1 Place several drops of the H_2SeO_3 solution (4.1) in the depression of a spot plate, and add four or five drops of asymmetric diphenylhydrazine (1% in glacial acetic acid). Mix with a stirring rod and allow to stand for several minutes. If a violet color has not appeared after this time, add one drop of HCl (2N) to increase the acidity. The appearance of a red-violet color indicates the presence of selenium, the intensity of the color deepening when the concentration of selenium is high (Note 2).

Note 2. The concentration of selenium in many synthetic lubricants and greases is so low that care must be taken to have enough sample in the bead to give the test for selenium. If only one drop of oil or an equivalent amount of grease is mixed with the

fusion mixture, the test is likely to be questionable, but if about ten drops or the equivalent amount of grease are mixed and a large bead is obtained, then a definite test will be given. Because of these low concentrations the color usually will not appear for several minutes; therefore, it is necessary to wait at least 5 minutes to be sure that the color reaction is negative or positive.

5.0 QUANTITATIVE DETERMINATION OF SELENIUM

5.1 OUTLINE OF METHOD.

5.1.1 The sample is oxidized by combustion in a bomb containing oxygen under pressure. Selenium, as selenate in the bomb washings, is determined gravimetrically as elemental selenium.

5.2 SAFETY.

5.2.1 Strict adherence to all of the provisions prescribed hereafter assures against explosive rupture of the bomb, or a blow-out, provided the bomb is of proper design and construction and in good mechanical condition. It is desirable, however, that the bomb be enclosed in a shield of steel plate at least 1/2 inch thick, or equivalent protection provided against unforseeable contingencies.

6.0 APPARATUS AND MATERIALS

6.1 Bomb, having a capacity of not less than 300 milliliters which will not leak during the test. It should be constructed so that quantitative recovery of liquids from the bomb after ignition may be readily achieved. The inner surface of the bomb may be made of stainless steel or other material that will not be affected by the combustion process or products. Materials used in the bomb assembly, such as the head gasket and lead-wire insulation, shall be resistant to heat and chemical action, and shall not undergo any reaction that will affect the selenium content of the liquid in the bomb. (A Parr No. 1102 Single-Valve Oxygen Combustion Bomb, or its equivalent, is recommended for these determinations).

6.2 Sample cup, platinum or inert metal or alloy designed to fit in the loop provided in one electrode in the bomb assembly, and weighing approximately 10 grams.

6.3 Firing wire, platinum, approximately No. 26 B. & S. gage.

6.4 Ignition circuit, capable of supplying sufficient current to ignite the cotton wicking or nylon thread without melting the wire. (CAUTION: The switch in the ignition circuit shall be a type which remains open, except when held in closed position by the operator.

6.5 Cotton wicking or nylon sewing thread, white.

6.6 Sulfur dioxide gas generator, consisting of (1) 125-milliliter capacity dropping funnel, (2) 250-milliliter Erlenmeyer-shaped suction flask, (3) a one-hole rubber stopper which holds the dropping funnel and fits in the neck of the suction funnel, and (4) an L-shaped glass delivery tube (3 millimeter outside diameter) which is attached to the delivery arm of the suction flask by a 1 inch length of rubber tube, the long arm of the L extending downward for delivery of SO_2 gas into the H_2SeO_3-containing solution.

6.8 Fritted glass filter funnel, Pyrex glass, Buchner type, with medium porosity fritted disc (similar to Corning Catalog No. 36060). A 10 millimeter fritted disc with 30 millimeter wall-height above the disc is convenient for this determination. A suction flask and rubber stopper to fit the filter funnel are also necessary.

6.9 Analytical balance, capable of weighing 0.1 milligram.

7.0 REAGENTS.

7.1 Sodium carbonate solution (5 percent). Dissolve 135 grams of $Na_2CO_3 \cdot 10H_2O$ or its equivalent in distilled water and dilute to one liter.

7.2 Oxygen, free of combustible material and sulfur or selenium compounds, available at a pressure of 40 atmospheres.

7.3 Saturated methyl orange solution. Prepare a saturated methyl orange solution by placing about 20 grams of methyl orange indicator in a small bottle with 50 milliliters of distilled water. Shake well, and allow to saturate overnight.

7.4 Wash solution. Pipette 1 milliliter of saturated methyl orange solution (7.3) into a one liter volumetric flask, and fill to the mark with distilled water.

7.5 Hydrochloric acid (sp. gr. 1.19).

7.6 Hydrochloric acid solution, (1:1). See Paragraph 3.6.

7.7 Sodium bisulfite, solid, anhydrous, reagent grade.

7.8 Nitric acid (sp. gr. 1.42), reagent grade.

7.9 White Oil, refined, sulphur-and selenium-free, or a pure dibasic acid ester such as dioctyl sebacate.

8.0 PROCEDURE.

8.1 PREPARATION OF BOMB AND SAMPLE. Cut a piece of firing wire 100 millimeters in length, coil the middle section (about 20 millimeters) and attach the free ends to the electrodes as described in the instruction manual supplied with the oxygen bomb. Arrange the coil so that it will be above and to one side of the sample cup. Insert between the loop of the coil a wisp of cotton or nylon thread of such length that one end will extend into the sample cup. Place about 5 milliliters of Na_2CO_3 solution in the bomb (Note 3), and rotate the bomb in such a manner that the interior surface is moistened by the solution. Weigh a 0.8 gram sample of the oil or grease in a freshly cleaned sample cup (Note 4), weighed to 0.1 milligram. (CAUTION: DO NOT USE MORE THAN 1 GRAM TOTAL OF SAMPLE OR OTHER SULFUR OR SELENIUM-FREE COMBUSTIBLE MATERIAL!)

Note 3. After repeated use of the bomb, a film may be noticed on the inner surface. This dullness should be removed by periodic polishing of the bomb. A satisfactory method for doing this is to rotate the bomb in a lathe at about 300 r.p.m. and polish the inside surface with grit number 2/0, or equivalent paper*, coated with light machine oil to prevent cutting, and then with a paste of grit-free chromic oxide* and water. This procedure will remove all but very deep pits and put a high polish on the surface. Before using the bomb it should be washed with soap and water to remove oil or paste left from the polishing operation.

*Emery polishing paper grit #2/0 may be purchased from the Behr-Manning Co., Troy, New York. Chromic oxide may be purchased from J. T. Baker & Co., Phillipsburg, N. J.

Note 4. The sample cup should be polished with the emery paper described in Note 3* to a high polished-surface both inside and out before each determination. The sample cup should not be touched with the hands after it has been cleaned, but rather should be handled with clean metal tweezers or forceps.

8.2 ADDITION OF OXYGEN. Place the sample cup in position in the electrode loop and arrange the cotton wisp or nylon thread so that the end dips into the sample. Assemble the bomb and tighten the cover securely with finger pressure, but under no circumstances should the cover be tightened with a wrench or mechanical device. (CAUTION: Do not add oxygen or ignite the sample if the bomb has been jarred, dropped, or tilted.) Attach the pressure regulator supplied with the bomb to the oxygen cylinder, taking care that the threads and fittings on both the tank and the regulator have been washed clean of traces of grease or dirt. Tighten the regulator on the tank with a large wrench. Remove the pressure relief valve from the top of the bomb and attach the delivery end of the regulator with moderate tightening, and admit oxygen slowly until a pressure of 35 atmospheres is recorded on the pressure regulator. Stop the oxygen flow, release the pressure in the oxygen line, and detach the oxygen inlet valve from the bomb. Replace the pressure relief valve and tighten with the fingers. Do not use a wrench to tighten this valve.

8.3 COMBUSTION. Immerse the bomb in a cold water bath. Connect the terminals to the open electrical circuit, and close the circuit to ignite the sample. Remove the bomb from the bath after 10 minutes. Release the pressure at a slow, uniform rate such that the operation requires not less than one minute. Open the bomb and examine the contents. If traces of unburned oil or sooty deposits are found, discard the determination and thoroughly clean the bomb before again putting it into use.

8.4 COLLECTION OF SELENIUM SOLUTION. If the combustion operation has been successful, all of the interior surfaces of the bomb, the sample cup, and the electrodes, will be covered with fine droplets of water (Note 5). Wash all parts of the interior, including the combustion capsule, check valve, and release valve, with a fine stream of distilled water containing methyl orange indicator. It is convenient to have the indicator-containing distilled water in a plastic wash bottle with a fine

*Emery polishing paper grit #2/0 may be purchased from the Behr-Manning Co., Troy, New York. Chromic oxide may be purchased from J. T. Baker & Co., Phillipsburg, N. J.

plastic delivery tip. Collect the washings in a 600 milliliter beaker, having a mark to indicate 150 milliliters. Use particular care to prevent loss of the liquid contents of the bomb. Remove any precipitate in the bomb by means of a rubber policeman. Wash the base of the electrodes until the washings are neutral to the indicator. (The volume of washings is normally in excess of 300 milliliters.) Place the sample cup in a 50 milliliter beaker and add 2 milliliters of HCl (1:1) and enough distilled water just to cover the cup. Heat the contents of the beaker to just below the boiling point for 3 or 4 minutes and add to the beaker containing the bomb washings. Wash the sample cup and the beaker thoroughly with distilled water. Remove any precipitate in the cup by means of a rubber policeman. Add the washings from the cup and the 50-milliliter beaker and the precipitate, if any, to the bomb washings in the 600-milliliter beaker. Filter through a rapid qualitative paper to remove particles of fuse wire or any other foreign material, and wash the filter thoroughly.

Note 5. If, upon opening the bomb, a large amount of fluffy white residue is found, the sample contained a silicate ester, disiloxane, or silicone base-oil. It has been shown that the presence of silicon-containing base-oils in the sample does not interfere with the selenium determination to an extent which would preclude use of the determination.

8.5 DETERMINATION OF SELENIUM.

8.5.1 Precipitation of the Selenium. Add sufficient concentrated HCl to the filtrate in the 600-milliliter beaker to show an acid reaction with the indicator. Place a large watch glass on top of the beaker and evaporate the contents (approximately 300 milliliters) down to 150 milliliters, as indicated by the mark on the side of the beaker. If silica is present, it will precipitate during boiling. Cool and filter the solution through a quantitative filter paper, the filter being washed with indicator-containing distilled water. Add an equal volume of concentrated HCl to the filtrate and cool to below 20°C. Maintain the solution at or slightly below this temperature during the subsequent addition of SO_2 gas. Prepare the sulphur dioxide gas generator described previously (6.8). Place 25 grams of solid $NaHSO_3$ reagent in the bottom of the suction flask, and fill the addition funnel with HCl (1:1). Set the generator in such a way that the end of the delivery tube reaches to the bottom of the beaker containing the acidified H_2SeO_3 solution. Allow the HCl (1:1) to flow onto the $NaHSO_3$ at a rate of about one drop per second or slower. Sulphur

dioxide is immediately evolved and passes through the delivery tube into the solution. Bubble the gas through the solution at this rate for about fifteen minutes. Selenium begins to precipitate immediately as a bright orange-red, finely divided material. After thoroughly saturating the selenium-containing solution, stop the flow of HCl into the gas generator, and raise the generator so that the delivery tube is above the surface of the selenium solution. With a wash bottle and rubber policeman remove all particles of selenium which cling to the delivery tube by washing them into the beaker. Cover the beaker with a watch glass and allow to stand for at least one hour, or overnight, to settle the precipitate.

8.5.2 Washing and Weighing the Selenium. Clean a fritted glass filter of medium porosity by successive washings with aqua regia, alcohol, and ether, and dry at 110°C. for one hour. Cool in a desiccator, and weigh to 0.1 milligram. Filter the supernatant solution and wash the selenium precipitate in the beaker successively with 20 milliliter portions of concentrated HCl, cold water, boiling water, ethyl alcohol, and finally ether, each of the wash liquids being passed through the fritted glass filter in turn. The selenium is changed from red to the black or gray modification by the hot water and is brought onto the filter at that time, using a rubber policeman to remove adhering particles from the walls of the beaker. After the last ether wash, remove the filter from the suction assembly, place in an oven at 110°C. for one hour, cool, and weigh to 0.1 milligram; this process is repeated until constant weight is achieved (Note 6). Calculate the selenium and the dilauryl selenide content of the sample (9.0).

Note 6. Selenium can be cleaned from the fritted glass filter by dissolving either in concentrated nitric acid or aqua regia, followed by washing with water, then alcohol, and finally ether. If there is a large quantity of selenium on the filter, about one half hour soaking is required to dissolve it completely.

8.6 DETERMINATION OF SMALL AMOUNTS OF SELENIUM.

8.6.1 In the event that the weight of selenium is below 10 milligrams, the weighing error becomes too great; therefore, the weight of sample is increased by oxidizing 2 consecutive samples before removing the contents of the bomb and proceeding with the selenium determination. Ignite the first 0.8 gram sample as described in Paragraphs 8.1 through 8.3. Open the bomb, remove the sample cup and treat as described in

Paragraph 8.4, but do not wash out the bomb or touch any of the interior surfaces. Wash down the tips of the two electrodes and sample cup with indicator-containing distilled water into a 600-milliliter beaker which will later be used to collect all of the bomb washings. Care must be taken to prevent loss of any of the residue remaining after the first combustion. Invert the bomb cover on a desk top, remove the fragments of fuse wire with clean forceps or tweezers, and insert a new fuse wire in the electrodes with a cotton wisp or nylon thread. Weigh a second 0.8 gram sample in a new, clean sample cup. Place the second sample in the electrode loop as described in Paragraph 5.2, and fire the bomb. In this manner, a sufficiently large sample can be combusted in the bomb to provide a weighable quantity of selenium in the final determination. Continue as described in Paragraphs 8.4 and 8.5.

8.7 BLANK. Make a blank determination on 0.3 to 0.4 grams of white oil or pure dibasic acid ester, such as dioctyl sebacate, by following the normal procedure, omitting the sample. Repeat this blank whenever new reagents are used.

9.0 CALCULATION.

9.1 SELENIUM CONTENT. Calculate the selenium content of the sample as follows:

$$\text{Selenium (percent)} = \frac{(A-B) \times 100}{W}$$

where: A = grams of selenium obtained.
B = grams of selenium obtained from blank (8.7).
W = weight of sample in grams.

9.2 DILAURYL SELENIDE. Calculate the dilauryl selenide content of the sample as follows:

$$\text{Dilauryl selenide (percent)} = \frac{(A-B) \times 5.679 \times 100}{W \times 0.88}$$

where: A = grams of selenium obtained.
B = grams of selenium obtained from blank (8.7).
W = weight of sample in grams.
5.679 = conversion factor from selenium to pure dilauryl selenide.
88% = dilauryl selenide content of commercial antioxidant samples.

SECTION 3

DETECTION AND DETERMINATION OF CORROSION PREVENTIVE AGENTS

METHOD OF ANALYSIS OF CALCIUM AND BARIUM PETROLEUM SULFONATES

1.0 SCOPE

1.1 This method of analysis describes procedures for the determination of mineral oil, calcium or barium sulfonate, calcium or barium carboxylate, basicity or acidity, inorganic salts, and average molecular weight of crude and refined calcium and barium petroleum sulfonates.

1.2 This method is modified from A.S.T.M. Method D1216-52T.

2.0 OUTLINE OF METHOD

2.1 This method of analysis of calcium and barium petroleum sulfonates is outlined in Figure 12.

3.0 APPARATUS

3.1 Vacuum oven, capable of operating at 70 to 100°C. under 3 millimeters of mercury absolute pressure.

3.2 Beaker, glass, with an inverted rim turned in 10 millimeters from the wall of beaker and pointed downward to a point 5 millimeters below the shoulder, and having a diameter of 65 to 75 millimeters, a height of 75 to 85 millimeters, and a wall thickness (approximately 1 millimeter) such that its weight is less than 70 grams.

3.3 Steam bath.

3.4 Muffle furnace, capable of operating at 800 to 1000°C.

3.5 Atmospheric ovens, capable of being maintained at 120°C. and at 70 to 80°C.

3.6 Graduated mixing cylinder with glass stopper, 250-milliliter capacity.

3.7 Water bath, capable of being maintained at 40 to 50°C. and at 25±0.2°C.

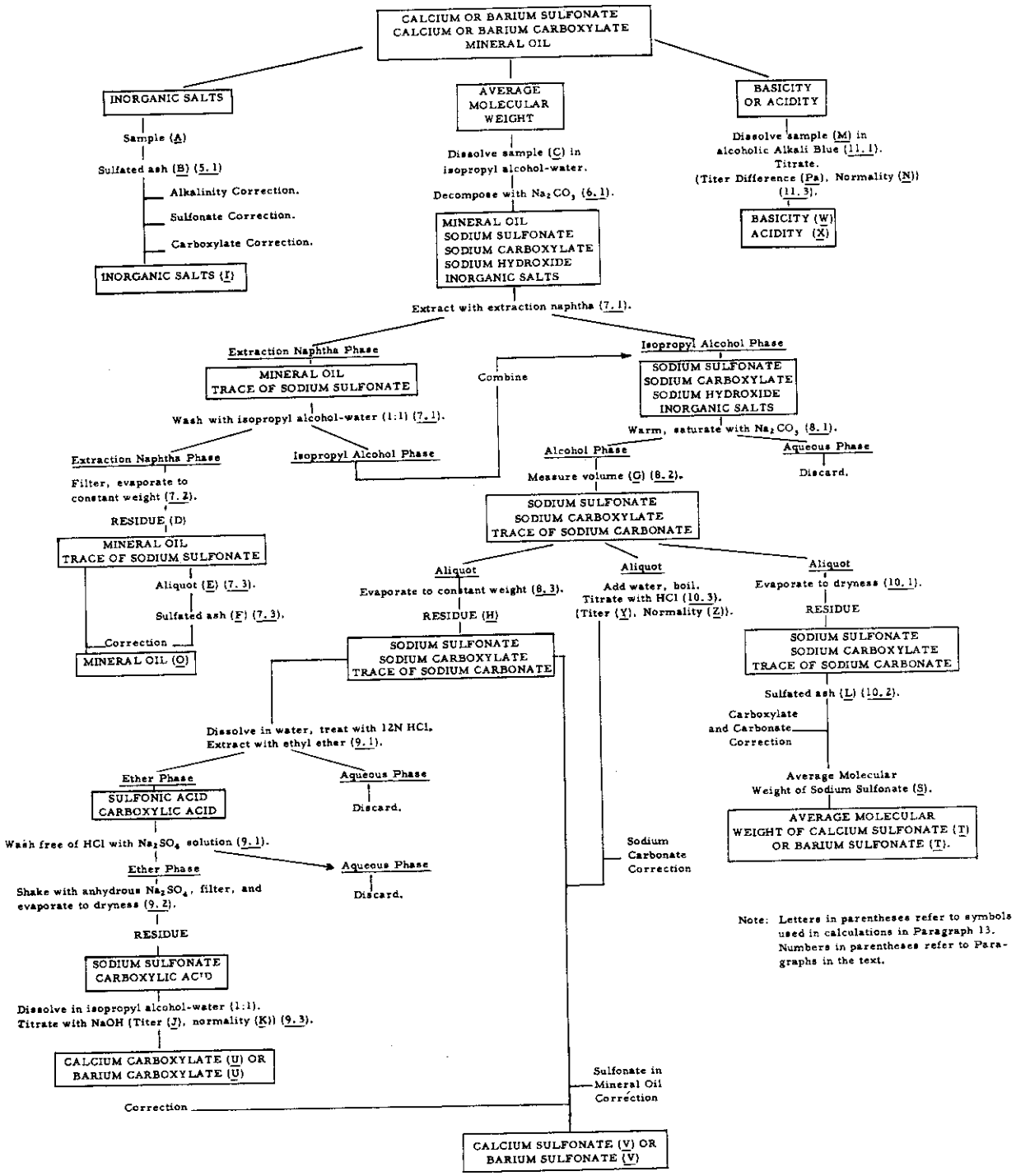


Figure 12. Outline of Method of Analysis of Calcium and Barium Petroleum Sulfonates.

3.8 Vacuum desiccator, shielded.

3.9 Distillation apparatus as described in A. S. T. M. Method D95, "Test for Water in Petroleum Products and Other Bituminous Materials."

3.10 Dish, platinum, approximately 50 or 100-milliliter capacity.

4.0 REAGENTS[1]

4.1 Sodium carbonate, anhydrous.

4.2 Sodium sulfate, anhydrous, crystalline.

4.3 Sodium sulfate solution (240 grams Na_2SO_4 per liter). Dissolve 240 grams of Na_2SO_4 in water and dilute to 1 liter.

4.4 Hydrochloric acid (12 N and standard 0.1 N).

4.5 Sulfuric acid (36 N).

4.6 Methyl orange indicator solution (1 gram per liter). Dissolve 0.1 gram of methyl orange in 100 milliliters of water.

4.7 Phenolphthalein indicator solution (10 grams per liter). Dissolve 1 gram of phenolphthalein in 100 milliliters of ethyl alcohol (50 percent).

4.8 Alkali Blue indicator solution. Dissolve 1.2 grams of Alkali Blue 6B[2] in 1500 milliliters of ethyl alcohol (95 percent). Alternatively, alcohol identified as "U.S. Treasury Dept. Specially Denatured Formula 30 (Regulation No. 3-1938)" may be used. Add 1000 milliliters of benzene and mix well. Store in a bottle having a stopper of cork or glass, but not rubber.

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[1] Unless otherwise indicated, it is intended that all reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. References to water shall be understood to mean distilled water.

[2] Alkali Blue 6B is available from Eimer and Amend, 635 Greenwich St., New York 14, N. Y.; or from Fisher Scientific Co., 717 Forbes St., Pittsburgh 19, Pa., or 2109 Locust St., St. Louis 3, Mo.

4.9 Acetone, reagent grade.

4.10 Benzene, reagent grade.

4.11 Ethyl ether, USP.

4.12 Isopropyl alcohol, refined grade (99 percent). The 99 percent concentration of isopropyl alcohol shall contain less than 0.9 percent water.

4.13 Isopropyl alcohol-water solution (1:1, v/v). Mix equal volumes of 99 percent isopropyl alcohol and water.

4.14 Ethyl alcohol (95 percent).

4.15 Extraction Naphtha. Boiling range 30 to 75°C; maximum nonvolatile impurities, 0.002 percent.

4.16 Standard sodium hydroxide solution (0.1 N). Prepare and standardize an 0.1 N aqueous, carbonate-free NaOH solution.

4.17 Standard potassium hydroxide solution (0.1 N, alcoholic). Add 6 grams of solid KOH to approximately 1 liter of anhydrous isopropyl alcohol (99 percent) in a 2-liter Erlenmeyer flask. Boil the mixture gently for 10 to 15 minutes, stirring to prevent the solids from forming a cake on the bottom. Add at least 2 grams of $Ba(OH)_2$ and again boil gently for 5 to 10 minutes. Cool to room temperature, allow to stand for several hours, and filter the supernatant liquid through a fine sintered-glass or porcelain filtering funnel; avoid unnecessary exposure to CO_2 during filtration. Store the solution in a chemically resistant dispensing bottle out of contact with cork, rubber, or saponifiable stopcock lubricant, and protected by a guard tube containing soda lime or soda asbestos (Ascarite). Standardize against pure potassium acid phthalate in about 100 milliliters of carbon dioxide-free water, using phenolphthalein to detect the end point.

5.0 SULFATED RESIDUE

5.1 Weigh 3 grams of the sample to the nearest 0.5 milligram in an ignited and tared platinum dish, designating this weight as A. Heat with a small flame until the contents ignite, and maintain a temperature

such that the contents will burn gently until only ash and carbon remain. Ignite this residue over a burner or in a muffle furnace at 800 to 1000°C. until oxidation of carbon is complete. (Carbon occluded in the residue may resist oxidation.) Cool and add 3 to 4 drops of 36N H_2SO_4. Expel the H_2SO_4 over a burner in a hood, but avoid heating strongly enough to cause spattering. When fuming ceases, cool and repeat the acid treatment. Then heat in a muffle furnace at 800 to 1000°C. to constant weight. Designate this weight as B. Cool in a desiccator prior to weighing.

6.0 CONVERSION OF CALCIUM OR BARIUM SULFONATE TO SODIUM SULFONATE

6.1 Introduce 125 milliliters of IPA-water (1:1, v/v)* into a 250-milliliter separatory funnel. Add, by means of a weighing bottle, 15 grams of the sample (C), weighed to the nearest 0.01 gram, and suspend this in the alcohol. Warm the funnel and contents to 40 to 50°C. under a tap or by immersion in a water bath. Add the calculated amount of anhydrous Na_2CO_3 necessary to convert the calcium or barium salts to the corresponding sodium salts (Note 1). Shake the contents of the funnel vigorously, and then allow to cool to approximately room temperature.

Note 1. Formulas for calculating the required amount of Na_2CO_3 are given in Paragraph 13.1.

7.0 MINERAL OIL.

7.1 Extract the alcoholic solution (6.1) six times (Note 2) with 30-milliliter portions of extraction naphtha, using two 250-milliliter separatory funnels and collecting the extraction naphtha extracts in a 500-milliliter separatory funnel. Retain any interface emulsion with the naphtha phase (Note 3). On completing the extractions, drain the alcoholic solution into a 250-milliliter mixing cylinder. Rinse each 250-milliliter separatory funnel with two 10-milliliter portions of IPA-water (1:1, v/v), and add the rinsings to the mixing cylinder. Wash the combined extraction naphtha extracts with 50 milliliters of IPA-water (1:1, v/v) and add the alcohol wash to the mixing cylinder.

*IPA = isopropyl alcohol.

Note 2. Continue extracting until the extraction naphtha is colorless, if this is not the case at the end of the sixth extraction.

Note 3. If three liquid phases are formed when the extraction naphtha is added, handle the two lower phases as if they were the alcohol solution referred to above.

7.2 Filter the combined extraction naphtha extracts through a small plug of cotton, placed in the vortex of a filter funnel, into a tared, inverted-rim beaker (3.2). Wash the separatory funnel and the filter with 20 to 30 milliliters of extraction naphtha, adding the washings to the beaker. Evaporate the extraction naphtha solution to dryness on a steam bath, and continue the heating for 15 minutes after the disappearance of the odor of extraction naphtha or alcohol. Cool the beaker and contents to room temperature, and bring to constant weight in a vacuum desiccator at room temperature and under 3 millimeters or less of mercury pressure (Note 4). Apply vacuum gradually and vent frequently to avoid spattering, particularly in the initial stages. Designate the weight of the oil residue as D.

Note 4. Difficulty in attaining constant weight may result from the presence of volatile oil, which circumstance would be further evidenced by an abnormally low total of all the constituents. In such cases, include a note of this circumstance in the analysis, and report the mineral oil as the difference between 100 percent and the sum of all the other constituents.

7.3 Weigh 1 to 2 grams of the oil residue (7.2) into an ignited and tared platinum dish, designating this weight as E. Carefully heat the dish over a small flame until the contents ignite, and maintain a temperature such that the contents will burn gently until only ash and carbon remain. Ignite this residue over a burner or in a muffle furnace at 800 to 1000°C. until oxidation of carbon is complete (carbon occluded in the residue may resist oxidation). Cool and add 3 to 4 drops of 36N H_2SO_4 over a burner in a hood, but avoid heating strongly enough to cause spattering. When fuming ceases, heat in a muffle furnace at 800 to 1000°C. to constant weight. Designate this weight as F. Cool in a desiccator prior to weighing.

8.0 SULFONATE.

8.1 Warm the mixing cylinder and contents (7.1) in a water bath at 40 to 50°C. Note the volume of solution in the cylinder, and weigh out the required amount of anhydrous Na_2CO_3 on the basis of 18 grams per 100 milliliters of solution. Cautiously add the Na_2CO_3 to the cylinder, a few grains at a time, in order to allow the dissolved extraction naphtha to boil off slowly. When danger of boiling is past, add the remainder of the Na_2CO_3 and shake the mixture vigorously. Allow to stand for a few minutes and repeat the shaking. If there is no excess of the solid Na_2CO_3, add an additional 1 to 2 grams of the alkali, and again shake vigorously. Allow the phases to separate, swirling the solution to dislodge any solid particles clinging to the upper part of the mixing cylinder. Replace the cylinder in the bath at 40 to 50°C. until separation into two layers is complete.

8.2 Remove the cylinder from the bath and allow it to cool to room temperature (3 to 4 hours). Note the volume, in milliliters, of the upper, alcoholic layer and record it as G. If the upper layer is cloudy, allow to stand overnight or filter through paper in a glass-stoppered Erlenmeyer flask.

8.3 Pipet a 50-milliliter aliquot of the clear alcoholic solution (Paragraph 8.2) into a tared 150-milliliter beaker (Note 5). Evaporate to dryness on a steam bath, adding small portions of isopropyl alcohol (99 percent) or acetone to aid in the removal of water. Dry to constant weight in a vacuum oven at 80°C. under less than 3 millimeters of mercury pressure, or in an atmospheric oven at 120°C. Designate the weight of the residue as H, and reserve it quantitatively for the procedure described below.

Note 5. Transfer the 25-milliliter aliquot, or aliquots, required in Paragraphs 10.1 and 10.3 simultaneously with the 50-millimeter aliquot for Paragraph 8.3.

9.0 CARBOXYLATE

9.1 Dissolve the sulfonate residue obtained in Paragraph 8.3 in two 100-milliliter portions of water, and transfer the solution quantitatively to a 500-milliliter separatory funnel. Wash the beaker with two 25-milliliter portions of water, and add the washings to the separatory funnel. Add 50 milliliters of 12N HCl to the funnel and shake vigorously. Allow the solution to cool, and extract the liberated acids with two 100-milliliter portions of ethyl ether, combining the ether extracts in a second

500-milliliter separatory funnel. Wash the combined ether extracts free of HCl by shaking with successive 50-milliliter portions of Na_2SO_4 solution containing methyl orange indicator, until a washing does not appear pink after shaking. Discard the salt washings.

9.2 Drain off as much of the aqueous layer as possible from the washed ether extract. Lay the separatory funnel on its side, and introduce about 10 grams of anhydrous Na_2SO_4. Make sure that the funnel mouth is free of Na_2SO_4 crystals before inserting the stopper. Shake the mixture vigorously for 3 to 4 minutes, venting frequently. Filter the ether solution through a small plug of cotton in the vortex of a filter funnel into a 250-milliliter Erlenmeyer flask. Wash the separatory funnel and the filter with 20 milliliters of ethyl ether and add the washings to the main ether solution. Evaporate the ether on a steam bath.

9.3 To the residue obtained in Paragraph 9.2, add 4 or 5 drops of phenolphthalein indicator and 50 milliliters of IPA-water (1:1, v/v) that has been previously neutralized to phenolphthalein. Warm, if necessary, to dissolve the residue, and titrate with 0.1N NaOH solution to a definite pink color. If the sample is so dark in color that it cannot be satisfactorily tested in this manner, determine the acidity according to A.S.T.M. Method D 664, Standard Method of Test for Neutralization Value (Acid and Base Numbers) by Potentiometric Titration. Designate the volume of the standard NaOH or alcoholic KOH solution used as J and its normality as K.

10.0 AVERAGE MOLECULAR WEIGHT

10.1 Pipet a 25-milliliter aliquot of the alcoholic sulfonate solution (Paragraph 8.2) into a tared ignited platinum dish (see Note 5 above). Evaporate to dryness on a steam bath, adding small portions of isopropyl alcohol (99 percent) or acetone to aid in the removal of water, which otherwise may cause spattering in the initial stages of ashing. The dry weight of the residue is taken as one half of the value of H as obtained in Paragraph 8.3.

10.2 Heat the residue obtained in Paragraph 10.1 over a small flame until it ignites, and maintain a temperature such that it will burn gently until only ash and carbon remain. Ignite this residue over a burner or in a muffle furnace at 800 to 1000°C. until oxidation of carbon is complete. (Carbon occluded in the residue may resist oxidation). Cool and add 3 to 4 drops of 36N H_2SO_4. Expel the H_2SO_4 over a burner in a

hood, but avoid heating strongly enough to cause spattering. When fuming ceases, cool, and repeat the acid treatment. Heat in a muffle furnace at 800 to 1000°C. to constant weight. Designate this weight as L. Cool in a desiccator prior to weighing.

10.3 Pipet a 25-milliliter aliquot of the alcoholic sulfonate solution (Paragraph 8.2) into a 250-milliliter beaker (see Note 5 above). Add 25 milliliters of water and 4 or 5 drops of phenolphthalein indicator. Heat to boiling, and discharge the pink color by titrating with 0.1N HCl. Repeat the boiling and the addition of 0.1N HCl until the solution no longer develops a pink color on repeated boiling. Designate the volume of standard acid used as Y and its normality as Z (Note 6).

Note 6. The purpose of Paragraph 10.3 is to increase accuracy by providing a correction for the small but appreciable amount of Na_2CO_3 retained in the alcoholic sulfonate solution. Its use is optional and will depend upon judgment in any individual case. If used, the two 25-milliliter aliquots required in Paragraphs 10.1 and 10.3 should be taken simultaneously. If not used, appropriate notes will be found in the calculations (Paragraphs 13.1 - 13.7) wherever applicable.

11.0 BASICITY OR ACIDITY

11.1 Transfer approximately 20 grams of the sample, weighed to the nearest 0.05 gram, to a 250-milliliter Erlenmeyer flask, designating this weight as M. Dissolve the weighed sample in 80 milliliters of Alkali Blue indicator solution.

11.2 If the solution turns red, discharge the color with at least 5 milliliters of 0.1N HCl from a buret. If necessary, add additional 2-milliliter increments of 0.1N HCl, and proceed with Paragraph 11.3. If the sample is acidic, as indicated by the indicator solution remaining blue, add 5 milliliters of 0.1N HCl and proceed with Paragraph 11.3. (Note 7).

Note 7. Free sulfonic acids may cause anomalous results by being determined by both the procedure of Paragraphs under 11.0 and as sodium sulfonate in the procedure of Paragraphs under 8.0.

11.3 Without delay, titrate the contents of the flask with 0.1N alcoholic KOH solution to a plum color. Designate the volume of the KOH solution used as P and its normality as N.

11.4 To another 80-milliliter portion of the Alkali Blue solution, add exactly the same volume of 0.1N HCl as was used in Paragraph 11.2, and titrate with 0.1N alcoholic KOH solution until the color just changes from blue to red. Designate the volume of KOH solution used as P_a.

12.0 INORGANIC SALTS

12.1 Calculate the inorganic salts by difference as directed in Paragraph 13.7.

13.0 CALCULATIONS. Calculate the results as follows, using the symbols defined in Paragraph 13.8.

13.1 SODIUM CARBONATE REQUIRED FOR DECOMPOSITION. Calculate the amount of anhydrous Na_2CO_3 required in Paragraph 6.1 for calcium or barium samples, as follows:

$$Na_2CO_3 \text{ for calcium samples, grams} = \frac{3 \times 106 \times BC}{136A}$$

$$Na_2CO_3 \text{ for barium samples, grams} = \frac{3 \times 106 \times BC}{233A}$$

13.2 AVERAGE MOLECULAR WEIGHT

13.2.1 Calculate the percentage of sodium carboxylate (or sodium carboxylate plus sodium carbonate), Q, contained in the crude sulfonate residue (Paragraph 8.3) as shown below. Consider the Y and Z terms to be zero if the procedure in Paragraph 10.3 was not used. A molecular weight of 333 is assumed for sodium carboxylate.

$$Q = \frac{333 \times JK \times 2}{20H} + \frac{53 \times YZ \times 2}{10H}$$

13.2.2 Calculate the percentage, R, of the sulfated residue, L, (Paragraph 10.2) which is derived from carboxylate (or from carboxylate plus carbonate) as shown below. Consider the Y and Z terms to be zero if the procedure in Paragraph 10.3 was not used.

$$R = \frac{71\ JK}{20L} + \frac{71\ YZ}{10L}$$

13.2.3 Calculate the average molecular weight of sodium sulfonate, S, as follows:

$$S = \frac{71 \times (100 - Q) \times H}{(100 - R) \times L \times 2}$$

13.2.4 Calculate the average molecular weight, T, of calcium or barium sulfonate as follows:

T = 2S - 6 (for calcium sulfonate)
T = 2S + 91 (for barium sulfonate)

13.3 MINERAL OIL. Calculate the percentage of mineral oil, O, as follows:

$$O = \frac{100D}{C} - \frac{100DFS}{71CE}$$

13.4 CARBOXYLATE. Calculate the percentage of calcium or barium carboxylate, U, as follows:

$$U = \frac{330JKG}{10 \times C \times 50} \quad \text{(for calcium carboxylate)}$$

$$U = \frac{379\ JKG}{10 \times C \times 50} \quad \text{(for barium carboxylate)}$$

13.5 SULFONATE. Calculate the percentage of calcium or barium sulfonate, V, as shown below. Consider the Y and Z terms to be zero if the procedure in Paragraph 10.3 was omitted.

13.5.1 For Calcium Sulfonate:

$$V = \frac{100\ GHT}{C \times 50 \times 2 \times S} + \frac{100DFT}{CE \times 142} - \frac{333UT}{330 \times 2 \times S} - \frac{53\ GYZT}{C \times 25 \times 10 \times 2 \times S}$$

13.5.2 For Barium Sulfonate

$$V = \frac{100\ GHT}{C \times 50 \times 2 \times S} + \frac{100\ DFT}{CE \times 142} - \frac{333\ UT}{379 \times 2 \times S} - \frac{53\ GYZT}{C \times 25 \times 10 \times 2 \times S}$$

13.6 BASICITY OR ACIDITY. Calculate basicity as percentage of calcium or barium hydroxide, W, or acidity as percentage of sulfuric acid, X, as follows:

$$W = \frac{37 \times (P_a - P) \times N}{10M} \quad \text{(for calcium sulfonate samples)}$$

$$W = \frac{86 \times (P_a - P) \times N}{10M} \quad \text{(for barium sulfonate samples)}$$

$$X = \frac{49 \times (P - P_a) \times N}{10M}$$

13.7 INORGANIC SALT. Calculate the percentage of inorganic salts, I, as calcium sulfate or barium sulfate, as follows:

$$I = \frac{100B}{A} - \frac{136V}{T} - \frac{136U}{757} - \frac{136W}{74} \quad \text{(for calcium sulfonate samples)}$$

$$I = \frac{100B}{A} - \frac{233V}{T} - \frac{233U}{757} - \frac{233W}{171} \quad \text{(for barium sulfonate samples)}$$

13.8 SYMBOLS. Listed below are definitions of the symbols used in the calculations above, and as noted in the procedures given in preceding sections. All weights refer to grams and all volumes to milliliters.

A = weight of sample taken for sulfated residue determination (Paragraph 5.1).
B = weight of sulfated residue (Paragraph 5.1).
C = weight of sample taken for conversion with sodium carbonate (Paragraph 6.1).
D = weight of mineral oil residue (Paragraph 7.2).
E = weight of oil residue taken for ignition (Paragraph 7.3).
F = weight of sulfated residue from mineral oil (Paragraph 7.3).
G = volume of alcoholic solution of sulfonate (Paragraph 8.2).
H = weight of impure sulfonate residue (Paragraph 8.3).
I = percentage of inorganic salts (Paragraph 13.7).
J = volume of NaOH solution used to titrate carboxylic acids (Paragraph 9.3).
K = normality of NaOH solution used to titrate carboxylic acids (Paragraph 9.3).

L = weight of ignited residue from impure sulfonate (Paragraph 10. 2).
M = weight of sample taken for basicity or acidity (Paragraph 11. 1).
N = normality of KOH solution used to titrate basicity or acidity (Paragraph 11. 3).
O = percentage of mineral oil (Paragraph 13. 3).
P = volume of KOH solution used to back-titrate sample (Paragraph 11. 3).
P_a = volume of KOH solution used to titrate acid blank (Paragraph 11. 4).
Q = percentage of sodium carboxylate (or sodium carboxylate plus sodium carbonate) in impure sulfonate (Paragraph 13. 2. 1).
R = percentage of L which was derived from carboxylate (or from carboxylate plus carbonate) (Paragraph 13. 2. 2).
S = molecular weight of sodium sulfonate (Paragraph 13. 2. 3).
T = molecular weight of calcium or barium sulfonate (Paragraph 13. 2. 4).
U = percentage of calcium or barium carboxylate (Paragraph 13. 4).
V = percentage of calcium or barium sulfonate (Paragraph 13. 5).
W = basicity as calcium or barium hydroxide (Paragraph 13. 6).
X = acidity as sulfuric acid (Paragraph 13. 6).
Y = volume of standard acid used to titrate impure sulfonate residue (Paragraph 10. 3), and
Z = normality of standard acid used to titrate impure sulfonate residue (Paragraph 10. 3).

SECTION 4

SEPARATION AND IDENTIFICATION OF SYNTHETIC GREASE COMPONENTS

SEPARATION AND DETERMINATION OF UREA THICKENERS

1.0 SCOPE.

1.1 This method describes procedures for the separation and determination of urea-type thickeners used in extreme high-temperature synthetic greases. The method is confined to determination of the carbon dioxide and nitrogen content of the urea thickener, with suggested qualitative tests for some of the possible aryl groups in the substituted urea compound. It is assumed in this method that substituted-urea thickeners are the only thickener or gelling agent present in the grease, the addition of other types of thickeners being unnecessary and detrimental to the high-temperature properties of greases compounded with urea thickeners (Note 1).

Note 1. It is intended that this method be used in close conjunction with Method 15, "Preliminary Qualitative Classification of Synthetic Greases." In Method 15 the analyst shall have established the presence of urea-type thickeners in the grease by use of the nitric acid-sulfuric acid ring test. If this test is positive, then Method 41 should be employed.

2.0 OUTLINE OF METHOD.

2.1 The urea thickener is isolated from the base-oil and other hexane-soluble additives by Soxhlet extraction with hexane or 1,1-dichloroethane. Further analysis of the thickener is obtained by hydrolysis with sulfuric acid to give amines and carbon dioxide. The latter is determined volumetrically, and the amines are recovered and reacted with benzene-sulfonyl chloride, yielding crystalline derivatives with characteristic melting points and solubilities to permit identification. Kjeldahl nitrogen determination on the urea thickener, coupled with identification of the amine and the amount of carbon dioxide evolved, assists in determining composition of the thickener. If the thickener possesses more than one type of amine substituent, solubility tests are employed to separate and identify the amines present.

3.0 SAMPLE.

3.1 The size of sample employed for this procedure shall be about 5 grams, weighed accurately to 1 milligram on an analytical balance.

Make the original sample of grease as uniform as possible. If the grease is soft, stir and mix with a glass or wood paddle in a beaker until uniform. If the grease is hard, scrape off surface layers with a clean spatula, and take the sample from the freshly exposed surface.

4.0 APPARATUS.

4.1 Centrifuge. A centrifuge is required which is equipped with a head, trunnion carriers, cups, and rubber cushions, capable of holding 100-milliliter capacity centrifuge tubes (such as A.S.T.M. pear-shaped oil tubes) and which can be controlled to give rotational speeds up to 1800 r.p.m. or higher.

4.2 Suction apparatus. This apparatus (illustrated in Figure 2, Method 15) provides a fast, convenient method for separating and transferring liquid layers from the centrifuge tube to a separatory funnel or other container for further treatment. The tubing is capillary type with 1 millimeter diameter bore, and the tip which is placed in the liquid is drawn out to a length of about 4 inches to provide a minimum of glass surface to disturb the contents in the tube. The 4 inch tip shall be 1 millimeter o.d. and 0.25 millimeter i.d. A standard A.S.T.M. pear-shaped 100-milliliter oil centrifuge tube is convenient for use in this method, although this is not essential to performance of the separation (Note 2). The 125-milliliter separatory funnel or receiving container is equipped with a two-hole rubber stopper which contains two sections of capillary tubing. Water aspirator vacuum is sufficient, since only low vacuum is needed to draw the liquid from the centrifuge tube into the funnel. A trap should be provided in the vacuum line. The capillary-bore three-way stopcock, opening to the air, provides a convenient means for controlling the rate of flow of liquid through the capillary tubing into the funnel.

Note 2. Any type of centrifuge tube of about 100-milliliter capacity which can be employed with the available centrifuge facilities will be adequate.

4.3 Drying oven. This oven should be capable of maintaining a constant temperature of 110°C.

4.4 Soxhlet extraction apparatus. Standard laboratory Soxhlet extraction chamber (preferably with a stopcock takeoff at the bottom of

the chamber for withdrawing samples of solvent), reflux Allihn condenser, and cellulose extraction thimbles which fit loosely in the chamber, should be provided. Standard taper ware is preferable. A hot plate shall be used for heating, or a heating mantle with a variable voltage transformer.

4.5 Kjeldahl digestion rack. A rack designed to hold standard size Kjeldahl flasks (whether micro or macro analyses are performed is optional, with the suggestion that micro analysis employs much less of the available sample) shall be provided. Electric heating with a variable voltage transformer is required, or gas heating. The digestion shall be carried out in a fume hood, or the apparatus must be equipped with a fume hood to eliminate poisonous vapors.

4.6 Kjeldahl distillation apparatus. Apparatus which will accommodate the Kjeldahl flasks employed in Paragraph 4.5 above, is required.

4.7 Carbon dioxide apparatus. A schematic drawing of the apparatus is given in Figure 13, and a photograph is shown in Figure 14. Operation of the apparatus is described in the text (6.2.2).

4.8 Melting point apparatus. This apparatus should allow temperature control to within 1°C. rise per minute. Either an aluminum-block type, electrically or gas heated, or a glass capillary type, immersed in a high-boiling liquid bath, may be employed.

4.9 Analytical balance, capable of weighing to 0.1 milligram.

5.0 REAGENTS

5.1 Hexane, purified grade. Technical grade hexane may be purified by distilling over sodium hydroxide or anhydrous sodium carbonate in a distillation column, and the fraction boiling from 63 to 69°C. shall be collected for use in this method.

5.2 1,1-Dichlorethane, reagent grade.

5.3 Sulfuric acid (sp. gr. 1.84), reagent grade.

5.4 Benzenesulfonyl chloride, reagent grade.

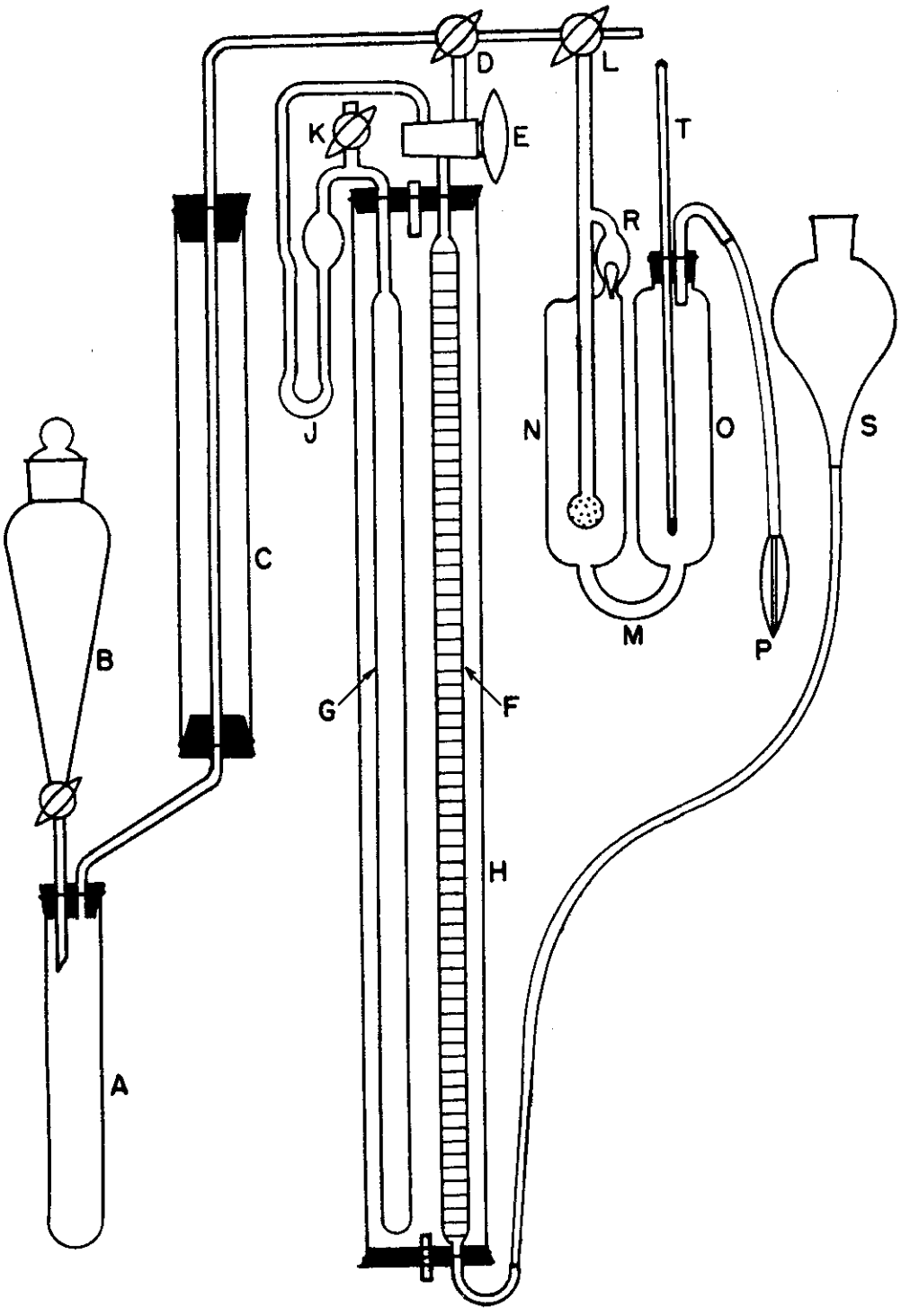


Figure 13. Schematic Diagram of CO_2-Determination Apparatus for Urea Thickeners.

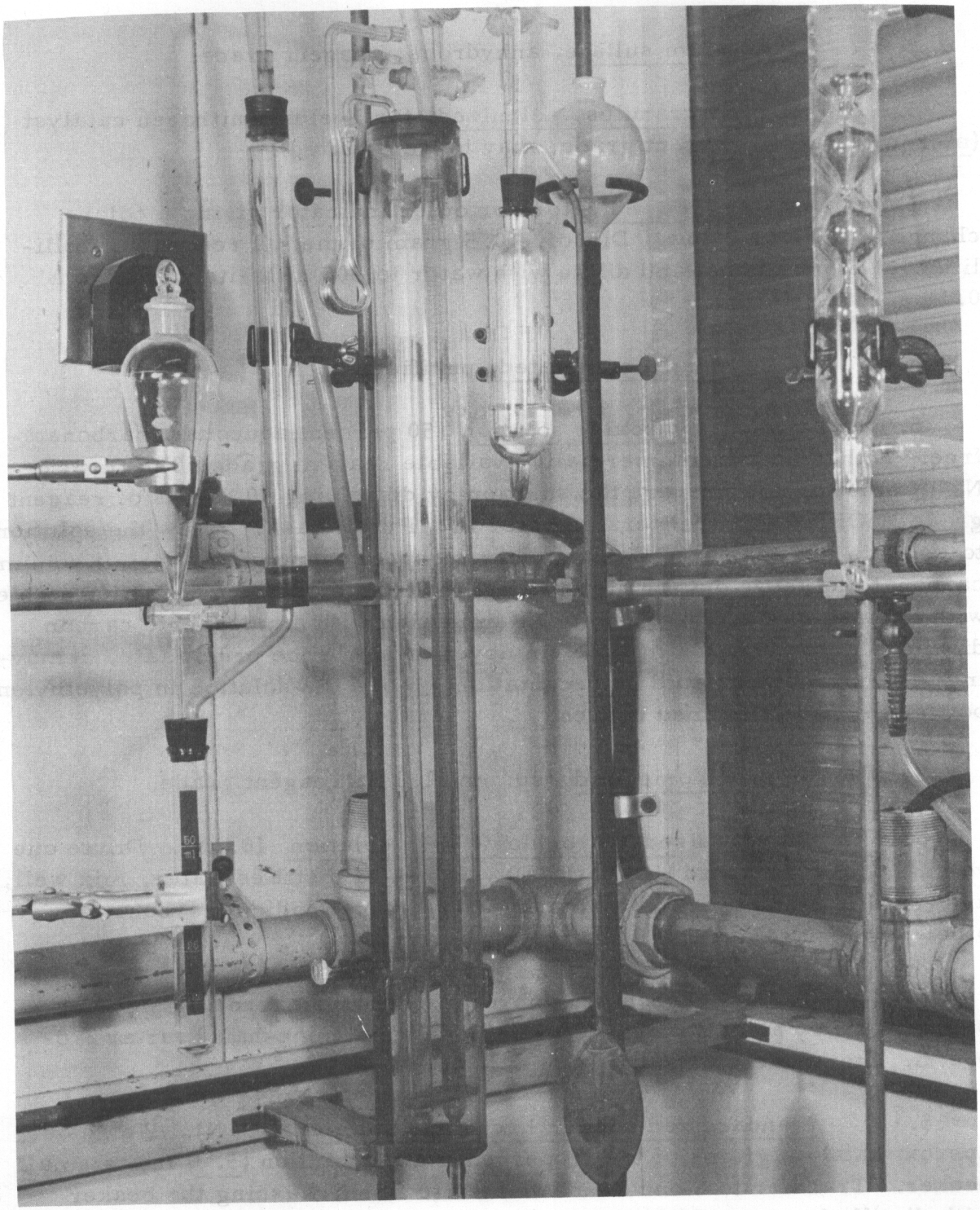


Figure 14. CO_2-Determination for Urea Thickeners.

5.5 Potassium sulfate, anhydrous, reagent grade.

5.6 Hengar granules, selenized, for Kjeldahl nitrogen catalyst (mercuric oxide, reagent grade, may be substituted).

5.7 Methyl red indicator, or other indicator giving a color change at pH 5 or below. Dissolve 0.5 gram of methyl red in 300 milliliters of ethyl alcohol and dilute with water to 500 milliliters to give a 0.1 percent solution.

5.8 Zinc metal, granulated, purified.

5.9 Sodium hydroxide solution (50 percent aqueous), carbonate-free. Either obtain commercially available reagent grade 50 percent NaOH solution, or prepare the solution by dissolving 50 grams of reagent grade NaOH in 50 milliliters of water in a Pyrex flask. Allow the solution to stand in the stoppered flask (rubber stopper) overnight to permit sodium carbonate to settle out. Filter through a Gooch or sintered-glass crucible with exclusion of air to prevent contamination with atmospheric carbon dioxide. Centrifugation may be employed to settle the precipitate, removing the supernatant liquid by decantation. Store the solution in polyethylene bottles, or paraffin-lined bottles.

5.10 Hydrochloric acid (sp. gr. 1.19), reagent grade.

5.11 Standardized hydrochloric acid solution (0.1N). Dilute one volume of concentrated HCl with 110 volumes of distilled water, mix well, and allow to stand overnight. Standardize against sodium carbonate or other primary standard.

5.12 Sodium carbonate, anhydrous, recrystallized, primary standard. Dry analytical grade sodium carbonate one-half hour at 270-300°C. Store in a closed bottle in a desiccator.

5.13 Standardized sodium hydroxide solution (0.1N). Weigh out approximately 8 grams of the 50 percent NaOH solution (5.9) into a small beaker. Transfer to a one liter volumetric flask, washing the beaker with distilled water. Make up to volume with distilled water, mix well, and standardize against potassium biphthalate or against the standardized 0.1N HCl (5.11).

5.14 Potassium biphthalate, anhydrous, reagent grade, primary standard.

5.15 Sulfuric acid solution (80 percent). Pour 43.5 milliliters of reagent grade H_2SO_4 slowly into 20 milliliters of distilled water.

5.16 Acidified water with indicator. Add approximately 1 milliliter of methyl red indicator solution (5.7) to 1 liter of distilled water, and add about 5 milliliters of HCl (sp. gr. 1.19).

5.17 Iron wire or filings, purified. Pieces approximately the size of a pin head are required.

5.18 Potassium hydroxide solution (5 percent).

5.19 Sodium hydroxide solutions (5 percent and 15 percent).

5.20 Hydrochloric acid solution (5 percent).

5.21 Sodium sulfate, anhydrous powder, purified.

6.0 PROCEDURE FOR SEPARATION AND DETERMINATION OF UREA THICKENERS

6.1 SEPARATION OF THE GREASE.

6.1.1 Isolation of the Urea Thickener. If urea-thickened grease has been indicated by Method 15, employ the following procedure for separating the thickener from the base-oil: weigh a 5 gram sample of the grease into a 100-milliliter A.S.T.M. pear-shaped oil centrifuge tube in the following manner: obtain the exact weight of the centrifuge tube to the nearest milligram and record this weight; add a little more than 5 grams of grease to the tube with a spatula (or by other convenient means, such as a hypodermic syringe), taking care that no grease touches the mouth of the tube. Break up any large pieces of grease to promote rapid dispersion; weigh the sample and centrifuge tube to the nearest milligram. Add 50 or 60 milliliters of hexane or 1,1-dichloroethane, stopper the tube with a cork or polyethylene stopper, and shake vigorously until all of the grease has been dispersed in the solvent. If necessary, heat the solvent to boiling by immersion in a steam or water bath, followed by shaking (Note 3). Repeated heating and shaking will

break down most synthetic lubricant greases, some being more resistant to this treatment than others (Note 4). Centrifuge at 1800 r.p.m. to settle out the urea thickener. Using the suction apparatus, place the tip of the capillary into the solvent, and slowly withdraw the liquid into a container of about 100-milliliter capacity, removing the last few milliliters very slowly to avoid drawing up any of the precipitate. It is unnecessary to remove the last one-half milliliter, as the remaining base-oil will be diluted and picked up in the washings. Add 15 milliliters of fresh solvent to the tube, shake to wash the precipitate thoroughly, and again centrifuge. Withdraw the supernatant wash solvent into the first solvent container. Repeat this washing with two more 10 milliliter portions of solvent. Place the centrifuge tube on a water bath to evaporate traces of solvent from the urea residue. A slow stream of air will speed removal of solvent. Dry the residue in an oven at 110°C. for 15 minutes. Cool in a desiccator and weigh to obtain the total insolubles (urea thickener) in the grease. Reserve this residue for positive determination of the type of urea thickener (6.2), and reserve the solvent phase for the determination of base-oils and solvent-soluble materials (Sections 2, 3, and 5).

Note 3. Caution should be exercised at all times when working with hexane and other volatile, flammable solvents. Under no conditions should solvents be heated in the vicinity of open flames. Always use a water bath to heat solvents in the centrifuge tube.

Note 4. In the event that the grease does not disperse readily in these solvents in the centrifuge tube, Soxhlet extraction may be employed to separate the base-oil and thickener. Weigh a Soxhlet extraction thimble (double weight preferred) contained in a stoppered glass vial to the nearest milligram. Weigh a 5 gram sample of the grease into the thimble, breaking the grease into as many pieces as practicable. Fill the boiling flask (usually 250-milliliter capacity) about half full with hexane or 1,1-dichlorethane, place the thimble in the chamber, and extract the grease overnight, maintaining a rapid rate of reflux. Check for completeness of extraction by withdrawing a few drops of solvent through the stopcock at the bottom of the extraction chamber onto a clean watch glass, and evaporate to dryness. The extraction should be continued until no trace of oil is visible on the watch glass. If necessary, add solvent through the top of the condenser to maintain at least 125 milliliters of solvent in the apparatus. When extraction is complete,

cool to room temperature and remove the boiling flask and thimble. Place the thimble on a watch glass and dry in an oven at 70-110°C. for about 15 minutes. Remove from the oven and cool in a desiccator. Place the thimble in the original weighing vial, stopper the vial, and weigh to the nearest milligram. Reserve this residue in the thimble for identification of the urea thickener (6.2), and reserve the solvent phase for determination of base-oils and solvent-soluble materials (Sections 2, 3, and 5).

6.1.2 Determination of the Base-Oil Fraction. Transfer the combined hexane or 1,1-dichlorethane extract and washings to a 250-milliliter round-bottom distillation flask and distill most of the solvent from the base-oil and additives, using a glass heating mantle or hot plate. When the volume of the solution is about 10 milliliters, cool the apparatus, and remove the distillation flask. To obtain the content of soluble materials in the grease, weigh a clean, dry Petri dish to the nearest milligram; transfer the solution to the Petri dish and wash out the flask with three successive 10 milliliter portions of solvent, washing the outside of the lip of the flask with solvent to remove traces of base-oils. Evaporate the remainder of the solvent on a steam bath with a stream of dry air. When the solvent has evaporated, dry at 110°C. for about 15 minutes. Cool the dish in a desiccator and weigh. Bring to constant weight by drying for another 15 minutes, cooling, and reweighing. Reserve the oil for analysis by paper and column chromatography (see Method 16 and Sections 2, 3, and 5).

6.1.3 Calculations. Calculate the content of residue (urea thickener) and solubles (base-oils) in the grease as follows:

$$\text{Residue (percent) (Urea thickener)} = \frac{P \times 100}{W}$$

where: P = weight of residue in grams.
W = weight of sample in grams.

$$\text{Solubles (percent) (Base-oils)} = \frac{R \times 100}{W}$$

where: R = weight of soluble material in grams.
W = weight of sample in grams.

6.2 DETERMINATION OF UREA THICKENER COMPOSITION.

6.2.1 Kjeldahl Nitrogen Determination

6.2.1.1 Procedure. Either a macro or micro procedure may be employed; micro methods have the advantage of requiring a smaller quantity of sample. However, many laboratories do not have adequate micro equipment; therefore, a macro procedure is presented here. Since most of the urea thickener must be used for the carbon dioxide determination (6.2.2) and for preparation of an amine derivative (6.2.3), it is well to conserve as much of the residue as possible, using a minimum amount for the nitrogen determination. For the nitrogen determination, remove the residue to a mortar and grind to a fine powder. Weigh a 1/2 to 1 gram sample of the residue to the nearest milligram and transfer to a dry 800 milliliter Pyrex Kjeldahl flask. Avoid having the powder touch the inner walls of the neck of the flask. Add 15 grams of anhydrous potassium sulfate powder, one or two Hengar granules (or 0.8 gram of mercuric oxide), and 25 milliliters of H_2SO_4 (sp. gr. 1.84). Place the flask in the digestion rack in a well-ventilated hood, and apply low heat until all initial frothing has ceased. A small piece of paraffin will assist in reducing extreme frothing. Gradually increase the heat until the acid boils rapidly, and continue this temperature until the solution has become colorless, and for an additional 15 minutes. Rotating the flask occasionally will bring some of the particles of carbon into contact with the solution. Stop heating and allow the flask to cool to room temperature, agitating it from time to time to prevent formation of a solid lump. Carefully add 200 milliliters of water and dissolve the solids completely. Again cool to room temperature. Pipet accurately 50 milliliters of standard 0.1N HCl solution into a 250 milliliter Erlenmeyer flask, and add a few drops of methyl red indicator solution. Place the flask under the delivery tube of the Kjeldahl distillation assembly in such a way that the delivery tube reaches several millimeters under the surface of the acid. Drop several granules of zinc into the digestion flask, and when everything is prepared for the distillation, carefully pour down the side, so as to form two layers, 50 milliliters of 50 percent NaOH. Quickly connect the Kjeldahl flask to the trap and condenser, and gently swirl until the contents are completely mixed. Turn up the heat and distill at a brisk rate about two-thirds of the solution. When distillation is complete, lower the acid-containing receiver (Note 5), and turn off the heat after some distillate has washed down the inside of the delivery tube. Rinse the condenser with a little water into the receiver, as well as the delivery tube. Add another drop or two of methyl red indicator solution to the receiver, and titrate excess acid with standard 0.1N NaOH (color

change from red to yellow). If extreme accuracy is desired a blank should be run, using a 1 gram sample of non-nitrogen-containing compound, such as sugar.

Note 5. The acid should not have changed color during the distillation; otherwise more NH_3 was generated than there was acid to neutralize it, and the determination must be run again, using a smaller sample.

6.2.1.2 Calculation. Calculate the percent of nitrogen in the urea thickener as follows:

$$\text{Nitrogen (percent)} = \frac{(S - T) \times 0.014 \times 100}{W}$$

where: S = milliequivalents of standard acid used.
T = milliequivalents of standard alkali used for back titration.
0.014 = milliequivalent weight of nitrogen.
W = weight of urea thickener in grams.

The nitrogen value under certain circumstances can be employed directly to indicate the type of urea thickener in the grease. Since the number of urea thickeners is limited, and the percent of nitrogen is a constant and different figure for each compound, then the nitrogen percent can be used to indicate the specific substituted urea; for example, the nitrogen content of sym-diphenyl urea is 13.2 percent, and the content of 1,4-bis-3-(p-biphenylyl-ureido)-benzene is 11.2 percent. If the composition of known commercial urea thickeners is known, the nitrogen content can be calculated and compared to the value obtained for the unknown. In this way the type of urea compound can be predicted without further analysis; however, the postulated compound can be verified by determining the carbon dioxide content of the thickener, and by characterizing the amines split from the compound during acid hydrolysis (6.2.2 and 6.2.3).

6.2.2 Carbon Dioxide Determination. The carbonyl group in the urea thickener is hydrolyzed from the arylamine groups and oxidized to carbon dioxide by 80 percent H_2SO_4; volume of the carbon dioxide evolved is measured in the apparatus diagrammed in Figure 13 and photographed in Figure 14. Description of a similar apparatus is given in Scott, W. W., Standard Methods of Chemical Analysis, Vol. 1, pp. 240-242.

6.2.2.1 Apparatus. The various parts of the apparatus are designated in Figure 13 as follows:

A = reaction tube. This is usually a 65-milliliter test tube.
B = separatory funnel for introducing acid.
C = condenser, filled with water. It is not necessary to have a running water condenser. The inner tube is constructed of Pyrex tubing, 7 millimeter o.d. and 5 millimeter i.d., and is cut off flush with the bottom of the rubber stopper connecting the condenser to reaction tube A.
D = stopcock, three-way.
E = stopcock, three-way.
F = 100-milliliter gas burette, graduated in tenths of a milliliter.
G = compensator tube, having about 75-100 milliliter capacity, and connected to a mercury manometer, J.
H = glass tube, 60 millimeter i.d. and long enough to contain tubes F and G. This tube is filled with water through a hole in the rubber stoppers at each end. The stopper at the top has two additional holes to accommodate tubing for F and G. The stopper at the bottom has another hole to accommodate tubing for F.
J = mercury manometer, with slightly enlarged bulb as indicated in the drawing.
K = stopcock, three-way.
L = stopcock, three-way.
M = caustic potash carbon dioxide absorption pipette. Other types of gas absorption pipettes may be employed in this apparatus.
N = bubbler section of M.
O = pressure equalizer chamber and reservoir for M. This is equipped with a rubber stopper, containing thermometer T and a glass tube which is attached to a rubber expansion bag P, the entire chamber being closed to the atmosphere.
P = expansion bag, attached to pressure equalizer O by rubber and glass tubing.
R = pressure relief valve, integrally incorporated in M.
S = leveling bulb for the gas burette, F, connected to F by heavy rubber tubing.
T = thermometer.

The tubing connecting C to D, D to E, E to J, J to G, F to E, D to L, and L to R is 8 millimeter o.d. capillary tubing. Separatory funnel B is used as a supply reservoir and addition pipette for the 80 percent H_2SO_4 solution. The test tube A holds the urea sample during acid treatment.

and the condenser C removes water, returning it to the reaction tube. The capacity of the system should be kept as small as possible by use of capillary tubing, except the tubing in the condenser which must be large enough to allow the condenser to return condensed water to the reaction tube. Before starting a run fill the condenser jacket, C, and the glass tube, H, with water and allow these to come to room temperature. Fill the gas burette with acidified water solution containing methyl red indicator through the leveling bulb, S, leaving enough space in the bulb so that it will not overflow. Fill the absorption pipette, M, half full with 5 percent KOH solution. The apparatus is now ready for determination of the apparatus factor (see 6.2.2.4) and the CO_2 determination.

6.2.2.2 Procedure. Weigh powdered urea thickener (6.2.1.1) after the determination of nitrogen, and transfer quantitatively to the reaction chamber, A, adding a piece of iron wire or filings about the size of a pin head. Close stopcock E, open the stopcock on the separatory funnel, and connect tube A to the rubber stopper holding the funnel and the condenser, C. Level the Hg columns in the manometer. Close the stopcock on the separatory funnel and open stopcock E. Add 10 milliliters of the 80 percent H_2SO_4 solution slowly into the reaction tube, A, then close the stopcock on the funnel. Fill the separatory funnel B full of water. Apply heat slowly to the reaction tube to promote reaction. Bring the solution to a full boil and continue heating for two hours. After removing the flame, cool the reaction tube, open the stopcock on the separatory funnel to flood the reaction tube, and lower leveling bulb S sufficiently to fill the reflux condenser and the attached capillary tubing with water. Close stopcock E and raise the leveling bulb until the water in the bulb is the same as the level in the gas measuring burette; then adjust the pressure in the gas measuring burette to the same pressure as that in the compensating burette by raising or lowering the leveling bulb as needed. Read and record the total volume of gas in the measuring burette. By proper manipulation of stopcocks D and L, and by raising and lowering the leveling bulb, run the entire volume of gas in the measuring burette into the absorption pipette and back again. Repeat at least three times. The valve R must be in proper position during this operation to force the gas through the bubbler. Sometimes it is necessary to tap the outside of the valve to position the glass valve in the tubing. Return the gas to the measuring burette, adjust the pressure as before, then read and record the volume of gas left in the measuring burette.

6.2.2.3 Calculation. Calculate the percent of CO_2 evolved from the urea thickener as follows:

$$\text{Carbon Dioxide (percent)} = \frac{(A - B) \times C \times 100}{W}$$

where: A = volume of gas before absorbing carbon dioxide.
B = volume of gas after absorbing carbon dioxide.
C = factor characteristic for the apparatus (see 6.2.2.4 below for determination of this factor).
W = weight of urea thickener in grams.

The CO content of the urea thickener can be determined by multiplying the CO_2 content by 0.636. As with the nitrogen value, the CO value under certain circumstances can be employed directly to indicate the urea thickener. Since the number of urea thickeners is limited, and the percent of CO in each of these compounds is a constant and different figure, then the CO percent can be used to indicate the specific urea compound. For instance, the CO content of sym-diphenyl urea is 13.2 percent (the same as the nitrogen content), and the content of 1, 4-bis-3-(p-biphenylyl-ureido)-benzene is 11.2 percent (the same as the nitrogen value). If the composition of known commercial urea thickeners is known, the CO content can be calculated and compared to the value obtained for the unknown. The postulated compound can be verified by determining the specific amines split from the amines split from the thickener by the acid hydrolysis (6.2.3).

6.2.2.4 Factor for carbon dioxide determination. The factor is determined by using a standard sample either of primary standard Na_2CO_3 or limestone of known composition, such as Argillaceous Limestone No. 1a from the National Bureau of Standards. The procedure is followed as described above (6.2.2.2). The factor is then calculated according to the following formula:

$$\text{Factor} = \frac{\text{wt. of standard sample} \times \text{percent } CO_2 \text{ in the sample}}{\text{ml. } CO_2 \text{ liberated.}}$$

When determining a new factor, stopcock K should first be opened to the atmosphere so that the pressure in the compensating burette is atmospheric. If it is necessary to make a new factor determination, it is well to do so before the series of determinations is started for which the factor is to be used. It is recommended that a periodic check determination of the factor be made.

6.2.2.5 Recovery of hydrolyzed amines. Having determined the carbon dioxide content of the sample, the hydrolyzate must be recovered in order to separate and identify the amine portion of the urea thickener.

Open the stopcock on the separatory funnel and stopcocks E and D, and raise the leveling bulb S so that the spent gas forces the diluted hydrolyzate back through the condenser, down into the reaction chamber, and up into the separatory funnel. When as much of the liquid has been forced back as possible, close the stopcock on the separatory funnel, lower the bulb, and close stopcocks E and D. Remove the separatory funnel and the reaction chamber, and pour the liquid into a 400-milliliter beaker. Evaporate the solution to 25 milliliters, cool, and pour into a 125-milliliter separatory funnel. Neutralize with 15 percent NaOH solution, using indicator test paper or litmus paper, and adding one milliliter in excess. Allow the solution to cool, add 50 milliliters of diethyl ether, close the funnel, and shake vigorously. Set the funnel aside in a vertical position until the phases separate. Drain the water phase and discard. Dry the ether phase by adding about 5 grams of dehydrating agent, such as anhydrous Na_2SO_4 powder, and shake well. After the powder has settled from the ether, decant the ether into a 250-milliliter beaker, taking care that none of the Na_2SO_4 is carried into the beaker. Evaporate the ether to dryness, leaving a residue of amines. Reserve this residue for preparation of derivatives for identification of the amines (6.2.3).

6.2.3 Identification of Amines from Hydrolysis of Urea Thickeners. To 5 milliliters of 5 percent NaOH solution in a test tube add 8 drops of the residue containing amines isolated from the hydrolyzed urea thickener (6.2.2.5), and 8 drops of benzenesulfonyl chloride.[1] Shake well, observe whether any reaction has occurred, and warm gently but not to the boiling point. Cool the solution and extract with 10 milliliters of diethyl ether. The aqueous layer contains salts of sulfonyl derivatives of primary amines, which can be precipitated by acidification with 5 percent HCl; the ether layer contains tertiary amines, sulfonyl derivatives of secondary amines, and some disulfonyl derivatives of primary amines. Treat the ether solution with 5 percent HCl. Tertiary amines form salts in the aqueous layer; the ether layer contains sulfonyl derivatives of secondary amines and disulfonyl derivatives of primary amines. Evaporate the ether and warm the residue with alcoholic KOH to decompose disulfonyl derivatives of primary amines. Dilute with distilled water. The primary amine deriva-

[1] Kamm, O., Qualitative Organic Analysis, New York: John Wiley & Sons, Inc., 1932, pp. 158.

tive is soluble in the diluted solution, and the derivative of the secondary amine is insoluble.[1] Each of the compounds isolated from the various fractions may be isolated, dissolved in an appropriate solvent, and recrystallized for melting point determinations. Identification of the specific amine or amines requires standard qualitative organic texts and reference books for the melting points of benzenesulfonyl derivatives and other derivatives which may be prepared as a means of identification.

[1] Kamm, O., Qualitative Organic Analysis, New York: John Wiley & Sons, Inc., 1932, p. 217. Other systematic schemes for the identification of amines and amine mixtures may be found in a number of standard qualitative organic texts and reference books.

SEPARATION AND DETERMINATION OF ALKALI SOAP THICKENERS

1.0 SCOPE

1.1 This method is intended to describe the quantitative separation and determination of alkali soap thickeners in synthetic greases. Lithium, sodium, and potassium soaps of stearic and 10-hydroxy-stearic acid or other fatty acids may be determined quantitatively by this method, after separation from the base-oil and other types of soap thickeners and gelling agents (Note 1). This method includes the determination of free fatty acid content of the grease. If sodium, lithium, or potassium metals or stearic or 10-hydroxy-stearic fatty acids have not been found by Method 15, it is unnecessary to use Method 42.

Note 1. It is intended that this method should be used in close conjunction with Method 15, PRELIMINARY QUALITATIVE CLASSIFICATION OF GREASES, in which qualitative identification of all possible soap thickeners and gelling agents in the grease has been established. Knowledge of the specific compounds present in the grease as determined by Method 15 will assist the analyst in determining which procedures and methods should be used for quantitative determination of gelling agents and thickeners. The analyst must judge whether certain procedures are necessary in view of the composition of the grease.

2.0 OUTLINE OF METHOD

2.1 The scheme of analysis for alkali soap thickeners in grease is shown in Figure 15. The grease is dispersed in hexane and hot isopropyl alcohol:water (1:1) solution. Base-oils are separated in the hexane, and soaps are held in the alcohol:water phase. The two phases are separated and are washed thoroughly with the other solvent. The hexane is set aside for determination of base-oils and fatty acids; the alcohol-water is taken for the determination of soap content. The soap is hydrolyzed with dilute hydrochloric acid and extracted with diethyl ether. Metals hydrolyzed from the soap are identified and determined in the aqueous phase, and fatty acids in the ether phase are recovered, identified, and determined.

3.0 SAMPLE

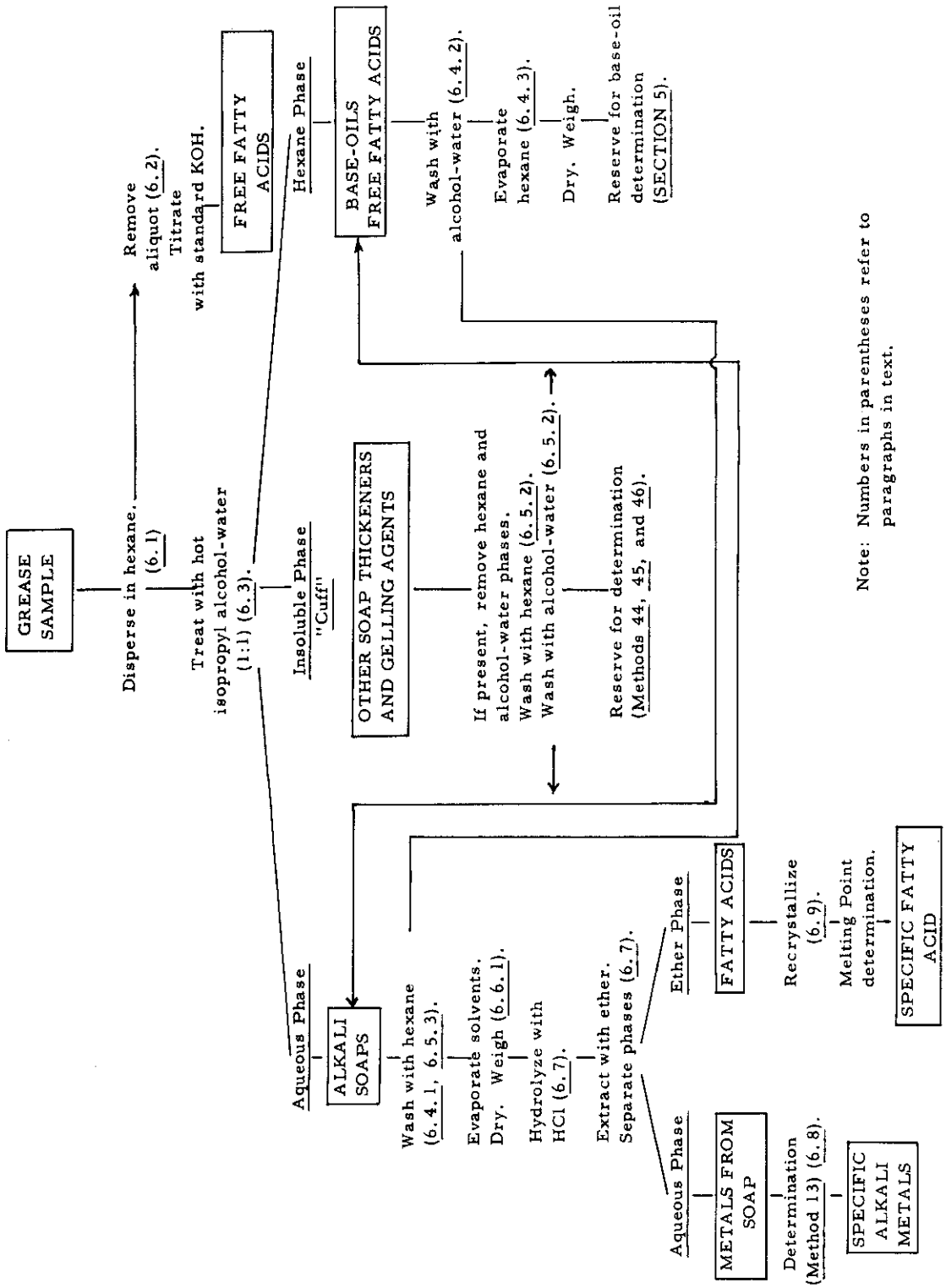


Figure 15. Scheme of Analysis for Determination of Alkali Soap Thickeners.

3.1 The size of sample employed for this procedure shall be about 5 grams, and shall be weighed accurately to 1 milligram on an analytical balance. The original sample of grease shall be made as uniform as possible. If the grease is soft, stir and mix with a glass or wood paddle in a beaker until uniform. If the grease is hard, scrape off the surface layers with a clean spatula, and take the sample from the freshly exposed surface.

4.0 APPARATUS

4.1 Centrifuge. A centrifuge is required which is equipped with a head, trunnion carriers, cups, and rubber cushions, capable of holding 100-milliliter capacity centrifuge tubes (such as A.S.T.M. pear-shaped oil tubes) and which can be controlled to give rotational speeds up to 1800 r.p.m. or higher.

4.2 Suction Apparatus. This simple apparatus (illustrated in Figure 2, Method 15) provides a fast, convenient method for separating and transferring liquid layers from the centrifuge tube to a separatory funnel or other container for further treatment. The tubing shall be capillary type with 1 to 2 millimeter diameter bore, and the tip shall be drawn out to a length of about 4 inches to provide a minimum of glass surface to disturb the contents in the tube. The 4 inch tip shall have a 1 millimeter o.d. and 0.25 millimeter i.d. A standard A.S.T.M. pear-shaped 100-milliliter oil centrifuge tube is convenient for use in this Method, although this is not essential to performance of the separation (Note 2). The 125-milliliter separatory funnel is equipped with a two-hole rubber stopper which contains two sections of capillary tubing. Water aspirator vacuum is sufficient, since only low vacuum is needed to draw the liquid from the centrifuge tube into the funnel. A trap should be provided in the vacuum line. The capillary-bore three-way stopcock, opening to the air, provides a convenient means for controlling the rate of flow of liquid through the capillary tubing into the container.

Note 2. Any type of centrifuge tube of about 100-milliliter capacity which can be employed with the available centrifuge facilities will be adequate.

4.3 Drying Oven. This oven should be capable of maintaining a constant temperature of 110°±5°C.

4.4 Melting Point Apparatus. This apparatus should allow temperature control to within 1°C. rise per minute. Either an aluminum-block type, electrically or gas heated, or a glass capillary type, immersed in a high boiling liquid bath, may be employed.

4.5 Porcelain Filter Crucibles (fine porosity).

4.6 Analytical Balance, capable of weighing to 0.1 milligram.

5.0 REAGENTS

5.1 Hexane, purified grade. Technical grade hexane may be purified by distilling over sodium hydroxide or anhydrous sodium carbonate and the fraction boiling from 63 to 69°C. shall be collected for use in this Method.

5.2 Isopropyl alcohol:water solution (1:1, v/v). Mix equal volumes of 99 percent reagent grade isopropyl alcohol and distilled water.

5.3 Hydrochloric acid solution (1:1, v/v). Pour one volume of reagent grade HCl (sp. gr. 1.19) into an equal volume of distilled water.

5.4 Hydrochloric acid solution (6N).

5.5 Diethyl ether, anhydrous, reagent grade.

5.6 Alcoholic methyl red indicator solution (1 gram per liter). Dissolve 0.5 gram of methyl red in 300 milliliters of ethyl alcohol (95 percent), and dilute with water to 500 milliliters.

5.7 Phenolphthalein solution (0.1 percent in ethanol).

5.8 Standard potassium hydroxide solution (alcoholic, 0.1N). Add 6 grams of chemically pure KOH to 1 liter of 99.8 percent reagent grade isopropyl alcohol, contained in a 2 liter Erlenmeyer flask. Boil the mixture gently for 10 to 15 minutes, stirring to prevent the solids from forming a cake on the bottom. Add at least 2 grams of chemically pure $Ba(OH)_2$ and again boil gently for 5 to 10 minutes. Cool to room temperature, stopper the flask, and allow to stand for several hours; filter the supernatant liquid through a sintered-glass or porcelain filtering funnel

(fine porosity). Avoid unnecessary exposure to CO_2 during the filtration. Store the solution in a chemically resistant bottle. Dispense in such a manner that it does not come in contact with cork, rubber, or saponifiable stopcock lubricant. Standardize frequently enough to detect normality changes of 0.0005N, by titration of 0.16 gram (accurately weighed) of analytical reagent grade potassium acid phthalate dissolved in 125 milliliters of CO_2-free distilled water, using phenolphthalein indicator.

5.9 Potassium acid phthalate, reagent grade, primary standard.

5.10 Acetone, reagent grade.

5.11 Nitric acid (sp. gr. 1.42), reagent grade.

5.12 Amyl alcohol, reagent grade, boiling point 132°C.

5.13 Sulfuric acid solution (4N).

5.14 Perchloric acid, 60-70% reagent grade, free from non-volatiles.

5.15 n-Butyl alcohol, reagent grade, boiling range 116-118°C.

5.16 Ethyl acetate, reagent grade, anhydrous, ethyl alcohol-free.

6.0 PROCEDURE

6.1 DISPERSION OF THE GREASE. Weigh a 5 gram sample of the grease in a 100-milliliter A.S.T.M. pear-shaped oil centrifuge tube in the following manner: obtain the weight of the centrifuge tube to the nearest milligram, and record; add a little more than 5 grams of grease to the centrifuge tube with a spatula or by other convenient means (such as a syringe), taking care that no grease touches the mouth of the tube. Break up any large pieces of grease to promote rapid dispersion in the solvent; weigh the sample and centrifuge tube to the nearest milligram. Add 50 to 60 milliliters of hexane, stopper the tube with a cork or polyethylene stopper, and shake vigorously until the grease is dispersed. If necessary, heat the hexane to boiling by immersion in a steam or boiling water bath, following by vigorous shaking (Note 3). Repeated heating and shaking will break down most synthetic lubricant greases, some being more

resistant to this treatment than others.

Note 3. Caution should be exercised at all times when working with hexane and other volatile, flammable solvents. Under no conditions should hexane be heated in the vicinity of open flames. Always use a hot water bath to heat hexane in the centrifuge tube.

6.2 DETERMINATION OF FREE FATTY ACIDS

6.2.1 Procedure. To obtain the free acid content of the grease, which is usually expressed in terms of free fatty acid, adjust the volume of the grease sample, which has been thoroughly dispersed in hexane, to exactly either 50 or 100 milliliters, mix to ensure homogeneity, and centrifuge at 1800 r.p.m. (or at the speed designated by the centrifuge manufacturer for the type of tube being employed) for ten minutes or until all insoluble material has been thrown down. Withdraw an aliquot of 10 milliliters from the tube, transfer to an Erlenmeyer flask of about 100 milliliters capacity, and titrate with standard alcoholic KOH with phenolphthalein indicator to a permanent pink color, shaking well after each addition of alkali.

6.2.2 Calculation. Calculate the percentage of free fatty acids (as stearic acid) in the grease sample as follows:

$$\text{Free fatty acid (percent) (as stearic acid)} = \frac{B \times C \times 0.285 \times 100}{W}$$

where: B = milliliters of KOH solution required for titration.
C = normality of KOH solution.
W = weight of sample in grams.

6.3 SEPARATION OF BASE-OIL AND ALKALI SOAP THICKENER. Add 50 milliliters of hot isopropyl alcohol-water (1:1) to the hexane solution of the grease (6.1), or to the remainder of the hexane solution after removing the aliquot for free acid titration (6.2.1). Stopper the tube with a cork or polyethylene stopper, and shake for several minutes. Maintain the solution at the boiling point of hexane for at least 5 minutes by immersion in a steam or boiling water bath, followed by further shaking. Centrifuge the tube at 1800 r.p.m. for 5 to 10 minutes, or until clear phases are obtained. If the grease contains only alkali soap thickeners, there should be none or a minimum amount

of insoluble material at the interface. Separate the phases using the suction apparatus described in Paragraph 4.2, and illustrated in Method 15. Draw the hexane phase, which contains base-oils and soluble additives, into a separatory funnel to be washed and retained for further analysis by paper and column chromatography (see Method 16 and Section 5). Withdraw the first 30 or 40 milliliters rapidly, taking care to immerse the tip of the suction tube only a few millimeters below the surface of the hexane. Withdraw the last portions of liquid very slowly to prevent removal of the alcohol-water phase from the centrifuge tube.

6.4 PROCEDURE IF ONLY ALKALI SOAPS ARE PRESENT.

6.4.1 Washing the Alcohol Phase. If there is a minimum of insoluble material at the interface, the grease contains only alkali soaps. After separating the hexane phase by suction, leave the IPA-water* phase in the centrifuge tube, add about 25 milliliters of hexane, heat to boiling, stopper, and shake for a few moments to remove residual oils from the IPA-water. Centrifuge and withdraw the hexane into the separatory funnel which contains the original hexane extract, taking care not to remove any of the lower phase. Wash the IPA-water phase a second time with 15 milliliters of hexane, centrifuging and adding the washings by suction to the previous hexane extracts. Place a few milliliters of hexane in a beaker and draw this hexane into the separatory funnel to rinse the suction tube. Allow the suction to continue for a moment to air-dry the tube.

6.4.2 Washing the Hexane Phase. Wash the combined hexane extracts in the separatory funnel by shaking with 20 milliliters of hot IPA-water solution. Allow the phases to separate, and withdraw the IPA-water, adding it to the original IPA-water extract. Repeat this washing. Reserve the combined IPA-water extracts for determination of alkali soap content (6.6 through 6.9).

6.4.3 Removing Hexane From the Base-Oils. Transfer the combined hexane extracts and washings to a 250-milliliter round-bottom distillation flask and distill most of the hexane from the base-oils and additives, using a glass heating mantle or hot plate. When the volume of the solution is about 10 milliliters, cool the apparatus, and remove the distillation flask. To obtain the content of hexane-soluble materials in the grease, weigh a clean, dry Petri dish to the nearest milligram;

* IPA = isopropyl alcohol.

transfer the solution to the Petri dish and wash out the flask with three successive 10 milliliter portions of hexane, washing the outside of the lip of the flask to remove traces of base-oils. Evaporate the remainder of the solvent on a hot water bath with a slow stream of air blowing across the surface of the solution. When all the hexane has evaporated, dry at 110 °C. for about 15 minutes. Cool the dish in a desiccator and weigh. Bring to a constant weight by drying for 15 minutes, cooling, and re-weighing. Reserve the oil for analysis by paper and column chromatography (see Method 16 and Section 5).

6.4.4 Calculation. Calculate the percent of hexane-solubles in the grease as follows:

$$\text{Hexane-solubles (percent)} = \frac{D \times F \times 100}{W}$$

where: D = weight of hexane-solubles in grams.
W = weight of sample in grams.
F = factor due to removal of aliquot from the hexane solution (6.2.1).

6.5 PROCEDURE IF INSOLUBLE GELLING AGENTS ARE PRESENT.

6.5.1 Removing the Alcohol-Water Phase. If there are insoluble materials, called a "cuff", at the interface between the two liquid phases, the grease contains either alkaline-earth soap thickeners, inorganic or organic gelling agents, or combinations of these materials. Remove the hexane phase by suction as described in Paragraph 6.3. Replace the funnel containing hexane with a clean 125-milliliter separatory funnel to receive the IPA-water phase. Place the centrifuge tube containing the cuff and IPA-water under the suction tube and, with no suction being applied, move the capillary tip of the suction tube through the cuff into the IPA-water. Apply suction and slowly withdraw the IPA-water (take care that none of the cuff is drawn into the tube). When only a few milliliters of IPA-water remain, turn off the vacuum by opening the stopcock above the trap to the air. Withdraw the capillary tip to a point several millimeters above the cuff and with a wash bottle, pipette, or medicine dropper wash off the tip of the suction tube with a few milliliters of hot IPA-water solution. Rinse out the suction tube by drawing several milliliters of hot IPA-water through the tube into the separatory funnel.

6.5.2 Washing the Cuff. Add 25 milliliters each of hexane and IPA-water solution to the centrifuge tube containing the cuff, heat to boiling in a steam bath, shake for several minutes to dissolve residual oils and alkali soaps, and centrifuge until both layers are clear and the cuff is well defined between them. Withdraw the hexane first, adding it to the first hexane extract. Next, withdraw the IPA-water phase as described previously (6.5.1), and add this to the first IPA-water extract. Wash the cuff again with 10 milliliters each of hexane and IPA-water. Reserve the cuff for determination of alkaline-earth soaps and gelling agents (see Methods 43, 44, and 45).

6.5.3 Washing the Alcohol-Water and Hexane Phases. Wash the combined IPA-water extracts once with 25 milliliters of hexane, heating, shaking, centrifuging, and separating as described previously (6.4.1). Add the separated hexane to the hexane washings. Wash the combined hexane extracts with 20 milliliters of hot IPA-water solution, separate by suction and add the washings to the combined IPA-water extract.

6.6. WEIGHT OF ALKALI SOAPS

6.6.1 Procedure. Transfer the combined IPA-water extract to a large glass crystallization or porcelain evaporating dish (Note 4). Place the dish on a steam or water bath and evaporate the solution to dryness, using a stream of air across the surface of the solution. The residue consists of alkali metal soaps. Weigh a Petri dish or other wide, flat container to 0.1 milligram and with a minimum quantity of distilled water transfer quantitatively the alkali soap from the large dish to the weighed Petri dish. Approximately 30 milliliters of water in about 5 milliliter portions is required to transfer the soap. Place the Petri dish on the water bath and evaporate to dryness, using air to remove the last traces of moisture. Continue heating on the bath, adding and evaporating 5 milliliter portions of acetone until constant weight is obtained. The weight of alkali soap is thereby obtained. If the elementary analysis (Method 13) has shown that only one alkali metal is present, the analyst may assume that the soap obtained is a single compound, the composition depending on which fatty acid has been found by Method 15.

Note 4. If it is desired to recover some of the isopropyl alcohol, transfer the IPA-water extract to a 250-milliliter round-bottom distillation flask. Distill off the bulk of the alcohol and transfer the remaining solution to the crystallization or evaporating dish.

6.6.2 Calculation. Calculate the percent of alkali soap in the grease as follows:

$$\text{Alkali soap(s) (percent)} = \frac{C \times 100}{W}$$

where: C = weight of alkali soap(s) in grams.
W = weight of sample in grams.

6.7 HYDROLYSIS OF ALKALI SOAP

6.7.1 Transfer quantitatively the alkali soap residue from the Petri dish to a 400-milliliter beaker with 5 milliliter portions of distilled water. Add 25 milliliters of HCl solution (1:1), cover the beaker with a clean watch glass, and heat to boiling for several minutes. Cool the solution, transfer to a 250-milliliter separatory funnel, add 50 milliliters of diethyl ether, close, and shake vigorously for several minutes. Set the funnel aside in a vertical position and allow the aqueous and ether phases to separate completely until they are almost clear. Remove the stopper and slowly drain the aqueous phase into a separatory funnel, leaving the ether phase in the first funnel. Add another 50 milliliters of diethyl ether to the aqueous phase in the second funnel, close and shake as before. Again separate the phases, receiving the aqueous phase in a 250-milliliter beaker, and add the ether to the first ether solution. Reserve the ether extract for the identification and/or determination of fatty acids (6.9), and the aqueous phase for the identification and/or determination of alkali metals (6.8).

6.8 DETERMINATION OF THE METAL CONTENT OF THE ALKALI SOAP.

6.3.1 Employ the flame tests described in Paragraph 11.2, Method 15, to determine the type of metals present in the aqueous phase. If the alkali metals have already been determined by Method 13, it is usually not necessary to determine the alkali soap metals isolated in Paragraph 6.7, unless the weight of alkali soap cannot be correlated with the weight of alkali metal. If complete analysis for these metals is required, analyze the aqueous solution in accordance with Paragraphs 7.4 through 7.8 in Method 13.

6.9 DETECTION OF FATTY ACID(S) FROM ALKALI SOAP.
The fatty acid(s) from the hydrolyzed soap (6.7) can be identified by the methods described in Paragraph 7.3, Method 15. An approximateion of

the weight of fatty acids evolved from hydrolysis of the alkali soap may be obtained by careful recrystallization of the fatty acid from the ether solution in a weighed Petri dish. Drain the fatty acid-containing ether from the separatory funnel into a 125-milliliter Erlenmeyer flask. Rinse the funnel thoroughly with two 10 milliliter portions of ether, adding the washings to the flask. Evaporate to dryness on a water bath, using an air stream. Re-dissolve the crystals in about 15 milliliters of diethyl ether, and transfer the solution quantitatively to a weighed Petri dish. Rinse the Erlenmeyer flask with two 5 milliliter portions of diethyl ether. Evaporate to dryness on a water bath, dry the crystals in a low temperature oven (50°C.) for about 1 hour, and weigh. Re-dry the crystals for another hour to bring to constant weight. In this manner the approximate weight of fatty acids from the alkali soap may be obtained; this value should correlate with the total metal content of the soap (6.8) to within a few percent. Identify the fatty acid by determination of melting point as stearic acid (m. p. 69°C.) or 10-hydroxystearic acid (m. p. 81°C.). In the event that mixtures of alkali soaps containing more than one fatty acid are employed in the grease, a situation which is unlikely, further complicated analysis such as paper chromatography or fractional crystallization will be required (Note 5).

Note 5. Methods for separation and determination of mixtures of two or more fatty acids employed in alkali soaps can probably be evolved using paper chromatography of hydroxamates of the acid mixture, or by employing fractional crystallization followed by identification of the acids in the fractions.

6.10 Calculations. Calculate the percent soap in the grease as follows:

$$\text{Alkali Soap (percent)} = \frac{M \times F \times 100}{W}$$

where: M = weight of metal in grams.

F = gravimetric factor depending on the metal and fatty acid found in the grease (Note 6).

W = weight of grease sample in grams.

Note 6. If the procedure was carried beyond Paragraph 6.6.2, in which the percent alkali soap content in the grease was determined, the following gravimetric factors should be used in determining the weight of alkali soap which would correspond with

the metal content of the hydrolysis mixture as determined by Method 13:

Lithium (10-hydroxystearate)	= % lithium x 44.15
Lithium stearate	= " x 41.84
Sodium (10-hydroxystearate)	= % sodium x 14.06
Sodium stearate	= " x 13.32
Potassium (10-hydroxystearate)	= % potassium x 8.66
Potassium stearate	= " x 8.25

SEPARATION AND DETERMINATION OF ALUMINUM AND ALKALINE-EARTH SOAP THICKENERS

1.0 SCOPE

1.1 This method is intended to describe procedures for the quantitative separation of alkaline-earth and aluminum soap thickeners from base-oils and other additives in synthetic greases, and for their quantitative determination after separation. The method is not restricted by the type of base-oil in the grease, nor is it affected by the presence of other types of gelling agents or thickeners (Note 1). This method includes the determination of free fatty acid content of grease.

Note 1. It is intended that this method should be employed in close conjunction with Method 13, QUANTITATIVE ELEMENTAL ANALYSIS, and Method 15, PRELIMINARY QUALITATIVE CLASSIFICATION OF SYNTHETIC GREASES. Use of these methods will establish the presence of aluminum or alkaline-earth soap thickeners and other thickeners and gelling agents, and the amount of metal from soap thickeners and gelling agents. The analyst must determine from Method 15 the proper procedure in using Method 43 most efficiently. If, for instance, no other gelling agents or soap thickeners are present except aluminum or alkaline-earth soaps, it is unnecessary to use the isopropyl alcohol-water (1:1) solution to separate inorganic gelling agents by the amyl acetate extraction; the base-oil is removed with hexane as described below, and determination of aluminum or alkaline-earth soap is carried out by weighing or by further chemical analysis. Judgment of the analyst is important in selecting the most direct, least time-consuming method of approach for quantitative analysis of each individual grease, based on his findings in Methods 13 and 15.

2.0 OUTLINE OF METHOD

2.1 A schematic outline of this method is presented in Figure 16. The grease is dispersed in hexane and centrifuged. Base-oils are removed with the hexane phase. Aluminum and alkaline-earth soaps are collected as a precipitate and weighed. The soap is hydrolyzed with dilute acid and metals evolved from the soap are determined quantitatively. Fatty acids from the soap are weighed and identified. If alkali soaps are present in the grease, hot isopropyl alcohol-water solution is used to

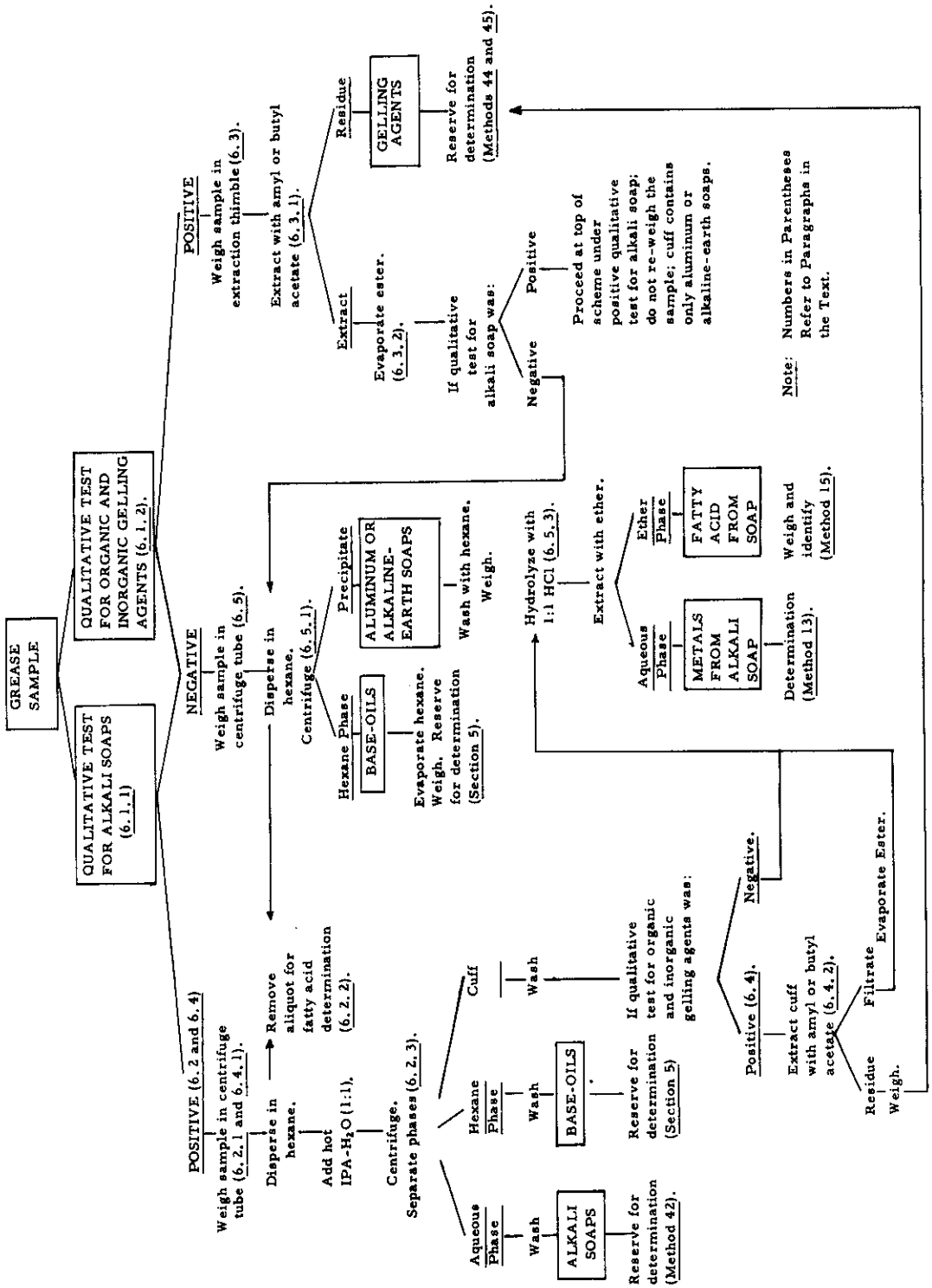


Figure 16. Scheme of Analysis for Aluminum and Alkaline-Earth Soap Thickeners.

separate them prior to determining the aluminum or alkaline-earth soaps. If bentone and/or other organic or inorganic gelling agents are present, they are separated from the aluminum and alkaline-earth soaps by extracting the latter with amyl or butyl acetate.

2.2 If Methods 13 and 15 have not been utilized to establish the presence of alkali soaps or organic and inorganic gelling agents in the grease, two preliminary qualitative tests for these groups of compounds must be performed. First, the presence of alkali soaps must be established by dispersing the grease in hexane and hot isopropyl alcohol-water (1:1) solution. If a residue is found on evaporating the alcohol-water solution, this indicates the presence of alkali soaps, and the separation procedure must be modified to allow for these soaps. Second, if the grease does not dissolve entirely in warm amyl or butyl acetate, a residue indicates the presence of organic and/or inorganic gelling agents. Figure 16 shows the procedures which must be adopted if either or both of these tests are positive.

3.0 SAMPLE

3.1 The size of sample employed for this procedure shall be about 5 grams, and shall be weighed accurately to 1 milligram on an analytical balance. The original sample of grease shall be made as uniform as possible. If the grease is soft, stir and mix with a glass or wood paddle in a beaker until uniform. If the grease is hard, scrape off the surface layers with a clean spatula, and take the sample from the freshly exposed surface.

4.0 APPARATUS

4.1 Centrifuge. A centrifuge is required which is equipped with a head, trunnion carriers, cups, and rubber cushions, capable of holding 100-milliliter capacity centrifuge tubes (such as A.S.T.M. pear-shaped oil tubes), and which can be controlled to give rotational speeds up to 1800 r.p.m. or higher.

4.2 Suction Apparatus. This apparatus (illustrated in Figure 2, Method 15) provides a fast, convenient method for separating and transferring liquid layers from the centrifuge tube to a separatory funnel or other container for further treatment. The tubing is capillary type with 1 to 2 millimeter diameter bore, and the tip which is placed in the liquid is drawn out to a length of 4 inches to provide a minimum of glass sur-

face to disturb the contents in the tube. The 4 inch tip has a 1 millimeter o.d. and 0.25 millimeter i.d. A standard A.S.T.M. pear-shaped 100-milliliter oil centrifuge tube is convenient for use in this Method, although this is not essential to performance of the separation (Note 2). The 125-milliliter separatory funnel is equipped with a two-hole rubber stopper which contains two sections of capillary tubing. Water aspirator vacuum is sufficient, since only low vacuum is needed to draw the liquid from the centrifuge tube into the funnel. A trap should be provided in the vacuum line. The capillary-bore three-way stopcock, opening to the air, provides a convenient means for controlling the rate of flow of liquid through the capillary tubing into the funnel.

Note 2. Any type of centrifuge tube of about 100-milliliter capacity which can be employed with the available centrifuge facilities will be adequate.

4.3 Drying Oven. This oven should maintain a constant temperature of 110°C.

4.4 Melting Point Apparatus. This apparatus should allow temperature control to within 1°C. rise per minute. Either an aluminum-block type, electrically or gas heated, or a glass capillary type, immersed in a high boiling liquid bath, may be employed.

4.5 Soxhlet Extraction Apparatus. Standard laboratory Soxhlet extraction chamber (preferably with a stopcock takeoff at the bottom of the chamber for withdrawing samples of solvent), reflux Allihn condenser, and cellulose extraction thimbles which fit loosely in the extraction chamber should be provided. Standard taper ware is preferable, because of ease of assembly, interchangeability, and elimination of rubber stopper fittings. A hot plate shall be used for heating, or a heating mantle with a variable voltage transformer.

4.6 Analytical Balance, capable of weighing to 0.1 milligram.

4.7 Claisen Distillation Apparatus. Standard laboratory distillation apparatus shall be provided with Claisen type distillation flask, West-type condenser, 105° receiving tube adapter, and receiving flask. Standard taper ware is preferable.

5.0 REAGENTS

5.1 Hexane, purified grade. Technical grade hexane may be purified by distilling from sodium hydroxide or anhydrous sodium carbonate, and the fraction boiling from 63° to 69°C. shall be collected for use in this Method.

5.2 Isopropyl Alcohol-Water Solution (1:1, v/v). Mix equal volumes of 99.8 percent reagent grade isopropyl alcohol and distilled water.

5.3 Standard Potassium Hydroxide Solution (alcoholic, 0.1N). Add 6 grams of chemically pure KOH to 1 liter of 99.8 percent reagent grade isopropyl alcohol, contained in a 2-liter Erlenmeyer flask. Boil the mixture gently for 10 to 15 minutes, stirring to prevent the solids from forming a cake on the bottom. Add at least 2 grams of chemically pure $Ba(OH)_2$ and again boil gently for 5 to 10 minutes. Cool to room temperature, stopper the flask, and allow to stand for several hours; filter the supernatant liquid through a sintered-glass or porcelain filtering funnel (fine porosity). Avoid unnecessary exposure to CO_2 during the filtration. Store the solution in a chemically resistant bottle. Dispense in such a manner that it does not come in contact with cork, rubber, or saponifiable stopcock lubricant. Standardize frequently enough to detect normality changes of 0.0005N, by titration of 0.16 gram (accurately weighed) of analytical reagent grade potassium acid phthalate dissolved in 125 milliliters of CO_2-free distilled water, using phenolphthalein indicator.

5.4 Potassium Acid Phthalate, reagent grade, primary standard.

5.5 Phenolphthalein Indicator Solution, (0.1 percent in ethanol).

5.6 Hydrochloric Acid (1:1, v/v). Pour one volume of concentrated, reagent grade HCl (sp. gr. 1.19) into an equal volume of distilled water.

5.7 Diethyl Ether, reagent grade, anhydrous.

5.8 Amyl Acetate, purified, boiling range 141 to 143°C. (butyl-acetate, purified or reagent grade, boiling range 124 to 126°C., may be substituted for amyl acetate).

6.0 PROCEDURE.

6.1 PRELIMINARY INSPECTION OF GREASE SAMPLE. The analyst should use Method 15 to establish the presence or absence of alkali soap thickeners, aluminum and alkaline-earth soap thickeners, and organic and inorganic gelling agents; in this way, the procedures outlined in Figure 16 can be accomplished more easily. If Method 15 has not been carried out, it is necessary to perform qualitative tests for alkali soaps and organic and inorganic gelling agents to avoid, if possible, the procedures for separating these compounds. These tests are given in Paragraphs 6.1.1 and 6.1.2 below.

6.1.1 Qualitative Test for Alkali Soap Thickeners. Place a 1 gram sample of grease in a 50-milliliter centrifuge tube, fill the tube half full with hexane, close with a cork or polyethylene stopper, and shake vigorously. Heat to the boiling point of hexane in a water bath (if necessary) to promote solution of the grease. When the grease is dispersed, add an equal volume of isopropyl alcohol-water (1:1), heat to boiling, close the tube, and again shake. Centrifuge at 1800 r.p.m. to separate the phases. With the suction apparatus draw the alcohol-water phase into a second centrifuge tube, using the technique described in Paragraph 10.1, Method 15. Wash the alcohol-water phase with an equal volume of hexane by heating and shaking. Centrifuge, separate the phases, and transfer the alcohol-water to a small crystallizing dish or a black-glazed evaporating dish. Evaporate to dryness on a boiling water bath. If there is an appreciable residue, alkali soaps are present, and the analysis for aluminum or alkaline-earth soaps should proceed according to Paragraph 6.2 (or Paragraph 6.4, if the following test for organic and inorganic gelling agents is positive).

6.1.2 Qualitative Test for Organic and Inorganic Gelling Agents. Place a 1 gram sample of grease in a small 50-milliliter centrifuge tube and fill the tube half full with amyl acetate. Close the tube and shake vigorously to disperse the grease. Warm if necessary. If the grease disperses completely in the solvent, leaving no insoluble material, it may be assumed that there are no organic or inorganic gelling agents in the grease. If organic or inorganic gelling agents are present, proceed with Paragraph 6.3 (or Paragraph 6.4, if the results of the preceding test for alkali soap thickeners was positive).

6.2 PROCEDURE IN THE PRESENCE OF ALKALI SOAP THICKENERS.

6.2.1 Dispersion of the Grease. Weigh a 5 gram sample of the grease, and proceed as described in Paragraph 6.1, Method 42.

6.2.2 Determination of Free Fatty Acids.

6.2.2.1 Procedure. Proceed as described in Paragraph 6.2.1, Method 42.

6.2.2.2 Calculation. Calculate the approximate percentage of free fatty acids according to the formula given in Paragraph 6.2.2, Method 42.

6.2.3 Separation of Base-Oils and Alkali Soaps. After withdrawal of the aliquot for analysis of fatty acids (6.2.2), treat the hexane dispersion of the grease as described in Paragraph 6.5, Method 42. Reserve the washed and dried cuff for the determination of aluminum and alkaline-earth soap thickeners as described below (6.5.4). The aqueous phase shall be reserved for the determination of alkali soap thickeners (Method 42), and the hexane phase for the determination of base-oils (6.5.3).

6.3 PROCEDURE IN THE PRESENCE OF ORGANIC AND INORGANIC GELLING AGENTS.

6.3.1 Separation of Gelling Agents from Base-Oil and Soap Thickeners. Weigh a 5 gram sample of grease into a Soxhlet extraction thimble (double weight thimble is preferred), using a small clean spatula to transfer the grease into the previously weighed thimble (Note 3). If a hard grease is being analyzed, break it into as many pieces as possible. Place the thimble in the Soxhlet apparatus and fill the 250-milliliter flat-bottom boiling flask about half full of pure amyl or butyl acetate. Extract the grease overnight, making sure that the liquid siphons periodically, draining the chamber completely, and does not simply leak a small stream of solvent continuously through the siphon tube. Check the completeness of extraction by occasionally withdrawing two or three drops of liquid through the stopcock onto a clean watch glass, and evaporate to dryness. When no residue is apparent on the watch glass, extraction is complete. Cool the apparatus to room temperature, and carefully lift the thimble from the chamber with tweezers or forceps, permitting solvent in the thimble to drain back into the chamber. Place the wet thimble in a small beaker or on a large watch glass, and dry at 105-110°C. for at least one hour. If a vacuum oven is available, the thimble may be dried

for a short period at 110°C. in the air oven, and may then be dried in vacuum at 50°C. for one hour. Cool the dried thimble in a desiccator, and weigh to obtain organic and inorganic gelling agents (Note 3). Reserve this residue for the determination of these compounds (Methods 44 and 45). Reserve the ester solution for separation of aluminum and alkaline-earth soap thickeners from base-oils (6.3.2).

Note 3. Weight of the extraction thimble will be more accurate if it is contained in a thin-wall ground-stoppered glass or polyethylene-stoppered vial. After cooling in a desiccator, the thimble may be slipped into the vial and weighed. This prevents moisture pickup while weighing.

6.3.2 Removal of Solvent From Soap Thickeners and Base-oils. Attach the 250-milliliter flat-bottom flask containing the ester solution of aluminum or alkaline-earth soap thickeners (6.3.1) to a Claisen distillation apparatus, and distill off most of the ester at a rate of about one drop per second. Remove the flask from the apparatus, and evaporate the remainder of the solvent on a steam bath, using a slow stream of dry air to hasten the process. (CAUTION: Always evaporate solvents in a fume hood or well-ventilated area!) When most of the solvent has been removed, as indicated by absence of the typical ester odor, a grease will usually have formed, which can be dried further by heating to 110°C. in a drying oven or to 50°C. in a vacuum oven. Reserve the residue of base-oil and soap thickener for their separation and determination (6.5.2).

6.4 PROCEDURE IN THE PRESENCE OF ORGANIC AND INORGANIC GELLING AGENTS AND ALKALI SOAP THICKENERS

6.4.1 Dispersion of the Grease. Proceed as described in Paragraph 6.1, Method 42. Determine and calculate free fatty acids according to Paragraphs 6.2.1 and 6.2.2, Method 42. Follow the procedures in Paragraphs 6.3 and 6.5, Method 42, to remove alkali soap thickeners and to obtain a clean, dry cuff. Since organic and inorganic gelling agents are present in the cuff, aluminum and alkaline-earth soaps must next be separated from the gelling agents (6.4.2).

6.4.2 Separation of Aluminum and Alkaline-Earth Soaps From Gelling Agents. Grind the dried and weighed cuff in a mortar, pulverizing it completely. Transfer as much of the powder as possible to a weighed Soxhlet extraction thimble (double weight thimble is recom-

mended) (Note 3), recording the aliquot part of the cuff which is used in the extraction and subsequent determination. Extract overnight, making sure that the liquid siphons periodically, draining the chamber completely, and does not simply leak a small stream of solvent continuously through the siphon tube. Test for completeness of extraction by occasionally withdrawing two or three drops of liquid through the stopcock onto a clean watch glass, and evaporate to dryness. When no residue is apparent on the watch glass, the extraction is complete (Note 4). Allow the apparatus to cool and lift the thimble carefully from the chamber with tweezers or forceps, permitting solvent in the thimble to drain back into the chamber. Place the wet thimble on a large watch glass, and dry at 105°-110°C. for at least one hour. If a vacuum oven is available, the thimble may be dried for a short period at 110°C. in the air oven, and may then be dried in vacuum at about 50°C. for one hour. Cool in a desiccator, place the dry thimble in a previously weighed tube (see Note 3), and weigh to obtain the organic and inorganic gelling agent content of the grease. It must be remembered that an aliquot of the total amount of cuff was used in the Soxhlet extraction. Reserve the gelling agents for determination by Methods 44 and 45, and reserve the ester solution of aluminum and alkaline-earth soaps for removal of the solvent (6.4.3).

Note 4. This extraction may require as much as 40 hours if the dried cuff is not ground up, or if the extraction chamber does not siphon properly.

6.4.3 Removal of Solvent From Aluminum and Alkaline-Earth Soap Thickeners. Attach the 250-milliliter flat-bottom flask containing the ester solution of aluminum or alkaline-earth soap thickeners (6.3.1) to a Claisen distillation apparatus, and distill off most of the ester at a rate of about one drop per second. Remove the flask from the apparatus and evaporate the remainder of the solvent on a steam bath, using a slow stream of dry air to hasten the process. (CAUTION: Always evaporate solvents in a fume hood or well-ventilated area!) When most of the solvent has been removed, as indicated by absence of the typical ester odor, dry the soap in a vacuum oven at 50°C. for one hour, or in an air drying oven at 110°C. for one hour. If possible, a slow stream of heated air introduced into the flask during drying speeds the process. Reserve the aluminum and alkaline-earth soaps for determination (6.5.4).

6.5 DETERMINATION OF ALUMINUM AND ALKALINE-EARTH SOAP THICKENERS.

6.5.1 Determination in Greases Containing No Other Soaps or Gelling Agents. Weigh a 5 gram sample of grease, or take the soap thickener-base-oil mixture after removing ester solvent (6.4.3) in a 100-milliliter A.S.T.M. pear-shaped oil centrifuge tube in the following manner: obtain the weight of the centrifuge tube to the nearest milligram, and record; add a little more than 5 grams of grease to the centrifuge tube with a spatula or by other convenient means (such as a syringe), taking care that no grease touches the mouth of the tube. Break up any large pieces of grease to promote rapid dispersion in the solvent; weigh the sample and centrifuge tube to the nearest milligram. Add 50 to 60 milliliters of hexane, stopper the tube with a cork or polyethylene stopper, and shake vigorously until the grease is dispersed. If necessary, heat the hexane to boiling by immersion in a steam or boiling water bath, followed by vigorous shaking (Note 5). Repeated heating and shaking will break down most synthetic lubricant greases, some being more resistant to this treatment than others. Centrifuge at 1800 r.p.m. to settle out aluminum and alkaline-earth soap thickeners. Using the suction apparatus, place the tip of the capillary into the hexane, and withdraw the liquid into a graduated container of about 100-milliliter capacity, removing the last few milliliters very slowly to avoid drawing up any of the precipitate. It is not necessary to remove the last one-half milliliter, as the remaining base-oil will be diluted and picked up in the washings. Add 15 milliliters of fresh hexane to the tube, shake to wash the soap precipitate thoroughly, and again centrifuge. Withdraw the supernatant wash hexane into the graduated container. Repeat this washing with two more 10 milliliter portions of hexane. Place the centrifuge tube on a water bath to evaporate traces of hexane from the soap residue. A slow stream of air will speed the removal of hexane. Dry the soap at 50°C. in a vacuum oven for one hour. Cool in a desiccator and weigh to obtain the total hexane insolubles in the grease, which are primarily aluminum and alkaline-earth soap thickeners. Reserve this residue for positive determination of these compounds (6.5.4), and reserve the hexane phase for the determination of free fatty acids (6.5.2), and base-oils (6.5.3).

Note 5. Caution should be exercised at all times when working with hexane and other volatile, flammable solvents. Under no conditions should hexane be heated in the vicinity of open flames. Always use a hot water bath to heat hexane in the centrifuge tube.

6.5.2 Determination of Free Fatty Acids.

6.5.2.1 Procedure. Adjust the volume of the hexane solution (6.5.1) to exactly 100 milliliters in the graduated container, mix to insure homogeneity, and withdraw an aliquot (10 milliliters will usually be sufficient). Transfer the aliquot to an Erlenmeyer flask of about 100 milliliter capacity and titrate with standard alcoholic KOH with phenolphthalein indicator to a permanent pink color, shaking well after each addition of alkali.

6.5.2.2 Calculation. Calculate the percentage of free fatty acids (as stearic acid) in the grease sample as follows:

$$\text{Free fatty acid (percent) (as stearic acid)} = \frac{B \times C \times 0.285 \times 100}{W}$$

where: B = milliliters of KOH solution required for titration.
C = normality of KOH solution.
W = weight of sample in grams.

6.5.3 Removing Hexane and Weighing the Base-Oil.

6.5.3.1 Procedure. Transfer the combined hexane extracts and washings to a 250-milliliter round-bottom distillation flask and distill most of the hexane from the base-oils and additives, using a glass heating mantle or hot plate. When the volume of the solution is about 10 milliliters, cool the apparatus, and remove the distillation flask. To obtain the content of hexane-soluble materials in the grease, weigh a clean, dry Petri dish to the nearest milligram; transfer the solution to the Petri dish and wash out the flask with three successive 10 milliliter portions of hexane, washing the outside of the lip of the flask to remove traces of base-oils. Evaporate the remainder of the solvent on a hot water bath with a slow stream of air blowing across the surface of the solution. When the hexane has evaporated, dry at 110°C. for about 15 minutes. Cool the dish in a desiccator and weigh. Bring to constant weight by drying for 15 minutes, cooling and reweighing. Reserve the oil for analysis by paper and column chromatography (see Method 16 and Section 5).

6.5.3.2 Calculation. Calculate the percent of hexane-solubles in the grease as follows:

$$\text{Hexane-solubles (percent} = \frac{D \times F \times 100}{W}$$

where: D = weight of hexane-solubles in grams.
W = weight of sample in grams.
F = factor due to removal of aliquot from the hexane solution (6.5.2.1).

6.5.4 Hydrolysis of Aluminum and Alkaline-Earth Soaps. Take the weighed residue after separating out alkali soaps (6.2), organic and inorganic gelling agents (6.3), or both types of thickeners and gelling agents (6.4), or the residue from the grease which contains only aluminum and alkaline-earth soap thickeners (6.5.1), and transfer the largest possible part to a mortar. Break up the residue into a powder and transfer this powder to a 125-milliliter weighed (to 1 milligram) 24/40 standard taper flat-bottom flask. Re-weigh the flask to obtain the weight of powder by difference; determine the aliquot part of the total weight of thickeners which has been taken for hydrolysis. Add about 50 milliliters of HCl (1:1), and attach the flask to a 24/40 standard taper Allihn condenser. Reflux the mixture one-half hour, or until the particles of soap have dissolved and the solution is clear. Allow the flask and contents to cool and transfer the liquid quantitatively to a 250-milliliter separatory funnel, washing the flask with several successive 10 milliliter portions of water, and with several 10 milliliter portions of diethyl ether. Add 50 milliliters of diethyl ether, stopper the funnel, and shake. Allow the funnel to stand until there is distinct separation of the two phases. Remove the stopper and slowly drain the aqueous layer into a second 250-milliliter separatory funnel. Repeat the ether extraction twice with 25 milliliters of ether, finally drawing off the aqueous layer into a 250 milliliter beaker, and adding the ether washings to the first ether extract. The aqueous phase contains aluminum and/or alkaline-earth metal salts, and the ether extract contains fatty acids from hydrolysis of the soaps. Reserve the aqueous phase for detection and/or determination of the metals (6.5.5), and the ether extract for identification of fatty acids (6.5.6).

6.5.5 Determination of Metal Content of Hydrolyzed Soaps.

6.5.5.1 Analysis of the salt-containing aqueous phase from hydrolysis of the soaps (6.5.3) may be approached in several ways, according to the accuracy desired by the analyst. Quantitative determination of the specific metals in the grease may already have been carried out by Method 13, in which event it is unnecessary to re-determine these metals in the hydrolysis solution; if, however, some of the metals such as aluminum and barium could have appeared in the grease through compounds

such as bentones or barium sulfonate, it is necessary that the metal content of the solution be determined. If other compounds containing these metals are absent in the grease, it is unnecessary to determine them in this solution, except as a check on the accuracy of the separation and as a verification of the analysis performed on the total grease by Method 13. If quantitative analysis of the metals in the solution is nevertheless desired, use Method 13, eliminating those steps which apply to determination of other metals than aluminum or alkaline-earths.

6.5.5.2 For the majority of synthetic greases, it is unlikely that more than one aluminum or alkaline-earth soap thickener will be employed in compounding the grease. Therefore it is usually unnecessary to attempt quantitative determination of each of the metals. It should suffice to identify the metal which is present by performing qualitative tests as described in Paragraphs 14.2.1 through 14.2.3, Method 15. Identification of the metal, coupled with the weight and the identification of the fatty acid hydrolyzed from the soap in Paragraph 6.5.6 below, provides an accurate measure of the aluminum or alkaline-earth soap content of the grease. The total weight of the soap thickener has been determined in Paragraph 6.5.1 as hexane-insoluble materials.

6.5.6 Determination of Fatty Acids Evolved From Hydrolyzed Soap. The fatty acid(s) from the hydrolyzed soap (6.5.4) can be identified by the techniques described in Paragraph 7.3, Method 15. An approximation of the weight of fatty acids evolved from hydrolysis of the aluminum and alkaline-earth soap thickeners may be obtained by careful recrystallization of fatty acid from ether solution in a weighed Petri dish. Drain the fatty acid-containing ether (6.5.4) from the separatory funnel into a 125-milliliter Erlenmeyer flask. Rinse the funnel thoroughly with two 10 milliliter portions of ether, adding the washings to the flask. Evaporate to dryness on a water bath, using an air stream. Re-dissolve the crystals of fatty acid in about 15 milliliters of diethyl ether, and transfer the solution quantitatively to a weighed Petri dish. Rinse the flask with two 5 milliliter portions of ether. Evaporate to dryness on a water bath, dry the crystals in a low temperature oven (50°C.) for about 1 hour, and weigh. Re-dry the crystals for another hour to bring to constant weight. In this manner the approximate weight of fatty acids from aluminum and alkaline-earth soap may be obtained; this value should correlate with the total metal content of the soap (6.5.5) to within a few percent. Identify the fatty acid by determination of melting point as stearic acid (m. p. 69°C.) or 10-hydroxystearic acid (m.p. 81°C). In the event

that mixtures of soaps containing more than one fatty acid are employed in the grease, a situation which is unlikely, further complicated analysis such as paper chromatography or fractional crystallization will be required (Note 6).

Note 6. Methods for separation and determination of mixtures of two or more fatty acids employed in aluminum or alkaline-earth soaps can probably be evolved, using paper chromatography of hydroxamates of the acid mixture, or by employing fractional crystallization followed by identification of the acids in the fractions.

6.6 CALCULATIONS.

6.6.1 Calculations for determination of aluminum or alkaline-earth soaps in a grease will depend upon the type of analysis carried out; that is, whether the total weight of soap present is determined by the metal content of the ash of the whole grease (Method 13), or by the metal content of the hydrolyzed soap (6.5.5), or simply by the weight of hexane-insolubles (6.5.1). The calculations for each of these approaches is given below (Note 7).

Note 7. Commercial soap thickeners, such as those used in compounding synthetic greases, are not pure compounds; aluminum stearate, in fact, does not exist in stoichiometric proportions, the commercial compound being closer to the composition Al(OH) Stearate)$_2$. Therefore account must be taken of these impurities. Free fatty acids contribute the highest percentage of impurity to commercial soaps and are determined in the hexane solution after dispersion of the grease. Other impurities are volatiles, salts, and moisture; these contribute from 1 to 2 percent of the total weight of soap thickener.

6.6.2 Soap Content From Weight of Hexane-Insolubles. Calculate the soap content of the grease as follows:

$$\text{Aluminum or Alkaline-Earth Soap Content (percent)} = \frac{A \times 100}{W \times Y}$$

where: A = weight of hexane-insoluble residue in grams.
W = weight of sample in grams.
Y = factor for impurities in commercial soap thickener products. This figure should include a correction for the amount of fatty acid found in the grease (6.2.2.1), and should include

about 2 percent of the weight of soap for other types of impurities (Note 7).

6.6.3 Soap Content From Weight of Metal Determined in Soap Hydrolyzate. Calculate the soap content of the grease as follows:

$$\text{Soap Thickener (percent)} = \frac{B \times N \times C \times 100}{W \times Y}$$

where: B = weight of metal found in aqueous hydrolyzate solution by Method 13.

N = factor for converting from the weight of metal to the weight of stearate soap. The following factors may be employed (St = Stearate):

Aluminum:	$Al(OH)St_2/Al$	= 22.65
Calcium:	$CaSt_2/Ca$	= 15.14
Strontium:	$SrSt_2/Sr$	= 7.47
Barium:	$BaSt_2/Ba$	= 5.13

W = weight of grease sample in grams.

Y = factor for impurities in commercial products (see Paragraph 6.6.2 and Note 7).

C = aliquot part of soap thickener residue which was used for the determination (6.4.2).

6.6.4 Soap Content From Weight of Metal Determined on Ash of Grease Sample. Calculate the soap content of the grease as follows:

$$\text{Soap Thickener (percent)} = \frac{D \times N \times 100}{W \times Y}$$

where: D = weight of metal found in the ash of the grease by Method 13.

N = factor for converting the weight of metal to the weight of stearate soap. The factors listed in Paragraph 6.6.3 apply.

W = weight of grease sample in grams.

Y = factor for impurities in commercial products (see Paragraph 6.6.2 and Note 7).

SEPARATION AND DETERMINATION OF INORGANIC GELLING AGENTS

1.0 SCOPE

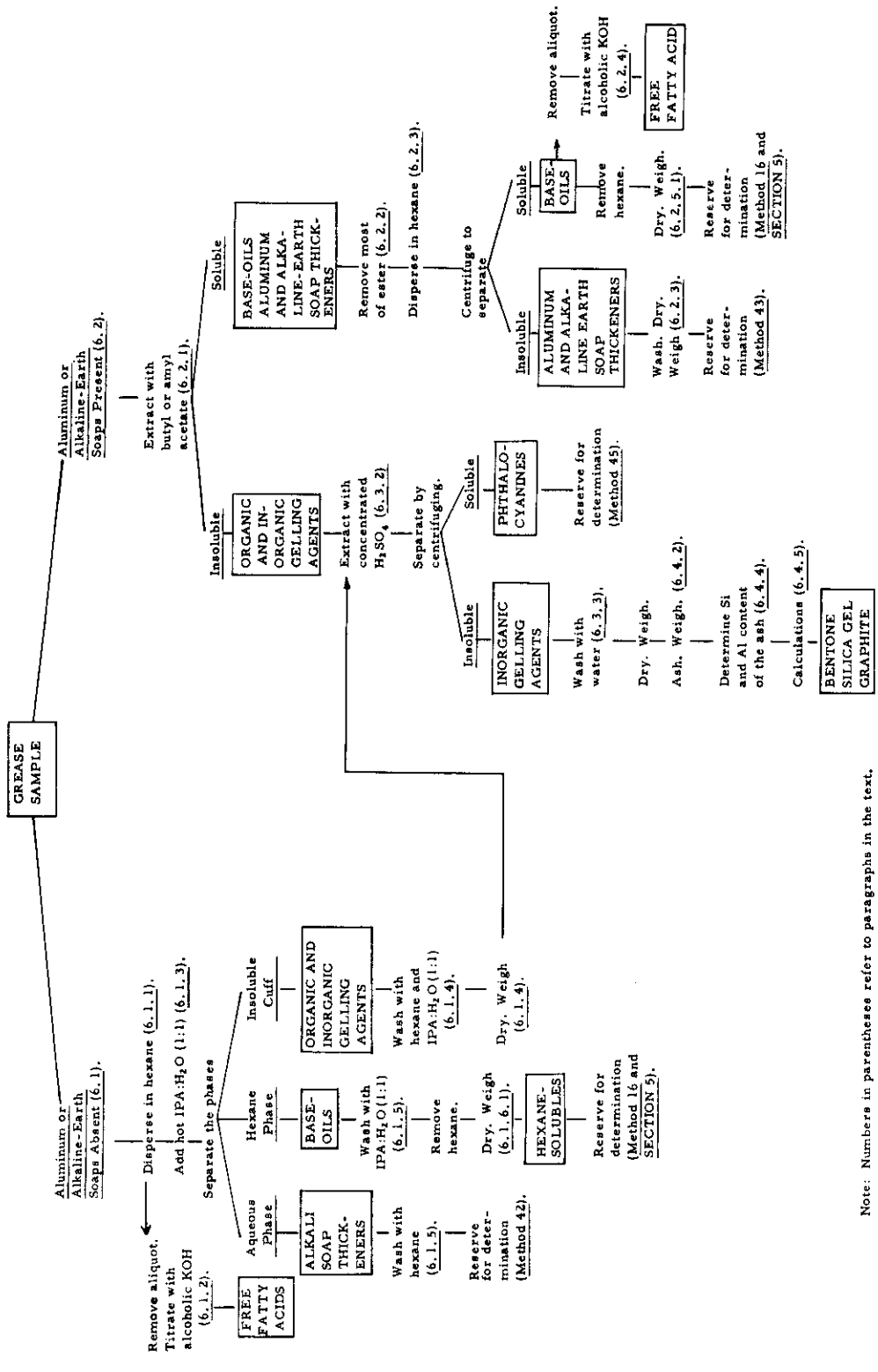
1.1 This method is intended to describe procedures for separation and determination of inorganic gelling agents in synthetic greases. This includes silica gel, graphite filler, and bentones (Note 1). Base-oil or other additives do not interfere in the method; however, some compounds present in small quantities, such as antioxidants or breakdown products, adsorb on bentones, imparting their color to the usually cream-colored bentone. The quantity of adsorbed materials is usually so small that the determination is not affected seriously. Other types of thickeners and gelling agents do not interfere with the method (Note 2).

Note 1. Bentones are montmorillonite clays, the surface of which is covered with an adsorbed layer of quaternary cations. The molecular weight and chemical structure of the adsorbed cation may be varied, but the compound most frequently employed in synthetic lubricant bentone-type gelling agents is dimethyldihexadecylammonium ion, having 34 carbons, from whence is derived the commercial name of the gelling agent, "Bentone-34".

Note 2. It is intended that this method should be used in close conjunction with Method 15, PRELIMINARY QUALITATIVE CLASSIFICATION OF GREASES, in which qualitative identification of soap thickeners and gelling agents in the grease has been established. Knowledge of the specific compounds present in the grease, as determined by Method 15, will assist the analyst in determining which procedures and methods should be used for quantitative determination of gelling agents and thickeners. The analyst is required to judge whether certain procedures are necessary in view of the composition of the grease. The procedures included in Method 13, QUANTITATIVE ELEMENTAL ANALYSIS, will also assist materially in the quantitative methods described herein for the determination of silicon and aluminum.

2.0 OUTLINE OF METHOD

2.1 The scheme of analysis for inorganic gelling agents in grease is shown in Figure 17. The grease is dispersed in hexane to remove base-oils, and in hot isopropyl alcohol-water solution (1:1) to remove alkali soap thickeners. Insoluble organic and inorganic gelling agents and alumi-



Note: Numbers in parentheses refer to paragraphs in the text.

Figure 17. Scheme of Analysis for Inorganic Gelling Agents.

num and alkaline-earth soap thickeners remain as a residue; the latter are removed by extraction with amyl or butyl acetate, the inorganic and organic gelling agents remaining as residue. Organic gelling agents, such as copper phthalocyanine, are separated by extraction with concentrated sulfuric acid. Fillers such as graphite are carried along with the inorganic gelling agents, and are determined in the method. Metal sulfide gelling agents, such as nickel, molybdenum, or copper sulfide are destroyed by the treatment with concentrated sulfuric acid. The sulfides are determined in Method 45. After removing aluminum and alkaline-earth soap thickeners and phthalocyanines, the residue contains only bentones, silica gel, and/or graphite filler. The presence of graphite is noted by the color of the residue, called the "cuff"; a black cuff indicates the presence of graphite. The cuff is ashed to remove carbon and volatile materials, and the silicon and aluminum contents of the ash are determined. Since aluminum in the ash can result only from bentone, the bentone content of the cuff can be calculated; since silica can result from both silica gel and bentone, the silicon stemming from bentone is calculated; the remaining silicon results from silica gel added to the grease. Graphite content of the grease is determined in the same manner, the volatiles stemming from bentone being calculated from the alumina content of the ash, and graphite forming the difference between this and the total volatiles found during ashing.

3.0 SAMPLE

3.1 The size of sample employed for this procedure shall be about 5 grams, and shall be weighed accurately to 1 milligram on an analytical balance. The original sample of grease shall be made as uniform as possible. If the grease is soft, stir and mix with a glass or wood paddle in a beaker until uniform. If the grease is hard, scrape off the surface layers with a clean spatula, and take the sample from the freshly exposed surface.

4.0 APPARATUS

4.1 Centrifuge. A centrifuge is required which is equipped with a head, trunnion carriers, cups, and rubber cushions, capable of holding 100-milliliter capacity centrifuge tubes (such as A.S.T.M. pear-shaped oil tubes) and which can be controlled to give rotational speeds up to 1800 r.p.m. or higher.

4.2 Suction apparatus. This simple apparatus (illustrated in Figure 2, Method 15) provides a fast, convenient method for separating and transferring liquid layers from the centrifuge tube to a separatory funnel or other container for further treatment. The tubing is capillary type with 1 to 2 millimeter diameter bore, and the tip which is placed in the liquid is drawn out to a length of about 4 inches to provide a minimum of glass surface to disturb the contents in the tube. The 4 inch tip has a 1 millimeter o. d. and 0. 25 millimeter i. d. A standard A. S. T. M. pear-shaped 100-milliliter oil centrifuge tube is a convenient type tube for use in this method, although this is not essential to performance of the separation (Note 3). The 125-milliliter separatory funnel is equipped with a two-hole rubber stopper which contains two sections of capillary tubing. Water aspirator vacuum is sufficient, since only low vacuum is needed to draw the liquid from the centrifuge tube into the funnel. A trap should be provided in the vacuum line. The capillary-bore three-way stopcock, opening to the air, provides a convenient means for controlling the rate of flow of liquid through the capillary tubing into the container.

Note 3. Any type of centrifuge tube of about 100-milliliter capacity which can be employed with the available centrifuge facilities will be adequate.

4.3 Drying oven. This oven should maintain a constant temperature of 110°±5°C.

4.4 Electric muffle furnace. Furnace capable of maintaining 1000°C., and equipped with a variable control device to adjust the temperature to ±25°C.

4.5 Soxhlet extraction apparatus. Standard laboratory Soxhlet apparatus with boiling flask, extraction chamber (preferably with a stopcock takeoff at the bottom of the chamber for withdrawing samples of solvent), reflux Allihn condenser, and cellulose extraction thimbles (double weight thimbles are recommended) which fit loosely in the extraction chamber. Standard taper glassware is preferable. A hot plate shall be used for heating, or a heating mantle with a variable voltage transformer.

4.6 Claisen distillation apparatus. Standard laboratory distillation apparatus with Claisen type distillation flask, West-type condenser, receiving tube 105° adapter, and receiving flask. Standard

taper glassware is preferable, because of its ease of assembly, interchangeability, and elimination of rubber stopper fittings.

4.7 Porcelain filter crucibles (fine porosity).

4.8 Analytical balance, capable of weighing to 0.1 milligram.

5.0 REAGENTS

5.1 Hexane, purified grade. Technical grade hexane may be purified by distilling over sodium hydroxide or anhydrous sodium carbonate and the fraction boiling from 63 to 69°C. shall be collected for use in this method.

5.2 Isopropyl alcohol:water solution (1:1, v/v). Mix equal volumes of 99.8 percent reagent grade isopropyl alcohol and distilled water.

5.3 Amyl acetate, purified, boiling range 141 to 143°C. (butyl acetate, purified or reagent grade, boiling range 124-125°C. may be substituted for amyl acetate).

5.4 Standard potassium hydroxide solution (alcoholic, 0.1N). See Paragraph 5.8, Method 42 for preparation of this reagent.

5.5 Phenolphthalein indicator (0.1 percent in 95 percent ethanol.

5.6 Potassium acid phthalate, reagent grade, primary standard.

5.7 Sulfuric acid. (sp. gr. 1.84) reagent grade.

6.0 PROCEDURE

6.1 Dispersion of the Grease.

6.1.1 Proceed as described in Paragraph 6.1, Method 42.

6.2 DETERMINATION OF FREE FATTY ACIDS

6.2.1 Procedure. If no soap-type thickeners have been identified in the grease by Method 15, the amount of free acid in the grease should

be negligible, and it is usually unnecessary to measure the free acid in the grease. If, however, soap-type thickeners have been identified by Method 15, a small amount of free fatty acid will have been added as an impurity in the soap thickener, and will be found in the hexane solution after dispersion of the grease. To determine the free acid content in the grease, proceed as described in Paragraph 6.2.1, Method 42.

6.2.2 Calculation. Calculate the approximate percentage of free fatty acids according to the formula given in Paragraph 6.2.2, Method 42.

6.3 PROCEDURE WHEN ALUMINUM AND ALKALINE-EARTH SOAPS ARE ABSENT.

6.3.1 Separation of Base-Oil and Alkali Soap Thickeners. Add 50 milliliters of hot isopropyl alcohol-water (1:1) to the hexane solution of the grease (6.1), or to the remainder of the hexane solution after removing the aliquot for free acid titration (6.2.1). Stopper the tube with a cork or polyethylene stopper, and shake for several minutes. Maintain the solution at the boiling point of hexane for at least 5 minutes by immersion in a steam or boiling water bath, followed by further shaking. Centrifuge the tube at 1800 r.p.m. for 5 to 10 minutes, or until clear phases are obtained. Inorganic and organic gelling agents, being insoluble in both solvent phases, form an insoluble "cuff" at the interface. Separate the phases, using the suction apparatus described in Paragraph 4.2. Draw the hexane into a clean 100-milliliter centrifuge tube to be washed and retained for further analysis by paper and column chromatography (see Method 16 and Section 5). Withdraw the first 30 or 40 milliliters rapidly, taking care to immerse the tip of the suction tube only a few millimeters below the surface of the hexane. Withdraw the last 20 milliliters slowly to prevent removing any of the cuff. Leave the last few milliliters in the tube, because the last traces of oil will be removed with the wash hexane. Replace the tube containing hexane with a clean 100-milliliter centrifuge tube to receive the IPA*-water phase. Place the tube containing the cuff and IPA-water phase under the suction tube and, with no suction being applied, move the tip of the tube through the cuff into the IPA-water, apply suction and slowly withdraw the IPA-water solution from below the cuff; take care that none of the cuff is drawn into the tube. When only a few milliliters of IPA-water remain,

*IPA=isopropyl alcohol.

turn off the vacuum by opening the stopcock above the trap. Lift the capillary tip a short distance above the cuff, and with a wash bottle, pipette, or medicine dropper wash off the tip with a few milliliters of hot IPA-water solution. Rinse the suction tube by drawing several milliliters of hot IPA-water through the tube into the centrifuge tube.

6.3.2 Washing and Weighing the Cuff. Add 25 milliliters each of hexane and IPA-water solution to the tube containing the cuff, heat to boiling in a steam bath, shake for several minutes to dissolve residual oils and alkali soaps, and centrifuge until both layers are clear and the cuff is well-defined between them. Withdraw the hexane first, adding it to the first hexane extract. Next withdraw the IPA-water phase as described previously (6.3.1), and add this to the first IPA-water extract. It is advisable to wash the cuff once more with 10 milliliters of each solvent. Wipe the outside of the centrifuge tube with a moist cloth to remove grease and dirt, and place the centrifuge tube containing the washed cuff in a drying oven at 110°C. for one hour. Upon removal from the oven, flush out the tube with a slow stream of dry air. Cool in a desiccator and weigh to obtain organic and inorganic gelling agents in the cuff. Reserve the cuff for the separation and determination of organic and inorganic gelling agents (Paragraphs 6.5 and 6.6).

6.3.3 Washing the Alcohol-Water and Hexane Phases. Wash the combined IPA-water extracts once with 25 milliliters of hexane by heating to the boiling point, stoppering the tube with a cork or polyethylene stopper, and shaking. Centrifuge and withdraw the hexane into the centrifuge tube with the original hexane extract, taking care not to remove any of the alcohol-water phase. Wash the IPA-water a second time with 15 milliliters of hexane, centrifuging and adding the hexane by suction to the previous hexane solution. Place a few milliliters of hexane in a beaker and draw this hexane through the capillary to rinse the tube. Allow the suction to continue for a moment to air-dry the capillary. Wash the combined hexane extracts with 20 milliliters of hot IPA-water solution with shaking. Centrifuge to separate the phases, withdraw the IPA-water phase into the centrifuge tube containing the original IPA-water extract, and wash the outside of the suction tube with a little fresh hexane. Reserve the IPA-water phase for determination of alkali soap thickeners (Method 42).

6.3.4 Determination of the Hexane-Soluble Fraction.

6.3.4.1 Procedure. Transfer the combined hexane extracts and washings to a 250-milliliter round-bottom distillation flask, and distill most of the hexane from the base-oils and additives, using a glass heating mantle or hot plate. When the volume of the solution is about 10 milliliters, cool the apparatus, and remove the distillation flask. To obtain the content of hexane-soluble materials in the grease, weigh a clean, dry Petri dish to the nearest milligram; transfer the solution to the Petri dish and wash out the flask with three successive 10 milliliter portions of hexane, washing the outside of the lip of the flask to remove traces of base-oils. Evaporate the remainder of the solvent on a hot water bath with a slow stream of air blowing across the surface of the solution. When the hexane has evaporated, dry at 110°C. for about 15 minutes. Cool the dish in a desiccator and weigh. Bring to constant weight by drying for 15 minutes, cooling, and re-weighing. Reserve the oil for analysis by paper and column chromatography (see Method 16 and Section 5).

6.3.4.2 Calculation. Calculate the percent of hexane-solubles in the grease as follows:

$$\text{Hexane-solubles (percent)} = \frac{D \times F \times 100}{W}$$

where: D = weight of hexane-solubles in grams.
W = weight of sample in grams.
F = factor due to removal of aliquot from the hexane solution (6.2.1). If no determination of free acid was made, no aliquot factor is necessary.

6.4 PROCEDURE WHEN ALUMINUM AND ALKALINE-EARTH SOAPS ARE PRESENT.

6.4.1 Separation of Gelling Agents From Base-Oil and Soap Thickeners. Weigh a 5 gram sample of the grease into a Soxhlet extraction thimble (double weight thimble is preferred), using a small clean spatula to transfer the grease into the previously weighed thimble (Note 4). If a hard grease is being analyzed, break it into as many pieces as possible. Place the thimble in the Soxhlet apparatus and fill the 250-milliliter flat-bottom boiling flask about half full of pure butyl or amyl acetate. Extract the grease overnight, making sure that the liquid siphons periodically, draining the chamber completely, and does not simply leak a small stream of solvent continuously through the siphon tube. Check the completeness of extraction by occasionally withdrawing two or three drops

of liquid through the stopcock onto a clean watch glass, and evaporate to dryness. When no residue is apparent on the watch glass, the extraction is complete. Allow the apparatus to cool to room temperature, and carefully lift the thimble from the chamber with tweezers or forceps, permitting solvent in the thimble to drain back into the chamber. Place the wet thimble in a small beaker or on a large watch glass, and dry at 105°-110°C. for at least one hour. If a vacuum oven is available, the thimble may be dried for a short period at 110°C. in the air oven, and may then be dried in vacuum at 50°C. for one hour. Cool the dried thimble in a desiccator, and weigh to obtain organic and inorganic gelling agents (Note 4). Reserve this residue for the separation and determination of organic and inorganic gelling agents (6.5). Reserve the ester solution for separation of aluminum and alkaline-earth soap thickeners from the base-oils (6.4.2).

Note 4. Weight of the extraction thimble will be more accurate if it is contained in a small thin-wall ground-stoppered glass or polyethylene-stoppered vial. After cooling in a desiccator, the thimble may be slipped into the vial and weighed. This prevents moisture pickup while weighing.

6.4.2 Removal of Solvent from Soap Thickeners and Base-Oil. Attach the 250-milliliter flat-bottom flask containing the ester solution of aluminum or alkaline-earth soap thickeners (6.4.1) to a Claisen distillation apparatus, and distill off most of the ester at a rate of one drop per second. Remove the flask from the apparatus, evaporate the remainder of the solvent on a steam bath using a slow stream of dry air to hasten the process. (CAUTION: Always evaporate solvents in a fume hood or well-ventilated area!) When most of the solvent has been removed, as indicated by absence of the typical ester odor, a grease will usually have formed, which can be dried further by heating at 110°C. in a drying oven, or to 50°C. in a vacuum oven.

6.4.3 Separation of Soap Thickeners and Base-Oil. Disperse the soap thickener-base-oil mixture after removing most of the ester solvent (6.4.2) in 30 milliliters of hexane, heat to boiling if necessary, and transfer the solution and soap precipitate to a 100-milliliter centrifuge tube, using several portions of fresh hexane to effect quantitative transfer. Centrifuge. Using the suction apparatus, slowly withdraw the hexane phase into a graduated container of about 100 milliliter capacity, removing the last few milliliters slowly to avoid drawing up any precipitate.

It is not necessary to remove the last one-half milliliter, as the remaining base-oil will be diluted and picked up in the washings. Add 15 milliliters of fresh hexane, shake to wash the precipitate thoroughly, and centrifuge. Withdraw the supernatant hexane into the graduated container. Repeat this washing with two more 10-milliliter portions of hexane, and place the centrifuge tube on a steam bath to evaporate traces of solvent. Dry the soap at 50°C. for one hour, cool in a desiccator, and weigh to obtain aluminum and alkaline-earth soap thickeners. Reserve for the determination of these thickeners (Paragraph 6.5.4, Method 43). Reserve the hexane solution of base-oils and additives for the determination of free fatty acid (6.4.4) and to obtain the weight of base oils (6.4.5).

6.4.4 Determination of Free Fatty Acids.

6.4.4.1 Procedure. Determine the free fatty acid content of the grease as described in Paragraph 6.2.1, Method 42.

6.4.4.2 Calculation. Calculate the percentage of free fatty acids in the grease according to Paragraph 6.2.2, Method 42.

6.4.5 Weight of Hexane-Solubles.

6.4.5.1 Procedure. To obtain the weight of hexane-solubles in the grease, proceed as described in Paragraph 6.3.4.1.

6.4.5.2 Calculation. Calculate the percent of hexane-solubles in the grease according to Paragraph 6.3.4.2.

6.5 SEPARATION OF ORGANIC AND INORGANIC GELLING AGENTS.

6.5.1 If organic gelling agents have been detected in the grease by Method 15, the residue after separating alkali soap thickeners (6.3.1) and aluminum and alkaline-earth soap thickeners (6.4.1) will be blue due to phthalocyanines, providing metal sulfide gelling agents or graphite fillers are absent. If the latter compounds are present, the blue color may be masked by the black color of these materials. When phthalocyanines have not been found by Method 15, it is unnecessary to perform the following separation step, and the analysis shall continue with Paragraph 6.6.1.

6.5.2 Place the washed, dried, and weighed cuff (6.3.2 or 6.4.1) in a mortar, and pulverize it completely. Transfer as much of the powder as possible to a weighed 25 milliliter centrifuge tube. Weigh the powder in the tube and record the aliquot part of the cuff which is used in the subsequent extraction and determination. Add 10 milliliters of concentrated H_2SO_4 and agitate gently. Phthalocyanines will dissolve readily, turning the acid a light brown color; inorganic gelling agents are insoluble. Centrifuge to settle the insoluble residue, and draw off the supernatant filtrate either with the suction apparatus employed in previous operations, or with a medicine dropper pipette. Place the acid in a 25-milliliter test tube. Wash the residue with a second 10 milliliter portion of acid, heat to about 60-70°C., and agitate to react metal sulfides. Again withdraw the acid and add to the first acid extract. Wash a third time with 5 milliliters of hot acid, and withdraw as before. Reserve the combined acid and wash acid for determination of phthalocyanine gelling agents and for detection of metals from sulfide gelling agents (Method 45).

6.5.3 Washing the Residue. Wash the residue from the H_2SO_4 extraction with four successive 10 milliliter portions of distilled water. Shake well to remove traces of acid. Centrifuge after each wash to settle the residue, draw off the water and reserve for determination of metals from sulfide gelling agents (Paragraph 6.5, Method 45). If traces of phthalocyanine remain in the residue, addition of water will cause reappearance of the blue color; should this occur, evaporate off all water, and extract the residue several more times with concentrated H_2SO_4. Wash again with water as described above. Dry the residue at 105-110°C. for one hour. Cool in a desiccator and weigh. The residue contains inorganic gelling agents, such as bentones, silica gel, and graphite filler; reserve the residue for the determination of these materials (6.6).

6.5.4 Calculation. Calculate the percentage of organic gelling agents (Phthalocyanine) in the grease as follows (if metal sulfides have been identified in the grease by Method 15, the calculation of organic gelling agents cannot be carried out at this point in the procedure):

$$\text{Organic gelling agents (Phthalocyanines) (percent)} = \frac{(A - B) \times F \times 100}{W}$$

where: A = weight of organic and inorganic gelling agents used in the H_2SO_4 extraction.
B = weight of inorganic gelling agents remaining after extraction.

Calculate the percentage of inorganic gelling agents in the grease as follows (if metal sulfides have not been identified in the grease):

$$\text{Inorganic gelling agents (percent) (Bentone, silica gel, graphite)} = \frac{C \times F \times 100}{W}$$

where: C = weight of residue after H_2SO_4 extraction.
F = aliquot part of gelling agents which was used for the H_2SO_4 extraction. (6.5.2).
W = weight of grease sample in grams.

6.6 DETERMINATION OF INORGANIC GELLING AGENTS AND GRAPHITE FILLER

6.6.1 By Method 15 the analyst shall have determined whether silica gel, bentones, or graphite filler are present in the grease. If only one of these compounds was found, it is unnecessary to carry the analysis further, since the weight of inorganic gelling agents found in Paragraph 6.5.3 and calculated in Paragraph 6.5.4 represents the compound detected in the qualitative analysis. However, if more than one compound was found, or if Method 15 was not employed, then it is necessary that the following procedures be carried out.

6.6.2 Ashing the Residue. If graphite is present in the grease, the residue after extraction of phthalocyanine with concentrated H_2SO_4 (6.5.2) will be black; if only silica gel and/or bentone are present, the residue will be white or cream-colored. Transfer the residue containing inorganic gelling agents and graphite filler (6.5.3) to a small, clean, weighed platinum crucible, breaking up lumps in the residue to a powder. Record the aliquot part of the residue which was transferred to the crucible. Ignite over a Meker burner or in a muffle furnace, starting at a low temperature until most of the carbon is burned off, and increasing the heat to dull redness for about 15 minutes. Remove the crucible from the heat, place in a desiccator to cool, and weigh. Re-ignite until constant weight is achieved. Record the weight loss of the residue. If the weight of ash remaining is very small, or negligible, graphite filler is present without silica gel or bentone. If there is a perceptible ash content, and the qualitative test for aluminum in Method 15 was negative, the ash is silica gel. In this case the weight lost during ashing and the weight remaining after ashing may be calculated as the actual weights of graphite and silica gel. Reserve the residue for determination of silicon and aluminum (6.6.4).

6.6.3 Calculations. Calculate the percentage of graphite and silica gel in the grease as follows (aluminum test in Method 15 negative):

$$\text{Graphite (percent)} = \frac{G \times F \times 100}{W}$$

where: G = weight lost by the residue during ashing.
F = aliquot of gelling agents which was used for the H_2SO_4 extraction (6.5.2) (Note 5).
W = weight of grease sample in grams.

$$\text{Silica gel (percent)} = \frac{H \times F \times 100}{W \times 0.90}$$

where: H = weight of ash remaining.
F = aliquot of gelling agents which was used for the H_2SO_4 extraction (6.5.2) (Note 5).
W = weight of grease sample in grams.
0.90 = factor determined from the actual SiO_2 content of commercial silica gel lubricant additives.

Note 5. An additional factor, F_1 may be required, which is the aliquot part of the dried residue which was transferred to the platinum crucible for ashing (6.6.2). This factor is usually not needed if a quantitative transfer is achieved.

6.6.4 Determination of Silicon and Aluminum in Ash. If Method 15 showed bentones in the grease with or without silica gel, it is necessary to determine both the silicon and aluminum content of the ash in order to obtain correct analyses for silica gel, graphite, and bentone. Determine the aluminum and silica contents of the ash, using Paragraphs 5.4 through 6.5, Method 13, omitting those procedures which apply to determination of iron and barium (Note 6). Record the percent of aluminum and silica found in the ash to use in calculating the bentone composition, graphite filler, and silica gel below.

Note 6. Bentones usually have about 5 percent Fe_2O_3; therefore in carrying out the silica and aluminum analyses, it is frequently useful to determine iron as a check on the presence of bentones in the grease.

6.6.5 Calculations. Calculate the percentage of bentone, graphite filler, and silica gel as follows (aluminum test in Method 15 positive):

F = aliquot part of gelling agents which was used for the H_2SO_4 extraction (6.5.2).
W = weight of grease in grams.

6.6.5.1 Bentone content of the grease. Calculate the bentone content of the grease as follows:

$$\text{Bentone (percent) (Note 7)} = \frac{I \times H \times 1.89 \times 6.93 \times F \times 100}{W}$$

where: H = weight of ash in grams.
I = percent aluminum found in ash (6.6.4).
1.89 = factor for converting aluminum to alumina.
6.93 = factor for converting alumina to bentone.
F = aliquot of gelling agents which was used for H_2SO_4 extraction (6.5.2) (see Note 5).
W = weight of grease sample in grams.

6.6.5.2 Silica gel content of the grease. Calculate the amount of silica which stems from the bentone present in the grease as follows:

$$\text{Silica from bentone (percent)} = \frac{I \times H \times 1.89 \times 3.194 \times F \times 1.00}{W}$$

where: 3.194 = factor for determining silica in bentone from alumina in bentone.

See Paragraph 6.6.5.1 for definition of remaining terms in the calculation.

Calculate the total amount of silica found in the grease as follows:

$$\text{Total silica in the grease (percent)} = \frac{J \times H \times F \times 100}{W}$$

where: J = percent silica found in the ash (6.6.4).
See 6.6.5.1 for definition of remaining terms in the calculation.

Deduct the amount of silica stemming from bentone from the total found in the grease to find the amount of silica gel added to the grease:

$$\text{Silica gel added to grease in addition to bentone (percent)} = \frac{(K - L)}{0.90}$$

where: K = total percent of silica found in the grease.
L = percent silica stemming from bentone.
0.90 = factor determined from the actual SiO_2 content of commercial silica gel lubricant additives.

6.6.5.3 Graphite content of the grease. Since bentone contains organic matter which is lost during ashing, the amount of organic matter stemming from bentone which is lost during ashing is calculated from the alumina content of the ash as follows:

$$\text{Organic matter stemming from bentone (percent)} = \frac{I \times H \times 1.89 \times 2.51 \times F \times 100}{W}$$

where: I = percent of aluminum found in ash (6.6.4).
H = weight of ash in grams.
1.89 = factor for converting aluminum to alumina.
2.51 = factor for determining organic matter in bentone from the alumina in bentone.
F = aliquot of gelling agents which was used for the H_2SO_4 extraction (6.5.2) (see Note 5).
W = weight of grease sample in grams.

Calculate the total amount of organic matter lost during ashing of the inorganic gelling agents:

$$\text{Total organic matter from inorganic gelling agents (percent)} = \frac{M \times H \times F \times 100}{W}$$

where: M = percent weight lost during ashing of inorganic gelling agent (6.6.2).
See Paragraph 6.6.5.1 for definition of remaining terms in the calculation.

Deduct the percent of organic matter stemming from bentone from the total found to obtain the amount of graphite filler in the grease:

$$\text{Graphite in grease (percent)} = N\text{-}O$$

where: N = total percent of organic matter in inorganic gelling agents in the grease.
O = percent volatiles stemming from inorganic gelling agents in the grease.

Note 7. The total percentages of silica gel, bentone, and graphite should total 100 percent of the H_2SO_4 insolubles. In the event that the results are not consistent, it is possible that other bentones than Bentone-34, containing different quaternary cations have been employed. In this case, reference may be made to WADC TR 54-464, Part I, pp. 10-41, for more extensive calculations based on different quaternary ammonium base contents in the bentone.

SEPARATION AND DETERMINATION OF ORGANIC GELLING AGENTS (AND METALS FROM METAL SULFIDES)

1.0 SCOPE

1.1 This method describes procedures for quantitative determination of organic gelling agents (phthalocyanines), and the metals evolved from metal sulfide gelling agents. Other gelling agents and soap thickeners are separated from the grease prior to determination of the organic gelling agents, and therefore do not interfere. Base-oils and hexane-soluble additives are also separated and do not interfere in the method (Note 1).

Note 1. It is intended that this method should be used in close conjunction with Method 15, PRELIMINARY QUALITATIVE CLASSIFICATION OF GREASES, in which qualitative identification of soap thickeners and gelling agents in the grease has been established. Knowledge of the specific compounds present in the grease, as determined by Method 15, will assist the analyst in determining which procedures and methods should be used for quantitative determination of organic gelling agents. The analyst is required to judge whether certain procedures are necessary in view of the composition of the grease.

2.0 OUTLINE OF METHOD

2.1 The scheme of analysis for organic gelling agents in greases is shown in Figure 18. The grease is dispersed in hexane to remove base-oils and hexane-soluble additives, and in hot isopropyl alcohol-water solution (1:1) to remove alkali soap thickeners. Organic and inorganic gelling agents form an insoluble "cuff" at the interface between the two phases. Aluminum and alkaline-earth soap thickeners are separated from the cuff by extraction with butyl or amyl acetate. Organic gelling agents are extracted from inorganic gelling agents with concentrated sulfuric acid, phthalocyanines being soluble. Inorganic metal sulfide gelling agents are partially destroyed by this treatment, the metals going into solution in the acid. Upon dilution of the acid with water, phthalocyanines are precipitated quantitatively, and are dried and weighed. Metals from sulfide gelling agents remain in solution and are analyzed by standard chemical procedures.

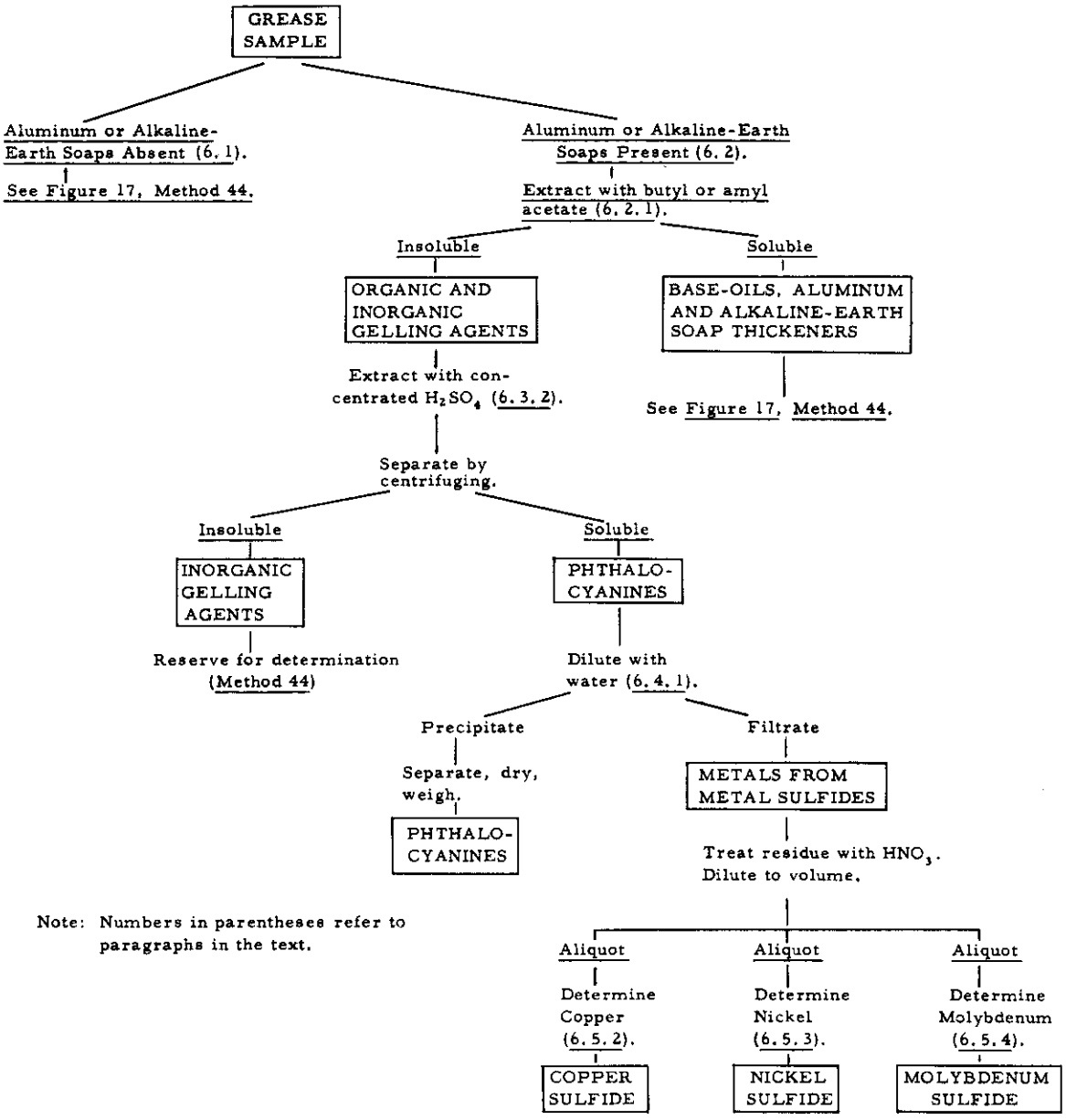


Figure 18. Scheme of Analysis for Organic and Metal Sulfide Gelling Agents.

3.0 SAMPLE.

3.1 The size of sample employed for this procedure shall be about 5 grams. Weigh accurately to 1 milligram on an analytical balance. Make the original sample of grease as uniform as possible. If the grease is soft, stir and mix with a glass or wood paddle in a glass beaker until uniform. If the grease is hard, scrape off the surface layers with a clean spatula, discard, and take the sample from the freshly exposed surface.

4.0 APPARATUS

4.1 Centrifuge. A centrifuge is required which is equipped with a head, trunnion carriers, cups, and rubber cushions, capable of holding 100-milliliter centrifuge tubes (such as A.S.T.M. pear-shaped oil tubes), and which can be controlled to give rotational speeds up to 1800 r.p.m. or higher.

4.2 Suction apparatus. This simple apparatus (illustrated in Figure 2, Method 15) provides a fast, convenient method for separating and transferring liquid layers from the centrifuge tube to a separatory funnel or other container for further treatment. The tubing is capillary type with 1 to 2 millimeter diameter bore, and the tip which is placed in the liquid is drawn out to a length of about 4 inches to provide a minimum of glass surface to disturb the contents in the tube. The 4 inch tip has 1 millimeter o.d. and about 0.25 millimeter i.d. A standard A.S.T.M. pear-shaped 100-milliliter oil centrifuge tube is convenient for use in this method, although this is not essential to performance of the separation (Note 2). The 125-milliliter separatory funnel or receiving container is equipped with a two-hole rubber stopper which contains two sections of capillary tubing. Water aspirator vacuum is sufficient, since only low vacuum is needed to draw the liquid from the centrifuge tube into the funnel. A trap should be provided in the vacuum line. The capillary-bore three-way stopcock, opening to the air, provides a convenient means for controlling the rate of flow of liquid through the capillary tubing into the container.

Note 2. Any type of centrifuge tube of about 100-milliliter capacity which can be employed with the available centrifuge facilities will be adequate.

4.3 Drying oven. This oven should maintain a constant temperature of 110°±5°C.

4.4 Melting point apparatus. This apparatus should allow temperature control to within 1°C. rise per minute. Either an aluminum block type, electrically or gas heated, or a glass capillary type, immersed in a high boiling liquid bath, may be employed.

4.5 Porcelain filter crucibles (fine porosity).

4.6 Analytical balance, capable of weighing to 0.1 milligram.

5.0 REAGENTS

5.1 Hexane, purified grade. Technical grade hexane may be purified by distilling over sodium hydroxide or anhydrous sodium carbonate, and the fraction boiling from 63 to 69°C. shall be collected for use in this Method.

5.2 Isopropyl alcohol:water solution (1:1, v/v). Mix equal volumes of 99.8 percent reagent grade isopropyl alcohol and distilled water.

5.3 Sulfuric acid (sp. gr. 1.84), reagent grade.

5.4 Nitric acid (sp. gr. 1.42), reagent grade.

5.5 Ammonium hydroxide solution (5 percent aqueous).

5.6 Ammonium hydroxide (sp. gr. 0.90), reagent grade.

5.7 Hydrochloric acid solution (0.5 percent aqueous).

5.8 Hydrochloric acid (sp. gr. 1.19), reagent grade.

5.9 Acetic acid, glacial, reagent grade.

5.10 Sulfuric acid solution (1:5, v/v). Pour one volume of concentrated sulfuric acid into 5 volumes of water.

5.11 Sodium bisulfite solution (5 percent aqueous).

5.12 Ammonium thiocyanate solution (10 percent aqueous).

5.13 Ammonium thiocyanate-sodium bisulfite solution (0.1 percent with respect to NH_4CNS and 0.01 percent with respect to sodium bisulfite).

5.14 Ethanol solutions (20 percent and 50 percent aqueous).

5.15 Hydrogen sulfide gas. This gas may be generated either from commercial preparations designed to deliver the gas on heating, or from FeS in dilute acid in a generator containing a trap to catch acid which might be swept along in the gas stream.

5.16 Lead acetate solution (4 percent aqueous). Dissolve 20 grams of the salt in 500 milliliters of warm water. Add a few milliliters of glacial acetic acid to clear the solution.

5.17 Alpha benzildioxime reagent. Prepare this reagent by boiling 10 grams of benzil with 8 to 10 grams of hydroxylamine hydrochloride in methyl alcohol solution. After boiling for three hours with reflux, filter off the precipitate, using quantitative filter paper. Dry the crystals, then wash them with hot water followed by a small amount of 50 percent alcohol solution. Dry at 110°C. for one hour. This precipitate consists of pure benzildioxime (m. p. 237°C.). Further yield may be obtained by boiling the filtrate with hydroxylamine hydrochloride. Prepare the reagent by dissolving 0.2 gram of the salt per liter of alcohol to which is added ammonium hydroxide (sp. gr. 0.90) to make 5 percent solution (sp. gr. 0.96)(50 milliliters per liter).

6.0 PROCEDURE.

6.1 PROCEDURE IN THE PRESENCE OF SOAP THICKENERS AND GELLING AGENTS.

6.1.1 If alkali soap thickeners have been shown to be present in the grease by Method 15, proceed as described in Paragraphs 6.1 through 6.3.4.2, Method 44, including dispersion of the grease, determination of free fatty acid, separation of base-oil and alkali soap thickeners, washing of each phase, and weighing the hexane-soluble fraction. The percents of free fatty acid and hexane-solubles are thereby determined, and the insoluble cuff containing organic and inorganic gelling agents and possible metal sulfide gelling agents and graphite thickener is obtained clean, dry,

and weighed for determination by this method (6.3).

6.2 PROCEDURE IN THE PRESENCE OF ALUMINUM AND ALKALINE-EARTH SOAP THICKENERS.

6.2.1 If aluminum or alkaline-earth soap thickeners have been shown to be present in the grease by Method 15, proceed as described in Paragraphs 6.4.1 through 6.4.5.2, Method 44, including separation of soap thickeners and base-oil from inorganic and organic gelling agents, separation of soap thickeners from base-oil, determination of free fatty acids, and weighing the hexane-soluble fraction. In this way, the percent of free fatty acid, hexane-insolubles, and soap thickeners is obtained, and the insoluble cuff containing organic and inorganic gelling agents and possible metal sulfide gelling agents and graphite thickener is obtained clean, dry, and weighed for determination by this method (6.3).

6.3 SEPARATION OF ORGANIC AND INORGANIC GELLING AGENTS.

6.3.1 If organic gelling agents have been detected in the grease by Method 15, the residue after separating alkali soap thickeners (6.1.1) and aluminum and alkaline-earth soap thickeners (6.2.1) will be blue due to phthalocyanines, providing metal sulfide gelling agents or graphite fillers are absent. If the latter compounds are present, the blue color may be masked by the black color of these materials.

6.3.2 Place the washed, dried, and weighed cuff (6.1.1 or 6.2.1) in a mortar, and pulverize it completely. Transfer as much of the powder as possible to a weighed 25-milliliter centrifuge tube. Weigh the powder in the tube and record the aliquot part of the cuff which is used in the subsequent extraction and determination. Add 10 milliliters of concentrated H_2SO_4 and agitate gently. Phthalocyanines will dissolve readily, turning the acid a light brown color; inorganic gelling agents are insoluble. Centrifuge to settle the insoluble residue, and draw off the supernatant filtrate either with the suction apparatus employed in previous operations, or with a medicine dropper pipette. Place the acid in a 25-milliliter test tube. Wash the residue with a second 10 milliliter portion of acid. Heat to about 70°C. and agitate to react metal sulfides. Again withdraw the acid and add to the first acid extract. Wash a third time with 5 milliliters of hot acid, and withdraw as before. Reserve the combined acid and wash acid for determination of phthalocyanine gel-

ling agents (6.4) and for detection of metals from sulfide gelling agents (6.5).

6.3.3 Washing the Residue. Wash the residue from the H_2SO_4 extraction with four successive 10 milliliter portions of distilled water. Shake well to remove traces of acid. Centrifuge after each wash to settle the residue, draw off the water, and reserve the water for determination of metals from sulfide gelling agents (6.5). If traces of phthalocyanine remain in the residue, addition of water will cause reappearance of the blue color; should this occur, evaporate off all water, and extract the residue several more times with concentrated H_2SO_4. Wash again with water as described above. Reserve the residue for further digestion with HNO_3 to destroy unreacted metal sulfides (6.5.1).

6.4 DETERMINATION OF PHTHALOCYANINE GELLING AGENTS.

6.4.1 Procedure. The combined extraction H_2SO_4 and wash acid from the separation of inorganic gelling agents (6.3) now contains phthalocyanine gelling agents and metals from hydrolyzed metal sulfide gelling agents. Pour the acid slowly and carefully into a 250-milliliter beaker containing about 100 milliliters of distilled water. Phthalocyanines precipitate immediately. Cool the resulting solution and filter through a weighed fritted glass filter funnel (fine porosity) with suction, or transfer to a large weighed centrifuge tube (100 milliliter capacity) and centrifuge until the solution is clear and phthalocyanine has been deposited. Remove the supernatant liquor by suction or decantation into a 250-milliliter beaker. Wash the insoluble phthalocyanines with three successive 10 milliliter portions of distilled water, filtering or centrifuging after each wash. Add the washings to the first wash liquid. Dry the filter funnel or the centrifuge tube with the residue at 110°C. for one hour, cool in a desiccator, and weigh. Repeat the drying and weighing until constant weight is achieved. Calculate the phthalocyanine content of the grease. Reserve the aqueous wash liquid for the determination of metals from metal sulfides (6.5) (Note 3).

Note 3. Phthalocyanines are extremely stable compounds, and further analysis for metal content, organic content, etc., is complicated and difficult. It is not usually necessary to determine these components, because phthalocyanines are isolated from other components by dissolving in H_2SO_4 and are recovered by precipitating by dilution with water.

6.5 DETERMINATION OF METALS FROM METAL SULFIDE GELLING AGENTS.

6.5.1 If the grease has been shown to have metal sulfide gelling agents by Method 15, metal ions from these gelling agents will be found in the filtrate after separation of precipitated phthalocyanines. Methods for the analysis of nickel, copper, and molybdenum are given below. In the event that these gelling agents are present, at the point in the analysis where phthalocyanines are separated from inorganic gelling agents by dissolving in concentrated H_2SO_4 (6.3.2), and the residue has been thoroughly washed with water to remove traces of H_2SO_4 and phthalocyanines (6.3.3), the residue contains inorganic gelling agents (silica gel, bentones) and possibly small amounts of unreacted metal sulfides. The residue should therefore be digested further to obtain all traces of metals from these unreacted sulfides. To the residue in a test tube add 5 milliliters of concentrated HNO_3, heat to boiling, and digest over a flame until any residue in the tube is white and the acid solution is clear. Add additional acid if necessary to bring unreacted sulfides into solution. When digestion is complete, cool the solution to room temperature, and pour the acid into the aqueous solution reserved from the precipitation and filtration of phthalocyanines (6.4.1). Wash the test tube thoroughly with water to effect quantitative transfer of all of the acid. Filter the aqueous solution through a quantitative filter paper, washing the beaker and paper thoroughly with warm water. Evaporate the filtrate down to about 60 milliliters on a hot plate, covering the beaker with a large watch glass to prevent loss of liquid by splattering. Cool to room temperature and reserve for the determination of copper (6.5.2), nickel (6.5.3), and molybdenum (6.5.4).

6.5.2 Determination of Copper From Metal Sulfide Gelling Agents. *

6.5.2.1 Procedure. Transfer the filtrate (6.5.1) quantitatively to a 100 milliliter graduated cylinder, using warm water to rinse the beaker. Dilute the solution to exactly 100 milliliters with water. With a pipette remove 25 milliliters of solution and transfer quantitatively to a 100 milliliter beaker. Reserve the remainder of the solution for the determin-

*This method is taken from Kolthoff, I. M., and Sandell, E. B., Textbook of Quantitative Inorganic Analysis, New York: The Macmillan Co., 1947, pp. 701-2.

ations of nickel and molybdenum (6.5.3 and 6.5.4). Add 5 milliliters of concentrated H_2SO_4 and evaporate on a hot plate until dense white fumes of SO_3 appear. Cool to room temperature, add 50 milliliters of water, and stir to dissolve any solids which may have appeared. Add dilute NH_4OH solution carefully until a precipitate appears. Add 10 milliliters of H_2SO_4 solution (1:5, v/v), dilute to 300 milliliters with water, and add 25 milliliters of a 5 percent solution of $NaHSO_3$. Heat nearly to boiling, and add slowly with stirring 15 milliliters of a 10 percent solution of NH_4CNS. Allow the solution to cool to room temperature and to stand for 2 hours. Filter through a previously cleaned, dried, and weighed filter crucible (Gooch, sintered-glass, or porous porcelain), and wash the precipitate about ten times with a cold solution containing 0.1 percent of NH_4CNS and 0.01 percent of $NaHSO_3$. Discard the filtrate. Wash the precipitate with 20 percent ethanol solution. Dry the precipitate to constant weight at 105-110°C. and weigh as CuCNS.

6.5.2.2 Calculation. Calculate the percent of copper and of copper sulfide in the grease sample as follows:

$$\text{Copper (percent)} = \frac{A \times B \times C \times 0.5224 \times 100}{D}$$

where: A = weight of copper thiocyanate recovered (6.5.2.1).
B = aliquot part of the solution of metals (from metal sulfides) taken for analysis (6.5.2.1).
C = aliquot part of the cuff recovered after grinding for analysis (6.3.2).
0.5224 = gravimetric factor for converting CuCNS to Cu.
D = weight of grease sample in grams.

$$\text{Copper Sulfide (percent)} = \frac{A \times B \times C \times 0.654 \times 100}{D}$$

where: A = weight of copper thiocyanate recovered (6.5.2.1).
B = aliquot part of the solution of metals (from metal sulfides) taken for analysis (6.5.2.1).

C = aliquot part of the cuff recovered after grinding for analysis (6.3.2).

0.654 = gravimetric factor for converting CuCNS to Cu_2S.

D = weight of grease sample in grams.

6.5.3 Determination of Nickel From Nickel Sulfide Gelling Agent. *

6.5.3.1 Procedure. From the volumetric solution measured in Paragraph 6.5.2.1 (from which an aliquot has been withdrawn for the determination of copper), withdraw a second 25 milliliter aliquot and transfer this quantitatively to a 100 milliliter beaker. Evaporate on a hot plate just to dryness, taking care near the end of the evaporation not to overheat any of the residue. Dissolve the residue with 10 milliliters of concentrated HCl and 20 milliliters of water. Heat to boiling and pass H_2S gas into the solution for 5 minutes. Dilute with water to 100 milliliters and again pass H_2S gas in for 5 minutes. Filter the solution through a quantitative filter paper, washing the paper thoroughly with dilute HCl solution (0.5%), and finally with a small amount of hot water. Again pass in H_2S gas, and if further precipitate appears filter this off in the same filter as previously used, washing the paper thoroughly. Wash the delivery tube of the H_2S generator with dilute acid and water to ensure quantitative recovery of the filtrate. Evaporate the filtrate down in a covered beaker on a hot plate to about 10 milliliters, cool to room temperature, and add concentrated NH_4OH until the solution is distinctly alkaline, using indicator test paper. Place the ammoniacal solution on a water bath and add about 10 milliliters of alpha benzildioxime reagent. Stir for 1 minute and allow the precipitate to settle. Add a further 5 milliliters of the reagent, and observe whether additional precipitate forms. If precipitate forms, stir and add another 5 milliliters of reagent. When precipitation appears to be complete, add 3 milliliters of the reagent, and continue heating for about 5 minutes. Filter through a previously cleaned, dried, and weighed filter crucible (Gooch, sintered glass, or porous porcelain), and wash thoroughly with 50 percent ethanol solution, followed by hot water. Dry one hour at 110°C., and weigh. Re-dry and weigh to bring to constant weight. The precipitate of $C_{28}H_{22}N_4O_4Ni$ contains 10.93 percent nickel.

*This method is taken from Scott, W. W., Standard Methods of Chemical Analysis, Volume One, Fifth Edition, edited by Furman, N. H., New York: D. Van Nostrand Co., Inc., 1939, pp. 617-18.

6.5.3.2 Calculations. Calculate the percent of nickel and of nickel sulfide in the grease sample as follows:

$$\text{Nickel (percent)} = \frac{E \times B \times C \times 0.1093 \times 100}{D}$$

where: E = weight of nickel alpha benzildioxime recovered (6.5.3.1).
B = aliquot part of the solution of metals (from metal sulfides) taken for analysis (6.5.3.1).
C = aliquot part of the cuff recovered after grinding for analysis (6.3.2).
0.1093 = gravimetric factor for converting nickel alpha benzildioxime to Ni.
D = weight of grease sample in grams.

$$\text{Nickel Sulfide (percent)} = \frac{E \times B \times C \times 0.169 \times 100}{D}$$

where: E = weight of nickel alpha benzildioxime recovered (6.5.3.1).
B = aliquot part of the solution of metals (from metal sulfides) taken for analysis (6.5.3.1).
C = aliquot part of the cuff recovered after grinding for analysis (6.3.2).
0.169 = gravimetric factor for converting nickel alpha benzildioxime to nickel sulfide (NiS).
D = weight of grease sample in grams.

6.5.4 Determination of Molybdenum From Molybdenum Sulfide Gelling Agent. *

6.5.4.1 Procedure. From the volumetric solution measured in Paragraph 6.5.2.1 (from which aliquots have been withdrawn for the determinations of copper and nickel), withdraw a third aliquot of 25 milliliters and transfer this quantitatively to a 100 milliliter beaker. Add 3 milliliters of concentrated H_2SO_4 and evaporate on a hot plate until dense white fumes of SO_3 appear. Cool to room temperature, add 50 milliliters of water, heat, and stir until all solids have dis-

*This method is taken from Scott, W. W., Standard Methods of Chemical Analysis, Volume One, Fifth Edition, edited by Furman, N. H., New York: D. Van Nostrand Co., Inc., 1939, pp. 589-90.

solved. Add 50 more milliliters of water if necessary to obtain a clear solution. Add dilute NH_4OH solution carefully until a faint precipitate appears. Add glacial acetic acid at the rate of 2.5 milliliters for each 100 milliliters of solution. Heat to near boiling and add lead acetate reagent slowly until no further precipitation occurs, then add about 5 percent reagent in excess. Allow the precipitate to settle a few minutes, and filter hot through a previously cleaned, dried, and weighed filter crucible (Gooch, or porous porcelain (fine)), refiltering the first portions if they come through the filter cloudy. Wash the precipitate with hot water until free of chlorides ($AgNO_3$ test) and lead acetate (sulfide test). Dry the crucible at low heat, then ignite at red heat for about 20 minutes. Cool in a desiccator and weigh. Re-ignite and cool until constant weight is achieved. The precipitate is weighed as $PbMoO_4$.

6.5.4.2 Calculations. Calculate the percent of molybdenum and molybdenum sulfide in the grease sample as follows:

$$\text{Molybdenum (percent)} = \frac{F \times B \times C \times 0.2614 \times 100}{D}$$

where: F = weight of lead molybdate recovered (6.5.4.1).
B = aliquot part of the solution of metals (from metal sulfides) taken for analysis (6.5.4.1).
C = aliquot part of the cuff recovered after grinding for analysis (6.3.2).
0.2614 = gravimetric factor for converting $PbMoO_4$ to Mo.
D = weight of grease sample in grams.

$$\text{Molybdenum Sulfide (percent)} = \frac{F \times B \times C \times 0.436 \times 100}{D}$$

where: F = weight of lead molybdate recovered (6.5.4.1).
B = aliquot part of the solution of metals (from metal sulfides) taken for analysis (6.5.4.1).
C = aliquot part of the cuff recovered after grinding for analysis (6.3.2).
0.436 = gravimetric factor for converting $PbMoO_4$ to MoS_2.
D = weight of grease sample in grams.

SECTION 5
SEPARATION, IDENTIFICATION, AND DETERMINATION OF BASE-OILS FROM SYNTHETIC LUBRICANTS AND GREASES

PRELIMINARY EXAMINATION OF THE BASE-OIL FRACTION FROM SYNTHETIC LUBRICANTS AND GREASES

1.0 SCOPE

1.1 This method describes a simple procedure for paper chromatographic examination of the base-oil fraction isolated from a synthetic lubricant by Method 16, or from a synthetic grease by Methods 41 through 45 and Method 16. The method provides a possible means for avoiding the partition separation (Method 52) which is necessary when complicated mixtures of base-oils (containing dibasic acid esters, silicate esters, disiloxanes, and/or silicone oils) are present. The method demonstrates whether any of the group of silicon-containing base-oils are present, and whether one of the group of dibasic acid esters is present. If only one of the two groups is found, Method 52 is not necessary; if both groups are found, Method 52 must be employed.

2.0 OUTLINE OF METHOD

2.1 The base-oil fraction obtained from treatment of synthetic lubricants and greases according to Method 16 is diluted with a suitable solvent, and a paper chromatogram of the oil is developed. The presence of dibasic acid esters is indicated by spots on the chromatogram at R_f-values of 0.50 and higher, and silicate esters, disiloxanes, and silicone oils are indicated by spots near the starting point at R_f-values of 0.05 or lower.

3.0 SAMPLE

3.1 The sample used in this method is obtained after treatment of the synthetic lubricant or grease to isolate base-oils from other additives, such as gelling agents, thickeners, antioxidants, etc. (see Paragraph 1.1).

4.0 APPARATUS.

4.1 Hydrometer cylinder, height 300 millimeters, diameter 50 millimeters, with expanded base. This cylinder is used for ascending paper chromatography, and is equipped with a #11 one-hole rubber stopper, through which a piece of wire with a hook at the end is placed. A glass rod which closely fits the hole in the stopper and which has four

horizontal short glass rods at the lower end may be substituted for the wire. The wire or glass rod shall be held in place by friction in such a way that it can easily be raised (to hold the entire paper strip in the atmosphere above the solvent) and lowered (to hold the paper with the lower edge in the solvent combination). This type of chromatographic cylinder is illustrated in Figure 6, page 110. Other types of cylinders with wide mouths may be substituted, providing the cylinder is made of glass and is tall enough to hold the paper and supporting clip (4.4) with about 2 inches of space for raising and lowering the paper.

4.2 Glass weights. Small glass weights, illustrated in Figure 6, are used to hold the paper straight in the chromatographic chamber (4.1).

4.3 Micro-pipets, capable of delivering 2.5 or 5 lambdas of solution (1 lambda = 0.000001 liter). A variety of sizes of micro-pipets from 1 to 50 lambdas capacity is recommended. (Micro-pipets and other micro supplies may usually be obtained from local chemical supply houses, or from microchemical equipment suppliers, such as Microchemical Specialities Co., 1834 University Ave., Berkeley 3, California).

4.4 Stainless steel clips, small metal spring-loaded clips similar to photographic clips, but having a jaw about 1 inch long.

4.5 Reagent spray, glass, bottle type, flat bottom, 50-milliliter capacity, with glass hooks and springs for securing. (A reagent spray similar to Microchemical Specialities Co., Catalog No. 2C-50, Type B, is satisfactory for this method).

4.6 Drying oven or low speed hot air fan, for evaporating solvents from paper strips.

5.0 REAGENTS.

5.1 Ethanol-acetone-water (12:3:8, v/v) solvent combination. Measure the volumes of each of the reagent grade solvents in separate graduated cylinders, and combine these in a glass-stoppered Erlenmeyer flask with shaking.

5.2 Rhodamine B solution (0.1 percent aqueous).

5.3 Benzene, reagent grade.

5.4 Diethyl ether, anhydrous, reagent grade.

5.5 Standard base-oil comparison solutions (1 percent in benzene or hexane):

(a) Dioctyl sebacate (abbreviated DOS).
(b) Dioctyl phthalate (abbreviated DOP).
(c) Dioctyl adipate (abbreviated DOA).
(d) Tetra(2-ethylhexoxy)silicate (abbreviated TOS).
(e) Hexa(2-ethylhexoxy)disiloxane (abbreviated HODS).
(f) Silicone DC-200(alkyl).
(g) Silicone DC-550(aryl).
(h) Chlorinated silicone (MLO-53-446).

5.6 Acetylcellulose paper. See Method 21 for preparation of this paper.

5.7 Blotting paper. Use any clean absorbent paper, such as brown paper towelling. Do not use tissue-weight paper.

6.0 PROCEDURE.

6.1 PREPARATION OF THE PAPER STRIP. Place a large piece of acetylated paper (see Method 21 for preparation of this paper) on a clean dry surface, like a glass plate, and mark on the sheet the following dimensions:

(a) Total length = 8-3/4 inches.
(b) Width = 1-1/4 inches.
(c) Width of tail = 3/16 inch.
(d) Length of tail = 1/2 inch.
(e) Length of paper to the diagonal cut 7-1/2 inches.
(f) Location of starting spot = 3/4 inch above bottom of tail and centered.

Use a soft lead pencil to mark these dimensions. With a scissors or razor blade and metal straight edge, cut the paper in the same shape as that illustrated in Figure 19. Always handle the paper with clean hands to avoid contamination and consequent misleading results.

6.2 PREPARATION OF THE OIL SAMPLE. Weigh into a 10 milliliter volumetric flask 0.1 gram of the oil fraction obtained from Method 16. Dilute to volume with benzene (or hexane) and mix well. The concentration of oil for this method should be about 1 percent; too dilute a solution will not yield detectable spots, and too concentrated a solution will cause the spot or spots of oils to spread out, overlap, and obscure each other.

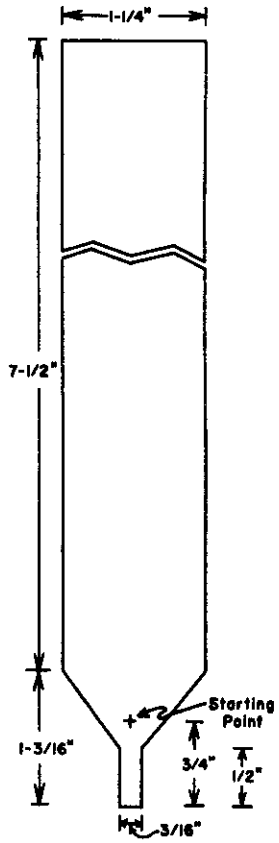


Figure 19. Paper Strip Used For Qualitative Identification of Dibasic Acid Esters, Silicate Esters, Disiloxanes, and Silicone Oils.

6.3 APPLICATION OF THE SAMPLE TO THE PAPER. Place the prepared paper strip (6.1) on a small piece of clean plate glass in such a way that the starting point, marked lightly on the paper with a pencil, is in the center of the glass. Dip the tip of a clean dry 2.5 or 5 lambda micro-pipet into the sample solution (6.2), and allow capillary forces to fill the pipet completely. In the case of viscous solutions, even though diluted with benzene or hexane, this sometimes requires a minute or so. When the pipet is full, remove from the solution, and wipe the outside of the tip with a piece of clean, dry, absorbent tissue in such a way that the tissue does not touch the opening at the tip of the pipet; otherwise some of the test solution would be absorbed into the paper, holding the pipet vertical and applying slight pressure. The solution will not drain until it contacts the paper; therefore it may be necessary to rotate the upper end of the pipet slightly to establish this contact. Allow the pipet to drain into the paper, remove the pipet, and hang the paper in air for a few moments to evaporate solvent. Clean the pipet by placing the tip in a suitable solvent, fill the capillary, and remove the solvent by touching the tip to tissue paper; repeat this procedure several times, and set the pipet aside to dry.

6.4 DEVELOPING THE CHROMATOGRAM. Prepare the solvent combination ethanol-acetone-water (12:3:8, v/v) by measuring 24 milliliters of ethanol in a graduated cylinder, 6 milliliters of acetone

in a second cylinder, and 16 milliliters of distilled water in a third cylinder. Combine the three solvents in a stoppered Erlenmeyer flask, shake to mix, and pour about 20 milliliters of the solvent combination into the hydrometer cylinder. Attach a stainless steel clip to the top of the paper strip, and hang the clip on the glass or wire rack in the stopper of the hydrometer cylinder. Adjust the height of the wire or glass rack so that when the stopper is in place, the entire paper strip will be suspended above the solvent combination. Allow the atmosphere in the cylinder to saturate with vapors of the solvent combination for about one hour (do not saturate overnight, because the oil in the paper will diffuse too far through the paper). At the end of the saturation period, lower the wire or glass rack so that the tip of the paper dips 2 or 3 millimeters below the surface of the solvent combination. Be sure that the paper hangs free in the cylinder, not touching the sides at any point (Note 1). Allow the chromatogram to develop (usually about 2 hours at room temperature) until the solvent front has reached a point about one inch from the top of the paper. At this point, quickly remove the stopper and paper from the chamber, lay the paper flat on a clean glass surface, mark the location of the solvent front with a soft lead pencil, taking care not to tear the wet paper, and hang the strip in a drying oven at 110°C. for 5 or 6 minutes, or in front of a hot air fan until the paper is completely dry.

Note 1. If the acetylcellulose paper does not hang straight in the chamber, particularly after saturating the paper and atmosphere, it may be necessary to add glass weights to the paper, as illustrated in Figure 6.

6.5 DETECTING THE SPOTS.

6.5.1 Adjusting the Spraying Apparatus. Fill the 50 milliliter spray reagent chamber about 2/3 full with Rhodamine B solution, assemble the spray, and attach the springs. The spray should be assembled so that air pressure applied will pass through the slot in the ground glass inner member into the channel in the ground glass outer member to force liquid up the capillary and out the orifice into the air jet in the spray head. An air pressure source should be available which can be controlled to deliver low pressures of air to the spray apparatus. With a short piece of rubber tube attach the spray air inlet to a glass tubing "T" (a three-way stopcock may be substituted for the "T") which is connected through rubber tubing to the air pressure source. Leave the extra arm of the "T" open when turning on the air and when not

spraying. To spray the reagent, turn on the air and simply place the finger on the extra arm of the "T" to force all of the air through the spray head. Hold the paper strip at a distance of about 10 to 12 inches in front of the sprayer. Direct the spray away from other apparatus to avoid unnecessary cleaning. Mount the spray apparatus with a clamp on a ring stand to provide permanent and secure positioning of the apparatus.

6.5.2 Spraying the Paper Strip. Remove the paper strip from the drying oven or the hot air fan, and place a second stainless steel clip at the bottom of the paper. Either hold the paper by hand, or suspend the paper and clips in a simple rectangular wire rack which is bent to hold this size paper strip. Turn on low air pressure, and spray the back side of the paper only until a uniform medium pink color has been applied to the entire side of the paper. It is well to practice spraying the paper with several trial paper chromatograms with known spots of DBAEs* present. Sufficient reagent should be applied that the DBAE will cause pink spots to appear on the opposite side of the paper; if too much reagent is applied, the reagent, even though in an aqueous solution, can creep through the paper and obscure any DBAE spots which might have appeared. Hang the paper to air-dry for 10 minutes, then dry in an oven or in front of the hot air fan until dry. Mark any pink spots which have appeared on the white side of the paper with a soft lead pencil by outlining the entire spot and marking the center of the spot. The color of all spots on the paper is identical; therefore this method cannot be used to determine specific compounds. In fact classes of compound are indistinguishable, since any oily material on the paper will cause formation of a pink spot.

6.6 DETERMINING THE R_f-VALUE. See Paragraph 6.6, Method 22, for a definition and determination of R_f-value of any spots which appear on the paper chromatogram. If a pink spot appears at an R_f-value of 0.52 or higher, dibasic acid esters are present in the oil (DOS has an R_f-value of 0.52, and other dibasic acid esters have higher values, the R_f-value increasing with decreasing molecular weight). If the starting point is surrounded by a solid spot or a "doughnut"-shaped spot, having a white center with a pink perimeter roughly the same size as the starting oil spot, silicon-containing base-oils are

*DBAE = dibasic acid ester.

present (none of the silicon-containing base-oils move farther from the starting point than R_f 0.05). With both types of oils present, it is mandatory to carry out Method 52 to separate the oils. If the starting point is completely clear, none of the silicon-containing oils are present, and it is unnecessary to perform the partition separation described in Method 52. Likewise, if no dibasic acid ester spots appear, Method 52 need not be employed.

6.7 COMPARISON WITH KNOWN COMPOUNDS. Make 1 percent solutions (in benzene or hexane) of each of the base-oil compounds encountered in synthetic lubricants and greases to prepare chromatograms for comparison with the unknown chromatogram. Chromatograph these solutions in the same manner as the unknown sample on individual strips of acetylcellulose paper. One of these chromatograms may be run in the same chamber and at the same time as the unknown, provided that the two pieces of paper do not touch during development. Comparison of the known oil spots with the unknown sample spots on the chromatogram assists in ascertaining the presence and identity of groups of compounds.

QUANTITATIVE COLUMN PARTITION CHROMATOGRAPHIC SEPARATION OF SYNTHETIC BASE-OIL GROUPS

1.0 SCOPE.

1.1 This method describes procedures for the quantitative separation of small samples of synthetic lubricants containing dibasic acid ester, silicate ester, disiloxane, and silicone base-oils. The method is applied to the analysis of base-oil fractions separated from synthetic greases (Section 4) and to the base-oil fraction obtained after separation of antioxidants and impurities by adsorption on silica gel (Method 16).

1.2 Other types of base-oils than those mentioned in Paragraph 1.1 above have not been studied; it is therefore difficult to predict accurately how these base-oils would perform under the conditions of the separation.

2.0 OUTLINE OF METHOD.

2.1 A chromatographic column of silica gel or other finely divided material is saturated with water to eliminate its adsorbent properties. A sample of unknown oil is placed in the column and partitioned by the use of a methanol-water (83:17, v/v) solvent combination. Dibasic acid esters (abbreviated DBAE) are dissolved slowly in the solvent combination and carried out of the column, while silicate esters, disiloxanes, and silicone oils remain in the column. The DBAEs are recovered by removal of the solvent by distillation. Silicate esters, disiloxanes, and silicone-oils are then eluted from the column by ether, followed by benzene. These oils are collected as a group and recovered by evaporation or distillation of the solvent.

3.0 SAMPLE.

3.1 To obtain quantitative results, it is necessary that most of the additives in the synthetic grease or lubricant be removed. This is done in the case of greases by the procedures described in Section 4, and in the case of lubricants by adsorption analysis (Method 16). The base-oil-containing fraction is dried and weighed in the above methods, and is then ready for column partition separation, provided the prelim-

inary paper chromatographic tests (Method 51) have indicated that such a separation is necessary.

4.0 APPARATUS

4.1 Chromatographic tube. The tube employed in these separations is illustrated in Figure 20, and consists of:

(a) Chromatographic column, Pyrex glass, 25 millimeter i.d. by a minimum of 350 millimeters long from the top to the fritted glass disc at the bottom of the chamber. The top has a 35/25 outer ball joint, and the bottom of the tube has three component parts:

(1) Coarse porosity fritted glass disc at the bottom of the chamber. The disc is approximately 25 millimeters in diameter.

(2) A short (10 millimeter) section below the fritted glass disc tapering from 25 to 5 millimeters diameter and connecting to a glass tube, 7 millimeter o.d. by 5 millimeter i.d. by 85 millimeters long, terminating in a drip tip.

(3) A 24/40 standard taper inner joint affixed to the 7 millimeter diameter tube at the base of the tapered section. The total length of this joint, including the standard taper is 70 millimeters, leaving about 10 millimeters of the inner tube and drip tip extending below the standard taper joint.

(b) Pressure chamber, Pyrex glass, 25 millimeters i.d. by 300 millimeters long, the bottom end having a 35/25 inner ball joint and the upper end tapering over a length of 20 millimeters to a narrow glass tube about 35 millimeters long by 8 millimeters o.d. with several knurls to hold rubber pressure tubing tightly. The solvent reservoir is fastened into the pressure chamber at the top and bottom with glass tubing (see below). A steel spring clamp secures the ball joint between the column and the pressure chamber when pressure is applied.

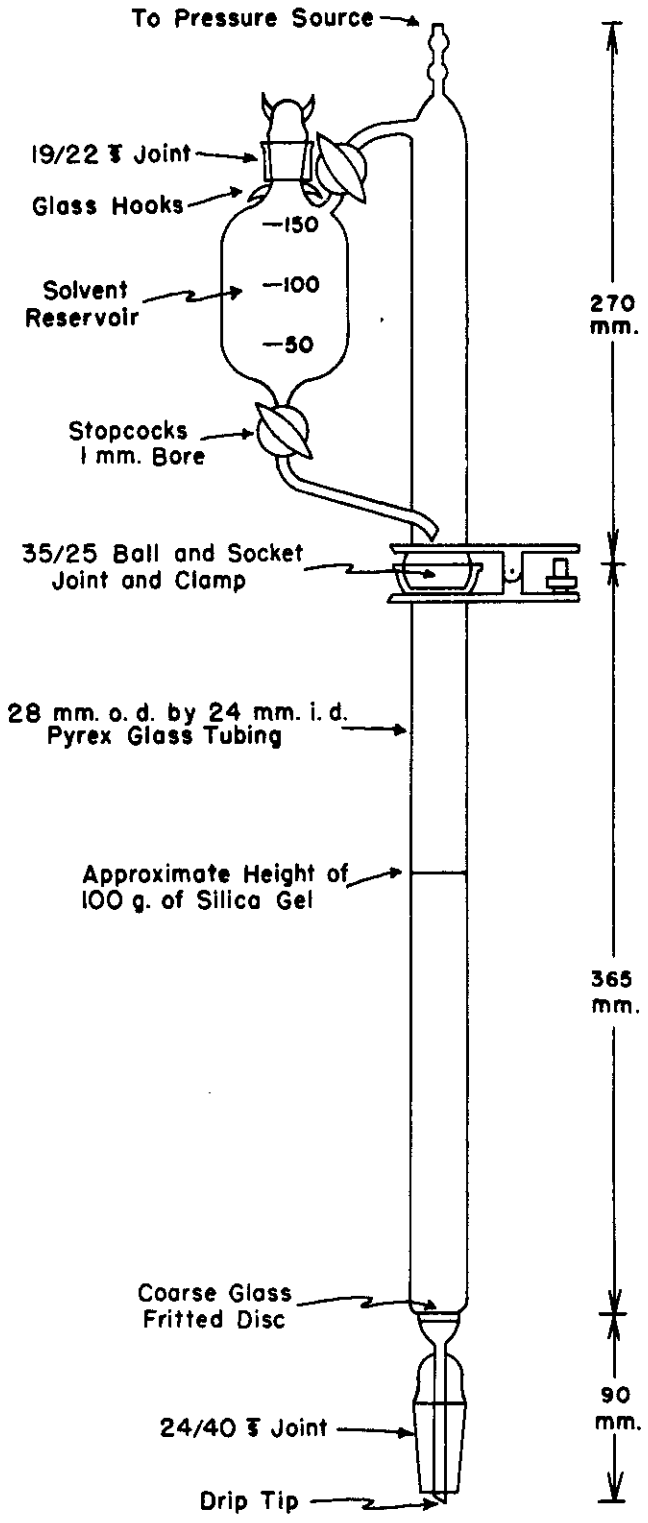


Figure 20. Chromatographic Tube with Solvent Reservoir and Constant Pressure Chamber.

(c) Solvent reservoir, Pyrex glass, permanently attached through glass tubing to the pressure chamber. The reservoir itself is a Pyrex glass section of a cylinder about 60 millimeters in diameter and having a capacity of about 250 milliliters. At the top is a 19/22 outer standard taper joint with glass hooks affixed to the base of the joint where it attaches to the reservoir. A matching inner joint with glass hooks provides tight closure of the reservoir. The bottom of the reservoir is tapered to and connected with a stopcock (1 millimeter bore), which in turn is connected to a glass tube (8 millimeter o. d.) bent at a 75° angle from vertical which enters the pressure chamber at a point about 35 millimeters above the ball joint. This is illustrated in Figure 20. The glass connecting tube extends through the wall of the chamber to the center, where it is bent vertical and terminates in a short drip tip. The upper part of the solvent reservoir has a sidearm stopcock (1 millimeter bore), which is connected to a glass tube (8 millimeter o. d.) bent horizontal above the stopcock, and which enters the pressure chamber near the tapered section, as illustrated in Figure 20. With this arrangement it is possible to apply pressure continuously to the liquid passing through the column, while re-filling the reservoir with solvents or while adding solvents from the reservoir to the column.

(d) Vacuum adapter tube, Pyrex glass with a 24/40 outer standard taper joint at the top, 24/40 inner standard taper joint at the bottom, and a sidearm suction tube for attachment of rubber vacuum tube. A drip tip is built into the center of these adapters.

(e) Receiving flasks, Pyrex glass with a 24/40 standard taper joint. A 1 liter capacity round-bottom distillation flask should be used for these procedures, and the flask should be marked at the 750 milliliter level before starting a separation run.

(f) Receiving tubes, for catching the ether and benzene fractions as they emerge from the column. Several types may be employed; 100-milliliter conical or pear-shaped A. S. T. M. oil centrifuge tubes have proven convenient. It is not necessary that these tubes have standard taper fittings, since the eluate can be caught easily from the drip tip of the vacuum adapter tube or from the drip tip of the column itself.

4.2 Pressure source. This pressure source can be provided in any convenient manner, such as with a high pressure cylinder of inert gas (nitrogen, air, argon, etc.), controlled with a sensitive pressure regulator which can control the pressure to within 1/2 p.s.i. at pressures between 1 and 5 p.s.i.

4.3 Distillation apparatus. A standard laboratory distillation apparatus shall be provided, such as a Claisen apparatus, with distilling head, West-type condenser, 105° receiving tube adapter, thermometer, and receiving flasks. Standard taper ware is preferable.

4.4 Drying oven, capable of maintaining a constant temperature of 110°C.

4.5 Analytical balance, capable of weighing to 0.1 milligram.

5.0 REAGENTS.

5.1 Methanol-water (83:17, v/v) solvent combination. Measure 747 milliliters of absolute reagent grade methanol in a graduated cylinder, and 153 milliliters of distilled water in a second graduated cylinder. Combine the two reagents in a glass-stoppered container with shaking to mix thoroughly. Store in the closed container until ready to start the separation. (CAUTION: Avoid breathing vapors of methanol and do not allow the alcohol to come in contact with the skin. This is an extremely poisonous reagent; reasonable precautions should be maintained at all times. Perform all operations with methanol in a fume hood, or in a well-ventilated area!).

5.2 Diethyl ether, anhydrous, reagent grade.

5.3 Benzene, reagent grade.

5.4 Silica gel, through 200 mesh, chromatographic grade. Davison silica gel No. 22-08-09-216, through 200 mesh, has been found satisfactory for these separations (Davison Chemical Corporation, Baltimore 3, Maryland). Other fine mesh inert column material, such as alumina, may be substituted.

5.5 Filter paper, coarse fiber, qualitative grade.

6.0 PROCEDURE.

6.1 PREPARATION OF THE COLUMN.

6.1.1 Mount the entire apparatus, including the column, pressure chamber and reservoir, vacuum adapter tube, and a 24/40 standard taper flask (about 250-milliliter capacity) on a rigid rack. Grease the ground glass fittings lightly with stopcock lubricant. Cut a circle from coarse filter paper which closely fits the inside diameter of the tube at the point where the glass frit is joined to the walls of the tube. Position the paper circle on the glass frit. Weigh 100 grams of silica gel in a 250-milliliter beaker. Raise the reservoir-pressure chamber and mount it to one side of the column. With a wide-mouth funnel, pour the gel into the chromatographic tube in an unbroken stream, directing the flow down the center of the tube. Remove the funnel, and tap the sides of the tube sharply with the hand or a stiff rubber paddle to settle the gel for about two minutes (or until there is no further visible settling of the gel). Replace the reservoir section after carefully wiping out any silica gel which might have fallen onto the ground glass surfaces of the ball joint. It is not necessary at this point to clamp the ball joint, nor to attach the pressure hose at the top of the pressure chamber.

6.1.2 Open the reservoir, close the stopcock at the bottom, and pour about 50 milliliters of distilled water into the reservoir. Be sure the vacuum tube adapter and flask are attached tightly to the bottom of the chromatographic tube. Attach the rubber vacuum tube to the adapter, and turn the aspirator vacuum on at a medium rate of water flow. Leaving the reservoir top off and the upper stopcock open, slowly open the stopcock at the bottom of the reservoir. Allow the water to drop onto the silica gel at a rate of about 1 drop per second until the upper 1/4 inch of the gel is wetted, then drain the water from the reservoir into the tube above the silica gel. The vacuum applied should be such that the water is adsorbed into the entire column of gel in about 20 minutes. Close the lower stopcock on the reservoir, and add about 125 milliliters of methanol-water (83:17, v/v) solvent combination. When about one milliliter of water remains above the surface of the gel, open the lower stopcock and drain about 110 milliliters of the solvent combination into the space above the gel, keeping the remaining solvent combination in the reservoir. Allow the solvent combination to enter the silica gel under vacuum. Meanwhile, weigh the sample oil (6.2.1) and continue as described below.

6.2 APPLICATION OF THE SAMPLE TO THE COLUMN.

6.2.1 Weigh a small glass weighing tube to about 0.01 gram, and add about 2.1 grams of the sample oil to the tube; weigh the tube and oil to 0.1 milligram. Raise the reservoir section to one side preparatory to pouring in the sample oil. When the last half milliliter of solvent combination is about to enter the gel, pour the sample oil onto the column. Be sure that the oil is poured quickly enough that no air is drawn into the gel; actually the rate of entry of the solvent into the gel should be slow enough that this will not happen. Also take care that a minimum of oil strikes the inside walls of the chromatographic chamber above the gel. Clamp the weighing tube at a 45° angle over the tube to drain for 10 minutes. When half of the oil has entered the gel, detach the vacuum hose from the adapter and allow gravity to pull the remainder of the oil into the gel. Meanwhile remove the weighing tube without touching the lip (which holds some oil), and weigh the empty tube. Record the difference in weights as the weight of oil sample taken.

6.2.2 When the last traces of oil are sinking into the silica gel, pour about 5 grams of dry silica gel through a funnel onto the wet column. Replace the reservoir after wiping out the ball joint, and add the remaining solvent combination in the reservoir at a rate of about 2 drops per second to the dry gel. The solvent will wet the gel completely, usually forming a few small air pockets at the interface between the two gel systems. Before all of the solvent combination has entered the gel, quickly remove the reservoir and with a long clean stirring rod stir the upper layer of gel slowly to remove most of the air bubbles. Do not allow the stirring rod to disturb the lower layer of gel, or part of the oil sample will be dislodged and the sealing procedure will have to be repeated (Note 1). It is not necessary to remove all of the visible air bubbles, particularly those which lay near the interface. During this stirring process, there still should be a few milliliters of solvent above the gel. Remove the stirring rod, allow the particles of gel to settle, and inspect the surface of the gel for small droplets of oil (Note 1). If no droplets are visible, the oil is sealed into the column, and the separation procedure may be started (6.3). Under no circumstances should the separation be started if there are droplets of oil on the surface of the gel.

Note 1. If droplets of oil have risen through the gel and emerged into the solvent, the solvent above the gel and the droplets must be drawn into the gel by vacuum, and further dry gel (5 grams) must be added to entrap these droplets. Add another 10 milliliters of solvent combination slowly, and repeat the stirring procedure to

remove air bubbles. Repeat the inspection after the stirred gel in the solvent has settled. Usually the procedure does not have to be repeated more than once to seal the oil into the column.

6.3 ELUTION OF THE BASE-OIL FRACTIONS.

6.3.1 From this point in the procedure it is necessary that the temperature in and around the chromatograph tube be held to 25°C. ± 1/2°C., and that the tube should not be subjected to drafts or other factors which would affect the equilibrium temperature conditions in the tube. Replace the reservoir on the chromatographic tube, secure the ball joint with the spring clamp, attach the hose from the pressure source to the top of the pressure chamber, and close the stopcock at the bottom of the reservoir. Measure in a glass-stoppered graduate 750 milliliters of solvent combination, and fill the reservoir from the cylinder. Close the reservoir with the cap, and secure with two springs under moderate tension. Remove the flask and vacuum adapter from the bottom of the tube, and clamp a 50-milliliter graduated cylinder at the outlet. Open the two stopcocks on the reservoir and fill the space above the gel with solvent combination. Turn on the pressure and adjust so that liquid emerges from the tube at a rate of 1 drop per second. When 40 milliliters of solvent have been collected in the 50-milliliter graduate, remove the graduate and quickly replace it with a 1 liter round-bottom standard taper flask, which has been previously marked at the 750 milliliter level. Do not fit the standard taper joints on the flask and tube together but leave a small air gap between them. Do not grease the standard taper joint on the flask--this joint should be cleaned with solvents before using--and avoid touching it to the greased joint on the tube. Continue the elution process until the reservoir is drained; at this time close both stopcocks on the reservoir, open the cap, and refill with solvent combination. Close the cap, open the stopcocks, and continue until the reservoir is again empty. Repeat the filling process until all 750 milliliters of solvent combination have been used.

6.3.2 When the reservoir is again empty, add 125 milliliters of diethyl ether to the reservoir, but do not add the ether to the pressure chamber until less than 1/2 milliliter of solvent combination remains above the surface of the gel. At this time add the ether quickly, continuing the application of pressure. Watch the level of the solvent combination in the receiving flask, and when it approaches 750 milliliters, prepare to remove and replace it with a 100-milliliter receiving tube.

The ether may be seen descending through the column of gel as an irregular dark line. When the lowest portion of this line comes near the glass frit, change receiving tubes. Set the 1 liter flask aside for the determination of DBAEs in the solvent combination (6.4.1).

6.3.3 When the ether has drained from the reservoir, close the stopcocks, open the cap, add 75 milliliters of benzene to the reservoir, and close the cap. When the volume of eluate (ether with some methanol-water) in the receiving tube has reached 100 milliliters, switch to a second 100-milliliter receiving tube. Set the full tube aside for determination of ether and benzene-soluble oils in the sample (6.4.2). When the last traces of ether are entering the silica gel, add the 75 milliliters of benzene to the column, and continue the pressure until no further liquid emerges. Remove the receiving tube (containing ether and benzene) for the determination of ether and benzene-soluble oils in the sample (6.4.2). Turn off the pressure, open the cap and stopcocks on the reservoir, attach the vacuum adapter and 250-milliliter flask on the bottom of the column, and dry the silica gel by applying vacuum until dry.

6.4 RECOVERING ELUTED OILS.

6.4.1 Dibasic Acid Esters.

6.4.1.1 Procedure. Attach the 1 liter flask containing 750 milliliters of solvent combination (with dissolved DBAEs in saturated solution) to a Claisen distillation apparatus. Do not grease the standard taper joint where the flask is attached to the apparatus. Distill off most of the methanol at a rate of 1 drop per second. When about 100 milliliters of liquid remain in the flask, stop the distillation, cool the flask enough for convenient handling, and remove it from the apparatus. Inspect the inside of the standard taper joint to see whether any oil has "crept" out of the flask. If this has occurred, the oil may be recovered by washing the outside and inside of the joint with hexane, catching the hexane and oil in a weighed Petri dish (take care not to spill any of the oil and solvent combination from inside the flask). Place the flask, which contains water, a little methanol, and any DBAEs, in a drying oven at about 95-100°C. to evaporate solvents. This usually requires overnight heating. When all water has been evaporated, cool, and rinse the oils from the flask with 4 successive 5 milliliter portions of hexane, catching the hexane in a weighed Petri dish. Rinse the outside of the

lip of the flask with a few milliliters of hexane to ensure complete recovery of the oil. Evaporate the hexane from the oil on a steam bath with a stream of dry air blowing across the surface of the solution. Dry the oil at 110°C. for 15 minutes, cool in a desiccator, and weigh. Reserve the oil for paper chromatographic identification of the DBAEs present (Method 53).

6.4.1.2 Calculation. Calculate the percent of DBAEs present in the oil as follows:

$$\text{Dibasic Acid Esters (percent)} = \frac{D \times 100}{W}$$

where: D = weight of dibasic acid esters recovered in the solvent combination.

W = weight of oil added to the column.

6.4.2 Silicon-Containing Base-Oils.

6.4.2.1 Procedure. Suspend both of the 100-milliliter receiving tubes (6.3.2 and 6.3.3) over a steam bath (to provide gentle heating until the volume has been reduced) with a clamp on a ring stand. Direct a slow stream of dry air into the tubes to sweep out evaporated solvent (use a fume hood). As the volume of solvent decreases, lower the tubes into the bath for greater heating, continuing to direct the air into the tubes. When the volume has been reduced to a few milliliters, transfer the tubes to a drying oven at 100°C. until the oils are dry. Rinse oil from the tubes with four successive 5 milliliter portions of hexane, catching the hexane in a weighed Petri dish. Rinse the outside of the lip of the tubes with a few milliliters of hexane to ensure complete recovery of the oil. Evaporate the hexane on a steam bath with a stream of dry air blowing across the surface of the solution. Dry the oil at 110°C. for 15 minutes. Cool in a desiccator, and weigh. Reserve the oil for paper chromatographic and wet chemical identification of the silicon-containing oils present (Method 54).

Note 2. Usually the second tube (which contains no water) dries in about 10 minutes. The first tube may have to be dried overnight, if an appreciable quantity of water is present.

6.4.2.2 Calculation. Calculate the percent of oils in the ether-benzene eluents as follows:

$$\text{Ether-benzene soluble oils (percent)} = \frac{E \times 100}{W}$$

where: E = weight of oils recovered from the ether-benzene eluents.
W = weight of oil added to the column.

IDENTIFICATION OF DIBASIC ACID ESTERS BY PARTITION PAPER CHROMATOGRAPHY

1.0 SCOPE.

1.1 This method describes procedures for the qualitative identification of dibasic acid esters (abbreviated DBAEs) from synthetic lubricants and greases after their separation from additives and from other base-oils. For the analysis of base-oils in synthetic lubricants, this method must be preceded by Methods 16, in which most additives are removed by adsorption chromatography, and Method 52, in which other base-oils are removed by partition chromatography. For the analysis of base-oils in synthetic greases, this method must be preceded by Methods 41 through 45 and by Methods 16 and 52, in which gelling agents and thickeners first are separated from the base-oils, and additives and other base-oils are then separated from DBAEs by adsorption and partition chromatography.

2.0 OUTLINE OF METHOD.

2.1 The DBAE oils, separated and isolated in Method 52, are diluted in hexane and benzene, and a sample is chromatographed on acetylcellulose (reversed phase) paper with the solvent combination methanol-acetone-water (37:9:21, v/v). This solvent combination divides the DBAEs present into three groups. If the group containing dioctyl adipate and dioctyl phthalate is present, a second chromatogram is developed with the solvent combination methanol-acetone-water (37:10:31, v/v) to distinguish between these DBAEs. If the first chromatogram showed DBAEs in the R_f-value range of 0.47 to 0.52, these could be one or more of four different compounds; a third chromatogram is therefore developed with methanol-acetone-water (4:1:4, v/v) to identify the compounds present from this group. If dibutyl phthalate or di-isoamyl adipate are present, their R_f-values are so close that the phthalate must be identified by wet chemical reaction. The third group which appears on the first chromatogram could be either dioctyl sebacate or dioctyl azelate. Since the R_f-values of these diesters are similar, it is necessary to hydrolyze the compounds, recover and crystallize the dibasic acids, and identify the diester by the melting point of the dibasic acid.

3.0 SAMPLE.

3.1 The oil sample used in this method must be obtained after prior treatment of the synthetic lubricant or grease to isolate the entire group of DBAEs (see Paragraph 1.1).

4.0 APPARATUS.

4.1 Hydrometer cylinder, height 300 millimeters, diameter 50 millimeters, with expanded base. This cylinder is used for ascending paper chromatography and is equipped with a #11 one-hole rubber stopper, through which a piece of wire with a hook at the end is placed. A glass rod which closely fits the hole in the stopper and which has four horizontal short glass rods at the lower end may be substituted for the wire. The wire or glass rod is held in place by friction in such a way that it can easily be raised (to hold the paper strip in the atmosphere above the solvent) and lowered (to hold the paper with the lower edge in the solvent combination.) This type of chromatographic cylinder is illustrated in Figure 21. Other types of cylinders with wide mouths may be substituted, providing the cylinder is made of glass and is tall enough to hold the paper and supporting clip (4.4) with about 2 inches of space for raising and lowering the paper.

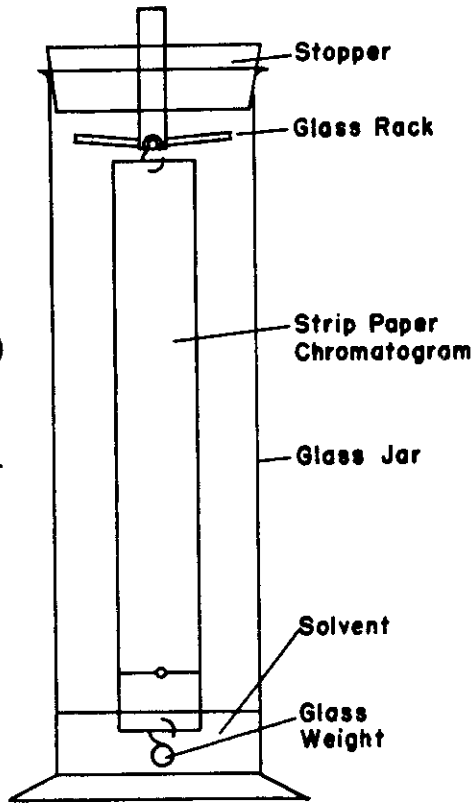


Figure 21. Apparatus For Ascending Paper Chromatography.

4.2 Glass weights. Small glass weights, illustrated in Figure 21, are used to hold the paper straight in the chromatographic chamber (4.1).

4.3 Micro-pipets, capable of delivering 2.5 or 5 lambdas of solution (1 lambda = 0.000001 liter). A variety of sizes of micro-pipets from 1 to 50 lambdas capacity is recommended. (Micro-pipets and other micro supplies may usually be obtained from local chemical supply houses, or from microchemical equipment suppliers, such as Microchemical Specialities Co., 1834 University Ave., Berkeley 3, California).

4.4 Stainless steel clips, small metal spring-loaded clips similar to photographic clips, but having a jaw about 1 inch long.

4.5 Reagent spray, all glass, bottle type, flat bottom, 50 milliliter capacity with glass hooks and springs for securing. (A reagent spray similar to Microchemical Specialities Co., Catalog No. 2C-50, Type B, is satisfactory for this method).

4.6 Drying oven, or low speed hot air fan, for evaporating solvents from paper strips.

4.7 Melting point apparatus. This apparatus should allow temperature control to within 1°C. rise per minute. Either an aluminum-block type, electrically or gas heated, or a glass capillary type, immersed in a high boiling liquid bath, may be employed.

4.8 Ultra-violet lamp. A Blak-Ray Model XX-4 long wave ultra-violet lamp (Ultra-Violet Products, Inc., South Pasadena, California) has proven satisfactory for illuminating samples of oil and paper chromatograms.

5.0 REAGENTS.

5.1 Solvent Combinations:

(a) Methanol-acetone-water (37:9:31, v/v).
(b) Methanol-acetone-water (37:10:21, v/v).
(c) Methanol-acetone-water (4:1:4, v/v).

Measure the volumes of each of the reagent grade solvents in separate graduated cylinders, and combine these in a glass-stoppered Erlenmeyer flask with shaking.

5.2 Rhodamine B solution (0.1 percent aqueous).

5.3 Resorcinol. Sublime resorcinol fresh for each determination.

5.4 Sulfuric acid (sp. gr. 1.84), reagent grade.

5.5 Sodium hydroxide solution (10 percent aqueous).

5.6 Potassium hydroxide solution (10 percent aqueous).

5.7 Hydrochloric acid solution (5 percent aqueous).

5.8 Diethyl ether, anhydrous, reagent grade.

5.9 Dibasic acid ester solutions (1 percent in benzene or hexane):

(a) Dioctyl Sebacate (DOS).
(b) Dioctyl Azelate (DOAz).
(c) Dioctyl Phthalate (DOP).
(d) Di-isoamyl Sebacate (DAS).
(e) Di-isoamyl Adipate (DAA).
(f) Dibutyl Sebacate (DBS).
(g) Dibutyl Phthalate (DBP).

5.10 Benzene, reagent grade.

5.11 Ethanol, absolute, purified grade.

5.12 Acetylcellulose paper. See Method 21 for preparation of this paper.

5.13 Blotting paper. Use any clean absorbent paper, such as brown paper towelling. Do not use tissue-weight paper.

PRELIMINARY PAPER CHROMATOGRAPHIC SEPARATION OF DIBASIC ACID ESTERS

6.0 PROCEDURE.

6.1 PREPARATION OF THE PAPER STRIP. Place a large piece of acetylated paper (see Method 21 for preparation of this paper) on a clean dry surface, like a glass plate, and mark on the sheet the following dimensions:

(a) Total length = 8-3/4 inches.
(b) Width = 1-1/4 inches.
(c) Width of tail = 3/16 inch.
(d) Length of tail = 1/2 inch.
(e) Length of paper to the diagonal cut = 7-1/2 inches.
(f) Location of starting spot - 3/4 inch above bottom of tail and centered.

Use a soft lead pencil to mark these dimensions. With a scissors or razor blade and metal straight edge, cut the paper in the same shape as that illustrated in Figure 22. Always handle the paper with clean hands to avoid contamination and consequent misleading results.

6.2 PREPARATION OF THE OIL SAMPLE. Weigh into a 10 milliliter volumetric flask 0.1 gram of the DBAE oil fraction obtained in Method 52. Dilute to volume with benzene (or hexane). The concentration of DBAE for this method should be about 1 percent; too dilute a solution will not yield detectable spots, and too concentrated a solution will cause the spot or spots of DBAEs to spread out and obscure each other.

6.3 APPLICATION OF THE SAMPLE TO THE PAPER. Place the prepared paper strip (6.1) on a small piece of clean plate glass in such a way that the starting point, marked lightly on the paper with pencil, is in the center of the glass. Dip the tip of a clean, dry 2.5 or 5 lambda micro-pipet into the sample solution (6.2), and allow capillary forces to fill the pipet completely. In the case of viscous solutions, even though diluted with benzene or hexane, this sometimes requires a minute or so. When the pipet is full, remove the tip from the solution, and wipe the outside of the tip with a piece of clean, dry, absorbent tissue in such a way that the tissue does not touch the opening at the tip of the pipet; otherwise some of the test solution would be absorbed into the paper. Place the tip on the starting point on the paper, holding the pipet vertical and applying slight pressure. The solution will not drain onto the paper until it contacts the paper; therefore it may be necessary to rotate the upper end of the pipet slightly to establish this contact. Allow the pipet to drain into the paper, remove, and hang the paper in air for a few moments to evaporate solvent. Clean the pipet by placing the

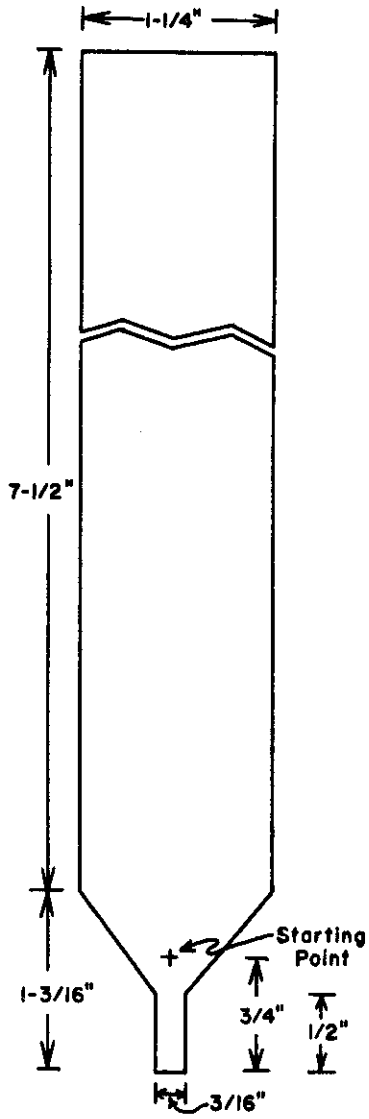


Figure 22. Paper Strip Used For Qualitative Identification of Dibasic Acid Esters.

tip in a suitable solvent, fill the capillary, and remove the solvent by touching the tip to tissue paper; repeat this procedure several times, and set the pipet aside to dry.

6.4 DEVELOPING THE CHROMATOGRAM. Prepare the solvent combination methanol-acetone-water(37:9:21, v/v) by measuring 37 milliliters of methanol in a graduated cylinder, 9 milliliters of acetone in a second cylinder, and 21 milliliters of distilled water in a third cylinder. Combine the three solvents in a glass-stoppered Erlenmeyer flask, shake to mix, and pour about 20 milliliters of the solvent combination into the hydrometer cylinder. Attach a stainless steel clip to the top of the paper strip, and attach the clip to the glass or wire rack in the stopper of the hydrometer cylinder. Adjust the height of the rack so that when the stopper is in place, the entire paper strip will be suspended above the solvent combination. Allow the atmosphere in the cylinder to saturate with vapors of the solvent combination for about 2 hours (do not saturate overnight, because the oil in the paper will diffuse too far through the paper). At the end of the saturation period, lower the rack so that the tip of the paper dips 2 or 3 millimeters below the surface of the solvent combination. Be sure that the paper hangs free in the cylinder, not touching the sides at any point (Note 1). Allow the chromatogram to develop (usually about 2 hours at room temperature) until the solvent front has reached a point about one inch from the top of the paper. Quickly remove the stopper and paper from the chamber, lay the paper flat on a clean glass surface, mark the location of the solvent front with a soft lead pencil, taking care not to tear the wet paper, and hang the strip in a drying oven at 110°C. for 5 or 6 minutes, or in front of a hot air fan until the paper is dry.

Note 1. If the acetylcellulose paper does not hang straight in the chamber, particularly after saturating the paper and atmosphere, it may be necessary to add glass weights to the paper, as illustrated in Figure 22.

6.5 DETECTING THE SPOTS

6.5.1 Adjusting the Spraying Apparatus. Fill the 50-milliliter spray reagent chamber about 2/3 full with Rhodamine B solution, assemble the spray, and attach the springs. The spray should be assembled so that air pressure applied will pass through the slot in the ground glass inner member into the channel in the ground glass outer

member to force liquid up the capillary and out the orifice into the air jet in the spray head. An air pressure source should be available, which can be controlled to deliver small pressures of air into the spray apparatus. With a short piece of rubber tube attach the spray air inlet to a glass tubing "T" (a three-way stopcock may be substituted for the "T"), which is connected through rubber tubing to the air pressure source. Leave the extra arm of the "T" open when turning on the air and when not spraying. To spray the reagent, turn on the air at low pressure and simply place the finger on the extra arm of the "T" to force all of the air through the spray head (or close the stopcock). Hold the paper strip at a distance of about 10 to 12 inches in front of the sprayer. Direct the spray away from other apparatus to avoid unnecessary cleaning. Mount the spray apparatus with a clamp on a ring stand to provide permanent and secure positioning.

6.5.2 Spraying the Paper Strip. Remove the paper strip from the drying oven or the hot air fan, and place a second stainless steel clip at the bottom of the paper. Either hold the paper by hand, or suspend the paper and clips on a simple rectangular wire rack which is bent to hold this size paper strip. Turn on low air pressure, and spray the back side of the paper only until a uniform medium pink color has been applied to the entire side of the paper. It is well to practice spraying the paper with several trial paper chromatograms with known spots of DBAEs present. Sufficient reagent should be applied that the DBAE will cause pink spots to appear on the opposite side of the paper; but if too much reagent is applied, the reagent, even though in an aqueous solution, can creep through the paper and obscure any DBAE spots which might have appeared. Hang the paper to air-dry for 10 minutes, then dry in an oven or in front of the hot air fan until dry. Mark any pink spots which have appeared on the white side of the paper with a soft lead pencil by outlining the entire spot and marking the center of the spot. The pink color of all spots on the paper is identical.

6.6 DETERMINING THE R_f-VALUE. See Paragraph 6.6, Method 22, for a definition and method of determination of R_f-value. Calculate the R_f-value of any spots which appear on the paper chromatogram. Table VI lists the R_f-values of various DBAEs in this solvent combination when run at room temperature (25°C.):

TABLE VI

R_f-Values of Dibasic Acid Esters With Solvent Combination Methanol-Acetone-Water (37:9:21, v/v).

Dibasic Acid Ester	Abbreviation	R_f-value
Dioctyl sebacate	DOS	0.12
Dioctyl azelate	DOAz	0.13
Dioctyl phthalate	DOP	0.30
Dioctyl adipate	DOA	0.34
Di-n-butyl sebacate	DBS	0.47
Di-isoamyl sebacate	DAS	0.49
Di-isoamyl adipate	DAA	0.52
Di-n-butyl phthalate	DBP	0.52

It may be seen from Table VI that the R_f-values fall roughly into three groups, so that when a spot is found on the chromatogram near one of these three groups, it is impossible to predict exactly which of the compounds in the group the spot represents. In some cases the spots may be identified by running a second chromatogram with a different solvent combination to obtain a second characteristic R_f-value for each diester, or in other cases chemical means must be employed to confirm the presence or absence of certain groups (such as phthalate) in the diester oil.

6.7 COMPARISON WITH KNOWN COMPOUNDS. Prepare a 1 percent (in benzene or hexane) solution of each DBAE to be used as a comparison material with the unknown oil. Chromatograph these solutions in exactly the same manner as the unknown sample on individual strips of acetylcellulose paper. Run one of these chromatograms in the same chamber and at the same time as the unknown, taking care that the two pieces of paper used in each chamber do not touch during development. Comparison of the known spots with the unknown sample spots on the chromatogram assists in ascertaining the presence and identity of groups of compounds.

7.0 SEPARATION AND IDENTIFICATION OF DIOCTYL SEBACATE AND DIOCTYL AZELATE.

7.1 DETECTION OF DIOCTYL SEBACATE AND DIOCTYL AZELATE. If a definite pink spot was detected in the vicinity of an R_f-value of 0.10 to 0.16 in the paper chromatographic determination (6.6), it is likely that the spot contains either DOS or DOAz. Since the R_f-values of these compounds are so similar, it is impossible to separate and positively identify them by further paper chromatography. Therefore it is necessary to hydrolyze a portion of the diester oil, recover the dibasic acid, and determine the melting point to distinguish which diester is present.

7.2 HYDROLYSIS OF THE DIESTER OIL. Place in a large Pyrex test tube 0.5 milliliter of the DBAE fraction from Method 52, 10 milliliters of 10 percent KOH solution, and a boiling chip. Suspend the test tube over a wire gauze with a clamp, and insert a finger condenser into the test tube so that it reaches about half way down the tube. Boil the mixture gently until all the oil has disappeared (about 1 hour). Disconnect the apparatus, cool the solution, and acidify with dilute HCl solution, using litmus or indicator test paper for this purpose. Add 10 milliliters of diethyl ether to the tube, stopper, and shake well. Allow the phases to separate, and decant the ether phase onto a large watch glass. Evaporate the ether slowly to dryness, and observe the crystals of dibasic acid which are formed. If clean, well-defined crystals are obtained, take their melting point. If the crystals are not satisfactory, take them up in a minimum of hot absolute ethanol or hot water, and recrystallize slowly in an Erlenmeyer flask. Dry the crystals at about 75°C. in a vacuum chamber or in a drying oven for about 10 minutes. Take the melting point of the dibasic acid. Azelaic acid has a melting point of 106.5°C., and sebacic acid 134.5°C. If other DBAEs were present when the oil was hydrolyzed, these dibasic acids will also be present during crystallization. The analyst must first identify these DBAEs (see Paragraphs 8.0 and 9.0); the resulting dibasic acids can then be separated from the azelaic or sebacic acid by fractional crystallization, the latter acids being much less soluble than other dibasic acids encountered in synthetic lubricants. The azelaic or sebacic acids can then be identified.

8.0 SEPARATION AND IDENTIFICATION OF DIOCTYL PHTHALATE AND DIOCTYL ADIPATE.

8.1 PAPER CHROMATOGRAPHIC IDENTIFICATION OF DIOCTYL PHTHALATE AND DIOCTYL ADIPATE. If a spot was detected near an R_f-value of 0.25 to 0.35 in the paper chromatographic determina-

tion (6.6), it is likely that DOA or DOP are present in the oil. Perform a paper chromatographic separation on the diluted sample of DBAEs (6.2) as described in Paragraphs 6.1 through 6.7, but now using the solvent combination methanol-acetone-water (37:10:21, v/v). With this combination DOP has an R_f-value of 0.32 and DOA has a value of 0.38. Comparison chromatograms should be run with pure solutions of DOP and DOA. If there is doubt about the identity of the DBAE because of diffuse spots covering a large area of the paper chromatogram, the following test will identify the presence of phthalate in the oil, indicating that the spot is DOP rather than DOA.

8.2 IDENTIFICATION OF PHTHALATE IN THE OIL.* Place several drops of the oil from the DBAE fraction from Method 52 in a microcrucible with freshly sublimed resorcinol, and add a few drops of H_2SO_4 (sp. gr. 1.84). Heat at a temperature not exceeding 130°C. for five minutes. When the reaction is complete, place the crucible and contents in 50 milliliters of distilled water to dissolve the reaction mixture. Make the solution alkaline with 10 percent NaOH solution, using litmus or indicator test paper for this purpose. If phthalic acid from a diester is present, a bright yellow fluorescence should be visible in the water. This fluorescence is a bright green when viewed in ultra-violet radiation. A blank should be employed to avoid any error which could arise from heating the reaction mixture in excess of 130°C.

9.0 SEPARATION AND IDENTIFICATION OF DI-n-BUTYL SEBACATE, DI-ISOAMYL SEBACATE, DI-ISOAMYL ADIPATE, AND DI-n-BUTYL PHTHALATE

9.1 PAPER CHROMATOGRAPHIC IDENTIFICATION OF THE DIESTERS. If a spot was detected near an R_f-value of 0.45 to 0.55 in the first paper chromatographic determination (6.6), it is likely that DBS, DAS, DAA, or DBP is present in the oil. Perform a paper chromatographic separation on the diluted sample of DBAEs (6.2) as described in Paragraphs 6.1 through 6.7, but using the solvent combination methanol-acetone-water (4:1:4, v/v). With this solvent combination, the following R_f-values may be obtained:

*This method is taken from Feigl, F., Spot Tests: Volume II, Organic Applications, New York: Elsevier Publishing Co., 436 pp., 1954.

Diester		R_f-value
Di-isoamyl sebacate	(DAS)	0.08
Di-n-butyl sebacate	(DBS)	0.11
Di-isoamyl adipate	(DAA)	0.18
Di-n-butyl phthalate	(DBP)	0.19

Comparison chromatograms should be run with pure solutions of these DBAEs. Identification of the diesters DAS and DBS is fairly certain from the R_f-values, particularly at these low values where R_f-values do not have the variation that occurs with substances at higher R_f-values. However, if a spot is found at R_f 0.18 or 0.19, it is impossible to identify the acid, except as one of two diesters, DAA or DBP. Presence of the phthalate ester may be proven as follows:

9.2 IDENTIFICATION OF PHTHALATE IN THE OIL. Proceed as described in Paragraph 8.2 to identify phthalate diester in the oil. If phthalate has already been identified in Paragraph 8.2, this phthalate may stem either from DOP or DBP, and it is necessary either (a) to assume that if DOP is present in the oil it is unlikely that DBP would be in the same oil, and that the spot at R_f 0.18 is DAA, or (b) to hydrolyze the diester oils by the technique described in Paragraph 7.2, and identify adipic acid in the hydrolyzate by its melting point (151°C.) after fractional crystallization from alcohol or hot water.

QUANTITATIVE DETERMINATION OF MIXTURES OF DIBASIC ACID ESTERS

1.0 SCOPE

1.1 This method is intended to suggest analytical procedures which may be employed for further identification and quantitative determination of mixtures of dibasic acid esters in synthetic lubricants and greases (Note 1). When more than one diester has been found by Method 53, quantitative determination of the exact amount of each diester is complicated and requires considerable further chemical analysis to establish these quantities. It is unlikely, however, that these determinations will be necessary for most synthetic lubricants and greases, since there are relatively few instances of the use of more than one diester in the base-oil.

Note 1. Method 53 employed paper chromatographic techniques to establish qualitatively the number of dibasic acid esters in a base-oil, and Method 52 measured quantitatively the weight of the diester fraction from the base-oil. The two methods give a quantitative measure of a specific diester only when one diester is found in the base-oil.

1.2 Specific analytical techniques for the quantitative determination of mixtures of dibasic acid esters have not been developed. However, several possible approaches and references are herein suggested by which this determination may be carried out:

(a) Adsorption chromatographic separation procedures could be developed in which the slight differences in adsorptive capacities of different diester compounds on a given adsorbent would be utilized to effect quantitative separation of mixtures of diesters.

(b) Hydrolysis of the diester compounds releases dibasic acids, which could be recovered for further analysis by a number of techniques (see Method 53 for qualitative hydrolysis of diesters to recover dibasic acids for melting point determination):

(1) Preparation of heavy metal salts of the dibasic acids, after separation of the dibasic acids.[1]

[1] Swann, M. M. H., "Determination of Dibasic Acids in Alkyd Resins," Analytical Chemistry 21, 1448-1453 (1949).

(2) Partition separation by column chromatography, followed by titration of the eluted dibasic acids in specific fractions of the eluate.[2]

(c) Counter-current distribution might be employed to effect quantitative separation and recovery of very complex mixtures of these compounds. However, this type of separation requires rather elaborate, though simply constructed, piece of apparatus.

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[1] Buch, M. L., Montgomery, R., and Porter, W. L., "Identification of Organic Acids on Paper Chromatograms", Analytical Chemistry 24, 489-491 (1952).

Higuchi, A., Hill, N. C., and Corcoran, B., "Chromatographic Separation and Determination of Dicarboxylic Acids, C_4 to C_{10}" Analytical Chemistry 24, 491-493. (1952).

Marvel, C. S., and Rands, R. D., Jr., "Separation of Organic Acids"; J. Am. Chem. Soc. 72, 2742. (1950).

Vandenheuvel, F. A., and Hayes, E. R., "Partition Chromatography of Aliphatic Acids," Analytical Chemistry 24, 960-965. (1952).

IDENTIFICATION AND DETERMINATION OF SILICATE ESTERS AND DISILOXANES BY PAPER CHROMATOGRAPHY

1.0 SCOPE

1.1 This method outlines procedures for paper chromatographic qualitative detection of silicate esters and disiloxane base-oils from synthetic lubricants and greases, after separating these oils from additives and other base-oils. For the analysis of these compounds in synthetic lubricants, this method must be preceded by Method 16 in which most additives are removed by adsorption chromatography, and by Method 52, in which other base-oils (with the exception of silicone oils) are removed by partition chromatography. For the analysis of these compounds in synthetic greases, this method must be preceded by Methods 41 through 45, and by Methods 16 and 52, in which gelling agents and thickeners first are separated from the base-oils, and then other additives and base-oils (with the exception of silicone oils) are separated from the silicate esters and disiloxanes by adsorption and partition chromatography.

1.2 This method has been studied with the silicate esters tetra(2-ethylbutoxy)silicate and tetra(2-ethylhexoxy)silicate, and with the disiloxanes hexa(2-ethylbutoxy)disiloxane and hexa(2-ethylhexoxy)disiloxane. The method cannot distinguish between mixtures of silicate esters, disiloxanes, and silicone oils, but does provide a means for determining whether silicate esters and disiloxanes as a group are present singly in a base-oil.

2.0 OUTLINE OF METHOD

2.1 The silicate ester, disiloxane, and silicone oil-containing fraction, separated and isolated in Method 52 from dibasic acid esters, is chromatographed on acetylcellulose (reversed phase) paper with the solvent combination ethyl acetate-tetrahydrofuran-water(1:6:4, v/v). This solvent combination will indicate the presence of silicate esters and disiloxanes only in the absence of silicone oils, the former compounds having R_f-values between 0.30 and 0.40. If silicone oils are present, they spread out in a broad band from the starting point to the secondary solvent front, thus obscuring silicate esters and disiloxanes. Techniques for distinguishing between the three classes of compounds when present in mixtures are given in Method 56.

3.0 SAMPLE

3.1 The oil sample used in this method must be obtained after prior treatment of the synthetic lubricant or grease to isolate the entire group of silicate esters, disiloxanes, and silicone oils (see Paragraphs 1.1 and 2.1).

4.0 APPARATUS

4.1 The apparatus employed in this method is the same as that described in Method 53, Paragraphs 4.1 through 4.6.

5.0 REAGENTS

5.1 Ethyl Acetate-tetrahydrofuran-water (1:6:4, v/v)solvent combination. Measure the volumes of each of the reagent grade solvents in separate graduated cylinders, and combine these in a glass-stoppered Erlenmeyer flask with shaking.

5.2 Rhodamine-B solution (0.1 percent aqueous).

5.3 Benzene, reagent grade.

5.4 Standard comparison solutions (1 percent in benzene or hexane):

(a) Tetra(2-ethylbutoxy)silicate (abbreviated THS).
(b) Tetra(2-ethylbutoxy)silicate (" TOS).
(c) Hexa(2-ethylbutoxy)disiloxane (" HHDS).
(d) Hexa(2-ethylhexoxy)disiloxane (" HODS).
(e) Silicone Oil, DC-200, 5 cs. (alkyl silicone).
(f) Silicone Oil, DC-550, (aryl silicone).
(g) Chlorinated silicone oil (MLO-53-446).

5.5 Acetylcellulose paper. See Method 21 for preparation of this paper.

5.6 Blotting paper. Use any clean absorbent paper, such as brown paper towelling. Do not use tissue-weight paper.

6.0 PROCEDURE.

6.1 PREPARATION OF THE PAPER STRIP. Prepare several strips of acetylcellulose paper as described in Paragraph 6.1, Method 53.

6.2 PREPARATION OF THE OIL SAMPLE. Weigh into a 10 milliliter volumetric flask 0.1 gram of the silicate-disiloxane-silicone oil fraction obtained in Method 52. Dilute to volume with benzene (or hexane). The concentration of oil for this method should be about 1 percent; too dilute a solution will not yield detectable spots, and too concentrated a solution will cause the spot or spots of oils to spread out and obscure each other.

6.3 APPLICATION OF THE SAMPLE TO THE PAPER. Proceed as described in Paragraph 6.3, Method 53.

6.4 DEVELOPING THE CHROMATOGRAM. Proceed as described in Paragraph 6.4, Method 53.

6.5 DETECTING THE SPOTS.

6.5.1 Adjusting the Spraying Apparatus. Proceed as described in Paragraph 6.5.1, Method 53.

6.5.2 Spraying the Paper Strip. Remove the paper strip from the drying oven or the hot air fan, making sure there is no solvent remaining in the paper, and place a second stainless steel clip at the bottom of the paper. Either hold the paper by hand, or suspend the paper and clips on a simple rectangular wire rack which has been bent to hold this size paper strip. Turn on low air pressure, and spray the back side of the paper only until a uniform medium pink color has been applied to the entire side of the paper. It is well to practice spraying the paper with several trial paper chromatograms with known spots of silicate esters, disiloxanes, and silicone oils present. Sufficient reagent should be applied that the oils will cause pink spots to appear on the opposite side of the paper, but if too much reagent is applied, the reagent, even though in an aqueous solution, can creep through the paper and obscure all spots which might have appeared. Hang the paper to air-dry for 10 minutes, then dry in an oven or in front of the hot air fan until dry. Mark any pink spots which have appeared on the white side of the paper with a soft lead pencil by outlining the entire spot and marking the center. The color of all spots on the paper is identical; therefore the detection method cannot be used to determine specific compounds. Any oily materi-

al on the paper will cause formation of a pink spot; hence, cleanliness is most important.

6.6 DETERMINING THE R_f-VALUE. See Paragraph 6.6, Method 22, for a definition and method of determination of R_f-value. Calculate the R_f-value of any spots which appear on the paper chromatogram. Table VII gives a list of R_f-values and a description of the appearance of the chromatogram with various compounds which could be present in the group:

TABLE VII

R_f-Values And Appearance of Paper Chromatograms of Silicate Esters, Disiloxanes, And Silicone Oils With the Solvent Combination Ethyl Acetate-Tetrahydrofuran-Water(1:6:4, v/v).

Compound	Abbreviation	R_f-value or Appearance of the Chromatogram
Tetra(2-ethylbutoxy)silicate	THS	Spot at 0.42.
Tetra(2-ethylhexoxy)silicate	TOS	Spot at 0.39.
Hexa(2-ethylbutoxy)disiloxane	HHDS	Large spot at 0.38.
Hexa(2-ethylhexoxy)disiloxane	HODS	Large spot at 0.31.
Silicone DC-550 (aryl)		Spot at the starting point, with faint spot at 0.25.
Silicone DC-200 (alkyl)		Wide spot extending from starting point to R_f 0.45; this oil would obscure all others present.
Silicone (chlorinated)		Wide spot extending from starting point to R_f 0.45; this oil would obscure all others present.

It will be apparent to the analyst after the first run with this solvent combination that the solvent combination itself is partitioned, forming a secondary front at R_f 0.45. This is why the above spots all stop at this R_f-value. It is evident from the above table why this method has only limited

use: when any of the silicone oils are present, it is impossible to determine whether silicate esters and disiloxanes are present. If, on the other hand, individual spots are found near R_f 0.30 to 0.45, with no tailing reaching back to the starting point, silicone oils are absent and one or more of the silicate esters and disiloxanes is present. This simplifies the chemical analyses for these compounds (Method 56).

6.7 COMPARISON WITH KNOWN COMPOUNDS: Prepare a 1 percent (in benzene or hexane) solution of each of the above oils to make comparison chromatograms. Chromatograph these solutions in the same manner as the unknown sample on individual strips of acetylcellulose paper. These chromatograms may be run in the same chamber and at the same time as the unknown, provided that the two pieces of paper used in each chamber do not touch during development. Comparison of the known spots with the unknown sample spots assists in ascertaining the presence and identity of groups of compounds. Reserve the remainder of the oil fraction from Method 52 for qualitative detection and determination of the types of silicate esters, disiloxanes, and silicone oils present in the oil (Method 56).

DETECTION AND DIFFERENTIATION BETWEEN SILICATE ESTERS, DISILOXANES, AND SILICONE OILS

1.0 SCOPE

1.1 This method describes procedures for the detection and differentiation between silicate esters, disiloxanes, and silicone oils in base-oils from synthetic lubricants after separation of the oils from additives and from other base-oils. For the analysis of these compounds in lubricants, this method must be preceded by Method 16, in which most additives are removed by adsorption chromatography and by Method 52, in which other base-oils, such as dibasic acid esters, are removed by partition chromatography. For the analysis of these compounds in greases, this method must be preceded by Methods 41 through 45, and by Methods 16 and 52, in which gelling agents and thickeners first are separated from the base-oils, and then other additives and base-oils are separated from silicate esters, disiloxanes, and silicone oils by adsorption and partition chromatography.

1.2 This method applies to the silicate esters tetra(2-ethylbutoxy)silicate and tetra(2-ethylhexoxy)silicate, the disiloxanes hexa-(2-ethylbutoxy)disiloxane and hexa(2-ethylhexoxy)disiloxane, and the silicone oils DC-550(aryl silicone), DC-200(alkyl silicone), and MLO-53-446(chlorinated silicone).

2.0 OUTLINE OF METHOD

2.1 The silicate ester-, disiloxane-, and silicone oil-containing fraction, separated and isolated in Method 52 from dibasic acid esters, is tested by a series of chemical reactions to establish the presence or absence of the three types of silicon-containing base-oils. The reactions do not distinguish between individual compounds in each type, but do indicate the presence of the type in the presence of the other types.

3.0 SAMPLE.

3.1 The sample used in this method is obtained after treament of the synthetic lubricant or grease to isolate the entire group of silicate esters, disiloxanes, and silicone oils (see Paragraphs 1.1 and 1.2).

4.0 APPARATUS

4.1 Reaction apparatus, consisting of a 125-milliliter round-bottom boiling flask, Allihn-type reflux condenser, and heating mantle. Standard taper ware (24/40) is preferable.

4.2 Muffle furnace, capable of maintaining 800°C., and equipped with variable control to adjust the temperature to ± 25°C.

4.3 Analytical balance, capable of weighing to 0.1 milligram.

5.0 REAGENTS

5.1 Sodium carbonate, anhydrous, reagent grade.

5.2 Sodium peroxide, reagent grade.

5.3 Hydrochloric acid solution (5 percent).

5.4 Ammonium molybdate solution (15 percent aqueous).

5.5 Benzidine solution (0.5 percent in glacial acetic acid).

5.6 Ammonium hydroxide (sp. gr. 0.90), reagent grade.

5.7 Sodium tetraborate, $Na_2B_4O_7 : 10H_2O$ crystals.

5.8 Sulfuric acid (sp. gr. 1.84), reagent grade.

5.9 Potassium dichromate solution (2 percent).

5.10 Nitric acid (sp. gr. 1.42), reagent grade.

5.11 Aluminum chloride, anhydrous, reagent grade.

5.12 N,N,N',N'-Tetramethyl-4,4'-diaminobenzophenone solution (2 percent in benzene). This reagent is obtainable from Distillation Products Industries, Eastman Organic Chemicals Department, Rochester, N. Y.

5.13 Benzene, reagent grade.

5.14 Acetic acid, glacial, reagent grade.

5.15 Diethyl ether, anhydrous, reagent grade.

5.16 Sodium hydroxide solutions (5 percent and 15 percent).

5.17 Hydrochloric acid (sp. gr. 1.19), reagent grade.

5.18 Acetic anhydride-pyridine (1:3, v/v) acetylating mixture. Mix the reagent grade chemicals in separate graduated cylinders, and pour together in a glass-stoppered Erlenmeyer flask with shaking.

5.19 Pyridine, reagent grade.

5.20 Alcoholic potassium hydroxide solution (0.5N.). See Paragraph 5.8, Method 42, for preparation of this reagent. Use 30 grams of KOH.

5.21 Butanol, reagent grade.

5.22 Isopropyl alcohol, anhydrous, reagent grade.

5.23 Standard hydrochloric acid solution (0.1N.). Dilute one volume of concentrated HCl with 110 volumes of distilled water, mix well, and allow to stand overnight. Standardize this solution against either a standard base or anhydrous sodium carbonate.

5.24 Sodium carbonate, anhydrous, recrystallized, primary standard. Dry analytical grade sodium carbonate 1/2 hour at 270-300°C. Store in a closed bottle in a desiccator.

5.25 Phenolphthalein solution. (0.1 percent in ethanol).

6.0 PROCEDURE.

6.1 Peroxide Fusion Method for Detection of Silicon. Mix 0.1 gram of anhydrous Na_2CO_3, 0.1 gram of Na_2O_2, and 3 drops of the silicate ester-, disiloxane-, and silicone oil-containing oil isolated in Method 52 into a smooth paste with a spatula in a spot plate depression. Make a 1/8 inch diameter loop in the end of a platinum wire, and clean the wire thoroughly by alternately dipping in dilute HCl and heating to

redness in a Bunsen burner flame, until no color is imparted to the flame by the wire. Dip the loop into the reaction paste and heat in the flame until all reaction has ceased (Note 1). Repeat this procedure until a 1/16 inch thick bead is formed. Heat for several minutes until it becomes water-white. Cool, unwind the wire, and drop the bead into a small platinum crucible containing 2 to 3 milliliters of distilled water. Warm over a burner until the bead has completely dissolved. Cut a 1 inch square piece of ashless filter paper and moisten the paper with the solution. Place a drop of ammonium molybdate solution on the paper, and warm over a burner or in an oven to evaporate excess moisture. With the paper still damp, place a small drop of benzidine solution over the ammonium molybdate spot. Wait one minute, then hold the paper over a watch glass containing a few drops of concentrated NH_4OH. The appearance of a blue spot indicates silicon in the oil.

Note 1. If a large quantity of dense black smoke is evolved during fusion, an aromatic compound such as a phenyl silicone oil is indicated.

6.2 SODIUM BORATE REACTION. Place several small crystals of $Na_2B_4O_7 : 10H_2O$ in a 3 inch test tube, add 4 or 5 drops of the oil, and 5 drops of concentrated H_2SO_4. Place the tube in a boiling water bath for 15 minutes, and observe the reaction from time to time. The appearance of a red to maroon colored deposit on the crystals indicates either silicate ester or disiloxane base-oils in the sample. There is no reaction with silicone base-oils.

6.3 POTASSIUM DICHROMATE-NITRIC ACID REACTION. Mix in a large test tube equal volumes (about 1/4 milliliter) each of the sample oil, 2 percent aqueous $K_2Cr_2O_7$ solution, and concentrated HNO_3. Shake well, heat slowly almost to the boiling point, and maintain this temperature for about 2 minutes. Under these conditions silicate esters and disiloxanes oxidize, indicated by a color change of the aqueous layer from orange to light blue or green (Note 2). Silicone oils do not react.

Note 2. Any oxidizable material in the base-oil will cause the color change, including dibasic acid esters, petroleum oils, and most of the organic additives used in synthetic lubricants; therefore, interpretation of the results of this test should be made with reservation, and should be supplemented with the results from Paragraphs 6.4 and 6.5 before definite conclusions are drawn.

6.4 SUBSTITUTED BENZOPHENONE REACTION. Heat 1/2 milliliter of the sample oil with approximately 0.1 gram of anhydrous $AlCl_3$ in a small test tube over a micro-burner until the reaction becomes self-sustaining. When the reaction has stopped, cool the tube and add 2 milliliters of N,N,N',N'-tetramethyl-4,4''-diaminobenzophenone solution. Silicate esters, disiloxanes, and dibasic acid esters immediately produce a wine-red solution; alkyl and chlorinated silicone oils give a bright orange precipitate; and aryl silicones develop this precipitate after 15 to 30 minutes. After waiting 30 minutes, add 5 milliliters of distilled water to the reaction mixture, shake well, and observe the color. Chlorinated silicone oils give a lime-green precipitate, aryl silicone oils give a royal-blue ether-insoluble solution, and alkyl silicone oils, silicate esters, disiloxanes, and dibasic acid esters give light colored precipitates ranging from tan to orange in color. This method thus not only distinguishes in the first step between silicone oils and the other types of silicon-containing base-oils, but in the second step distinguishes between the three classes of silicone oils themselves.

6.5 HYDROLYSIS OF SILICATE ESTERS. If the preceding reactions or the paper chromatographic procedures described in Method 55 have established that the oil contains either silicate esters or disiloxanes, distinguish between these two classes of compound by placing 1 milliliter of the oil in a large test tube with about 5 milliliters of glacial HAc. Place a finger condenser in the test tube and heat the mixture with reflux, maintaining the original volume of liquid by adding further acid if necessary. If there is deposition of white silica particles, silicate esters are present in the oil; if there is formation of a water-white gel, disiloxanes are present. Formation of this gel usually requires a minimum of 1 hour and a maximum of 3 hours' heating. If silicone oils are present in large amounts, the reaction will be delayed, but silica will deposit after 4 or 5 hours' heating if silicate esters are present in more than trace amounts.

7.0 QUANTITATIVE DETERMINATION OF SILICATE ESTERS BY HYDROLYSIS.

7.1 HYDROLYSIS OF THE SILICATE ESTER. If silicate esters or disiloxanes have been found by Methods 55 or 56, weigh to the nearest milligram the remaining silicon-containing oil sample isolated in Method 52 in a weighed 125-milliliter flat-bottom distillation flask. If the sample weighs 2 grams or less, add 10 milliliters of glacial HAc to the flask; if the sample is over 2 grams, add 20 milliliters of acid. Attach the flask to a reflux condenser, but do not grease the standard taper joints. Boil

gently under reflux for 3 hours. Inspect the contents occasionally. If a clear thick gel has formed, disiloxanes are present in excess, and the reaction should be discontinued. If there is evidence of the deposition of white silica particles, silicate esters are present, and the boiling should be continued. Cool the flask, remove from the apparatus, and decant the liquid layer from the flask through an ashless quantitative filter paper into a 125-milliliter separatory funnel. Extract the contents of the flask with five successive 15-milliliter portions of diethyl ether, filtering each wash into the separatory funnel through the quantitative filter paper. Retain as much of the residue in the flask as possible during the extraction procedure. Reserve the residue for determination of silica (7.3). Reserve the ether extract in the separatory funnel for determination of alcohols hydrolyzed from the silicate ester (7.2).

7.2 DETERMINATION OF ALCOHOLS HYDROLYZED FROM SILICATE ESTERS.

7.2.1 Recovery of the Alcohol. Add 25 milliliters of 15 percent NaOH solution to the separatory funnel (containing HAc and alcohols hydrolyzed from the silicate esters) (7.1), close the funnel, and shake vigorously for several minutes, holding the stopper in tightly with the hand. Pressure in the funnel should be relieved occasionally by holding the funnel in an inverted position for a moment, and slowly opening the stopcock, letting the ether vapor under pressure escape. Check with litmus paper to be sure that the ether and aqueous phases are alkaline; if not, add more NaOH solution. Set the funnel aside in a vertical position until the two phases separate. Drain the aqueous phase into a second separatory funnel. Add 20 milliliters of diethyl ether to the second funnel, and extract the aqueous layer, discarding the water after the extraction. Add the wash ether to the first ether extractions. Wash the ether layer in the first funnel with 2 successive 20 milliliter portions of distilled water, discarding the water. Drain the ether into a 300 milliliter ground-stoppered Erlenmeyer flask. Wash the funnel with two successive 20 milliliter portions of ether, and add these to the Erlenmeyer flask. Add about 20 grams of anhydrous Na_2SO_4 to the ether, close the flask, shake, and allow to stand for about 1 hour, shaking occasionally. When dry, decant the ether in increments into a 250-milliliter (or smaller) 24/40 standard taper Erlenmeyer flask which is equipped with a cap having glass hooks for securing with springs. Place the flask on a steam bath and evaporate, using a stream of dry air to sweep ether vapors out of the flask (in

a fume hood). When most of the ether in the flask has been removed, rinse the Na_2SO_4 with two successive 10-milliliter portions of diethyl ether, add the ether to the Erlenmeyer flask, and again evaporate to dryness.

7.2.2 Determination of the Alcohol by Acetylation.* To the Erlenmeyer flask containing alcohols after evaporating ether (7.2.1), pipette exactly 3 milliliters of acetic anhydride-pyridine (1:3, v/v) acetylation mixture. Place the flask on a steam bath for 1 hour. Stopper with the springs attached, but relieve the pressure in the container from time to time throughout the digestion period. Remove the flask and wash the stopper and walls with 5 to 6 milliliters of distilled water. Stopper again and heat on the steam bath for 2 minutes. Cool the flask, wash the stopper and walls with 10 milliliters of n-butanol. Titrate the solution with 0.5N alcoholic KOH to a phenolphthalein end-point. Determine the free acid in the sample by repeating the procedure (7.2.1 and 7.2.2), using pyridine instead of acetic anhydride-pyridine (1:3, v/v) solution, and adding 5 milliliters of neutral ethanol just prior to titration to homogenize the solution. Shake well and titrate with 0.5N alcoholic KOH. Calculate the volume of alkali required to neutralize the acidity of 1 gram of the sample.

7.2.3 Blank. Run a blank sample in the manner described in Paragraph 7.2.2, omitting the ethanol.

7.2.4 Calculations. Calculate the amount of alcohol (as 2-ethylhexanol-1) recovered from the silicate ester as follows:

$$\text{2-Ethylhexanol-1 (percent)} = \frac{(B - (A-C) \times W) \times N \times 0.130 \times 100}{W}$$

where: B = volume of standard KOH used for the blank determination (7.2.3).

A = volume of standard KOH used for titrating the sample (7.2.2).

C = calculated volume of alkali required to neutralize the acidity of 1 gram of the sample (W) (7.2.2).

* See Off, C. L., Porter, W. L., and Willits, C. O., "Determining the Hydroxyl Content of Certain Organic Compounds. Macro- and Semimicromethods," Ind. Eng. Chem., Anal. Ed. 17, 394-7 (1945); and Steyermark, A., Quantitative Organic Microanalysis, New York: The Blakiston Company, 1951, pp. 302-3.

N = normality of the standard KOH solution.
0.130 = milliequivalent weight of 2-ethylhexanol-1.
W = weight of sample in grams.

Multiplication of the percent 2-ethylhexanol-1 by 1.045 will give the percent silicate ester in the sample.

7.3 DETERMINATION OF SILICA FROM SILICATE ESTERS.

7.3.1 Procedure. Place the residue in the 125 milliliter flat-bottom flask (7.1) on a steam bath to evaporate ether, using a stream of dry air to remove vapor from the flask. Evaporate water from the residue by placing the flask on a hot plate at low temperature. A small watch glass on the flask will prevent loss of any residue due to sputtering. Gradually increase the heat when sputtering ceases until a dry powder remains in the flask. Cool the flask in a desiccator and weigh to the nearest milligram. Subtract the weight of the flask from the weight of flask and residue to obtain the weight of residue. Transfer as much of the residue to a small weighed platinum crucible as possible, and reweigh the flask to obtain the weight of residue transferred to the crucible. Record the aliquot part of the total weight of the residue which was taken for the determination of silica. Place the crucible in a warm muffle furnace and increase the heat to 800°C., holding this temperature for 2 hours. Remove the crucible from the furnace, cool in a desiccator, and weigh. Re-place in the hot muffle furnace for another hour, cool in a desiccator, and re-weigh. Repeat this procedure until constant weight is achieved. The ash is SiO_2.

7.3.2 Calculation. Calculate the weight of silicate ester (as tetra(2-ethylhexoxy)silicate) from the weight of silica as follows:

$$\text{Tetra(2-ethylhexoxy)silicate (percent)} = \frac{C \times F \times 9.09 \times 100}{W}$$

where: C = weight of silica obtained on ashing.
F = aliquot part of the residue used in ashing.
9.09 = conversion factor from silica to silicate ester.
W = weight of sample taken for hydrolysis.

IDENTIFICATION OF SILICONE OILS IN SYNTHETIC LUBRICANTS AND GREASES

1.0 SCOPE

1.1 This method describes procedures for detection and differentiation between three types of silicone oils (alkyl, aryl, and chlorinated) in base-oils from synthetic lubricants after separation of the oils from additives and from other base-oils. For the analysis of these compounds in lubricants, this method must be preceded by Method 16, in which most additives are removed by adsorption chromatography, and by Method 52, in which other base-oils are removed by partition chromatography. For the analysis of these compounds in greases, this method must be preceded by Methods 41 through 45, and by Methods 16 and 52, in which gelling agents and thickeners first are separated from base-oils and additives and dibasic acid esters are then separated from silicate esters, disiloxanes, and silicone oils by adsorption and partition chromatography.

1.2 This method applies to the silicone oils DC-200 series (alkyl), DC-550 (aryl), and to a chlorinated silicone (designated by WADC as MLO-53-446).

2.0 OUTLINE OF METHOD.

2.1 The silicone oil-containing fraction (which also contains silicate esters and disiloxanes), separated and isolated in Method 52 from dibasic acid esters, is tested by a series of chemical reactions to establish the presence or absence of the three types of silicon-containing base-oils. Reaction with anhydrous aluminum chloride, followed by addition of a substituted benzophenone and dilution with water, gives a characteristic color for each type of silicone oil. The procedures are identical with those carried out in Method 56.

3.0 SAMPLE.

3.1 The sample used in this method is obtained after treatment of the synthetic lubricant or grease to isolate the entire group of silicate esters, disiloxanes, and silicone oils (see Paragraphs 1.1 and 1.2).

4.0 REAGENTS.

4.1 Reagents employed in this method are identical with those described in Paragraphs 5.1 through 5.13, Method 56.

5.0 PROCEDURE.

5.1 QUALITATIVE IDENTIFICATION OF SILICONE OILS. The procedures described in Paragraphs 6.1 through 6.4, Method 56, shall be employed for the qualitative identification of silicone oils.

5.2 QUANTITATIVE DETERMINATION OF SILICONE OILS. Quantitative determination of silicone oils has not been accomplished by simple chemical means, either wet chemical or chromatographic. If maximum accuracy is necessary, high-temperature combustion in oxygen is recommended. However, in lieu of the complicated equipment necessary for this type of analysis, reasonably accurate results can be achieved by using the weight of oil eluted after partition separation of silicon-containing oils from dibasic acid esters (Method 52), followed by the qualitative identification of any silicone oil eluted (Method 56). If a single silicone oil is identified along with negative tests for other silicon-containing oils, then the weight obtained by Method 52 is the weight of the silicone oil, and further quantitative measurement is unnecessary. If mixtures of silicon-containing base-oils are found, the above method of analysis is not applicable, and quantitative determination of silicone oils must be based on differences in weight (after determining other silicon-containing compounds) or must be found by more complicated combustion methods.