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DEVELOPMENT OF SCHEMATIC ANALYTICAL PROCEDURES FOR SYNTHETIC LUBRICANTS AND THEIR ADDITIVES

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FOREWORD

This report was prepared by the Organic-Analytical Section, Chemical Division, of the Denver Research Institute, University of Denver, Denver, Colorado, under USAF Contract No. AF 33(616)-2204. The contract was initiated under Project No. 7331, "Hydraulic Fluids", Task No. 73313, "Hydraulic Fluids", formerly RDO No. 613-15, "Hydraulic Fluids and Lubricants", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Mr. V. A. Lauer acting as project engineer.

ABSTRACT

General properties and methods for the identification, determination, and separation of components of synthetic greases and synthetic lubricants are presented and discussed.

Included in these components are inorganic and organic gelling agents, soap and urea type thickeners, and such additives as antioxidants. A schematic analytical procedure for the separation of grease components is presented along with the application of paper chromatographic methods for the identification and separation of antioxidants in greases and synthetic lubricants.

Initial investigations for the separation and identification of dibasic acid esters in synthetic lubricants are presented.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

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INTRODUCTION

Rapid developments in the field of aircraft engineering, particularly in the military field, as well as in the fast-extending transportation industry as a whole, have caused a considerable increase in the severity of operational conditions of our machines and instruments; this is particularly the case with the high altitude and high speed turbo-prop operations of the Air Force with their extreme temperature and climatic changes.

These developments have consequently induced a considerable change in the operational characteristics and performance requirements of lubricants used in aircraft engines performing under extreme conditions. In most cases the fundamental requirements have been to obtain low volatility at elevated temperatures, low viscosity at low temperatures, and good viscosity-temperature properties. The demand for lubricants to serve at temperatures from below -65°F. to temperatures as high as 400°F. was most satisfactorily met by lubricants with synthetic base-oils.

In view of these experiences the military forces regard the synthetic lubricant field with a great deal of promise, and the Air Force as well as the Bureau of Aeronautics has been very active in promoting and sponsoring research and development work in this field since the start of the last world war. The increasing number and type of synthetic lubricants, greases, and hydraulic fluids manufactured in this country as well as abroad have revealed more and more the necessity for development of methods for their identification and determination, in other words, for their analysis.

Chemical analysis of synthetic lubricants and their additives was neglected in the beginning of this development because emphasis was placed primarily on determination of the rheological and lubricating performance of the synthetic compounds rather than on the qualitative and quantitative separation of their components. This lack of analytical methods is felt particularly in those cases when a quick and relatively simple identification is desired for the purpose of production control, field control, classification of samples of unknown origin, or in the case of field accidents.

Field laboratories and also control laboratories are often remote from their central laboratories, and circumstances may require a quick answer, thus not allowing time for shipment of samples to well-equipped analytical laboratories. Therefore, in such cases methods of analysis are desirable which will permit the identification and determination of synthetic lubricants, greases, and their additives with relatively simple methods and techniques and with the greatest possible accuracy.

The incentive of the investigations presented in this report was to develop a schematic analytical procedure for synthetic lubricants and greases which would meet the requirements suggested above: namely, (1) to avoid the use of elaborate and expensive optical equipment, (2) be applicable to the majority of synthetic lubricants and greases, and (3) have an acceptable accuracy and reproducibility.

Considering the complexity of the organic compounds used in the preparation of modern lubricants, e.g., monobasic and dibasic acid esters, silicone polymers, phosphate esters, polyester, fluorinated compounds, as well as the numerous* other additives, different types of gelling agents, viscosity improvers, etc., it may seem very questionable whether there would be any hope of finding simple methods for the determination and identification of such compounds. It would appear even more difficult to establish a schematic analytical procedure similar to the analytical schemes used in inorganic analysis or in the standard routine analysis of petroleum-based lubricants and greases. Since by contractual specifications the analytical scheme must also avoid colorimetric methods which would require photocolorimeters (such as the Fisher photo-colorimeter or the Beckman spectrophotometer) and restrict itself to the use of Nessler tubes or a Duboscq colorimeter, the task becomes even more difficult.

Most of the analytical work on synthetic lubricants or their additives done to date employed elaborate optical methods such as infrared spectrophotometry, X-ray diffraction, and even mass spectroscopy. Since these data were of no specific value for the present contract, it was necessary to develop in most cases new and

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* A brief account revealed that no less than 3300 antioxidants, corrosion preventive agents, etc., have been investigated for their feasibility in the past few years.

simpler methods, applying techniques used successfully in other fields of chemistry, as for example partition paper chromatography or counter current distribution, etc. In view of these facts and the complexity of the materials involved, the question whether an over-all schematic analytical procedure can be developed which would be applicable for all combinations of synthetic lubricants, must be viewed with considerable doubt. This, however, does not preclude the derivation of procedures and methods of more restricted scope.

Any schematic procedure would, therefore, necessarily be more a tentative and rather general guide for the less experienced analyst than a rigid scheme or working manual. An analogous situation is encountered in a related field, the analysis of plastic materials, where many authors on the subject considered a rigid analytical scheme as rather confusing and misleading. Such schematic procedures should first give indications as to the general nature of the components involved. From these indications the analyst must then decide for himself which further method of approach he will have to choose in order to solve his problems most effectively. This will depend very much upon the experience and analytical skill of the investigator. Therefore, the schematic procedures developed in the course of our investigations should not be considered as rigid rules but rather as general guides of approach which in certain cases will have to be modified or adapted to the specific problems.

However, this does not imply that the less experienced analyst should not use these schematic approaches closely until he has acquired sufficient experience to adapt the methods adequately to the specific problems with which he must deal. It was for this reason, to make the analyst who is not necessarily specialized in the field of lubricants more acquainted with the materials involved, that we have discussed the different components and their properties more in detail than would be necessary for a specialist in this field. Following the general discussion of a compound in the body of this report the possible methods of analysis are presented, followed by an experimental section for each related group of compounds.

The complexity of the subject made it necessary to break down the general attack into two major parts:

Part I. Analysis of synthetic lubricant greases, particularly the gelling agents and other additives, including their separation from the base-oils.

Part II. Analysis of synthetic lubricants proper and base-oils from greases, and their additives.

A projected Part III was intended to cover the analysis of synthetic hydraulic fluids and degradation products from synthetic lubricants. This part, however, will be the incentive of a possible later program.

It was intended to adapt whenever possible the methods developed for analysis of specific compounds as well as the separation techniques to the standard ASTM methods used in routine petrochemical analysis; however, in the course of the investigations it was necessary to introduce new techniques (as for example partition paper chromatography) which hitherto have not been standardized. Although in all cases these methods do not have the accuracy of optical methods or other standard methods because of sources of error inherent in their basic principles, they are relatively simple, have good reproducibility, in many cases have excellent qualitative selectivity, and their quantitative accuracy is fully adequate for the purpose intended. As in many such circumstances the simplification must sacrifice a certain amount of accuracy.

Because of the numerous compounds involved, it was obvious that development of an analytical procedure for the determination and identification of grease and lubricant components could be achieved only gradually. Thus the investigation could not be concluded in the course of a single year's program. Development of the analytical procedure for greases could be accomplished in one year to an extent where a fairly detailed schematic procedure for gelling agents, thickeners, and their separation from base-oils in different combinations could be presented.

Among the additives, emphasis has been placed on the development of identification and separation methods for antioxidants in greases and lubricants. It is believed that this goal has been resolved at least in principle, and the feasibility of the techniques demonstrated. This framework must, of course, be expanded further to include more of the numerous types of antioxidants and also corrosion inhibitors.

From the different types of synthetic lubricants, analysis of dibasic acid esters and their separation from other components and from mixtures of esters themselves has been attacked first, and the separation and analysis resolved to a large extent. Other analytical problems, e.g. the analysis of polymers and phosphorus compounds, could not be attacked in detail; and, therefore, these procedures are rather tentative and based upon the limited experiences gained to date.

A further extended program would have to complete the current investigations, establish further their feasibility, fill in gaps, and refine the results achieved so far. It is obvious that with rapid developments in the field of synthetic lubricants, new combinations and new specific compounds will require the development of new experimental methods and eventually require the modification of some of the schematic procedures. We are aware of these limitations on the methods developed and are open to constructive suggestions or advice from interested parties in this respect.

We acknowledge the Lubricants Section of the Materials Laboratory of the Wright Air Development Center for their helpful cooperation in furnishing test samples of greases and lubricants of different specification and in keeping us informed upon recent developments in the synthetic lubricant field. Acknowledgment is also given to the companies and research institutions who have furnished samples of antioxidants, corrosion inhibitors, and other additives necessary for our investigations.

PART I

ANALYSIS OF GREASES WITH MINERAL AND SYNTHETIC BASE-OILS

1.0 INTRODUCTION

Development in the field of synthetic lubricants with specifications for extreme temperature or pressure conditions has also induced a high degree of development in grease research and technology.

The conventional definition of a grease as the colloidal product obtained when mineral oils are thickened by addition of the metallic salt of a fatty acid (soap) no longer conforms to the complexity of modern greases. In these greases the mineral oils are replaced partially or completely by synthetic lubricants, e.g. dibasic acid esters, polyglycols, polysiloxanes, etc., and the conventional alkali soaps are replaced either by improved alkali metal soaps such as Li-stearates or hydroxystearates, by alkaline-earth soaps like aluminum-stearate, or partially by inorganic or organic gelling agents like bentones, phthalocyanines, silica gel, etc.

If such gelling agents are used for the preparation of greases, the mineral or synthetic base-oil is gelled by minute size inorganic or organic particles of platelet-like shape which bind the organic base-oil in oriented layers. Such greases are real gels by their physical nature and do not depend upon the maintenance of a matrix to hold the oil. Thus the conventional definition of a grease no longer conforms to such compositions, and the chemical and physical behavior of these new type greases is essentially different from the older type. Consequently, the methods of analysis used for the older type soap greases must be modified, since not only the gelling materials are of different chemical nature but also because of the nature of certain types of base-oils and additives present. Thus the method of analytical approach will depend upon the type of gelling agent or thickener present. The type of gelling agents present in a grease is at the same time a feasible base for a practical classification of greases for the analyst.

1.1 CLASSIFICATION OF GREASE TYPES FROM THE ANALYTICAL VIEWPOINT

The most feasible classification of greases for the analyst will be based on the type of gelling agent or thickener used in the preparation of the grease, because this determines the method of separation he will have to choose. This type of classification is based on the colloidal characteristics of the mixture rather than on performance characteristics and is, therefore, not necessarily related to the specification-types of the Air Force.

According to these colloidal characteristics the modern type greases can be divided into the following groups:

1.1.1 Greases With Mineral and/or Synthetic Base-Oils, Plus Inorganic Gelling Agents

The gelling agents in this type of grease consist of platelet-shaped inorganic particles (e.g., montmorillonite from clay) which have been made lipophilic and water repellant by coating the surface of the platelets with long-chained hydrocarbon compounds. In this way the platelets acquire a brush-like structure (see Figure 1). Under the influence of polar agents like alcohols, acetone, etc., the side chains can be dissolved by organic hydrocarbons or other synthetic base-oils.

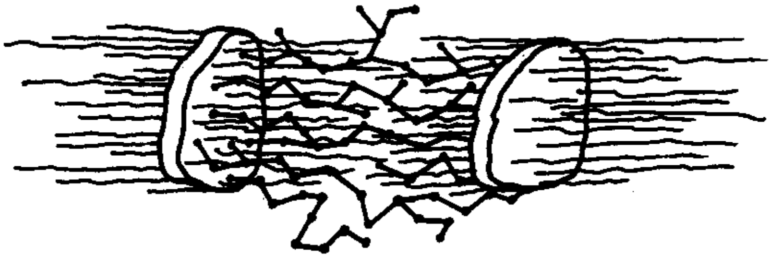


Figure 1. Brush-Type Inorganic Gelling Agent Platelets (Schematic) With Adsorbed Base-Oil Molecules.

The organic solvents are adsorbed to the surface of the platelets, thus forming a stable colloidal structure, quite different from the micell structure in metallic soaps. Since in this type of gelling agents, of which bentones are typical examples, the major part (about 65%) is of inorganic nature, they can be considered as inorganic gelling agents.

1.1.2 Greases With Mineral and/or Synthetic Base-Oils Plus Organic Gelling Agents

The gelling agents in these greases consist mostly of pigment-type compounds with relatively flat-shaped molecules, of which phthalocyanines are typical examples.

As in the case of the bentones, there is much evidence that the phthalocyanine molecule does not act merely as a flat-shaped pigment, similar to graphite for example, but that the chelating properties of such strongly resonating molecules probably contribute to the gelling activity. This is particularly the case if amino salts are used as polar wetting agents. In such cases the phthalocyanine molecule platelets may act similarly to the bentone platelets and can, therefore, be considered as similar gelling agents. Because the major part of these gelling agents is of organic nature (80-90%), they can be considered as organic gelling agents.

1.1.3 Greases With Mineral Oil and/or Synthetic Base-Oils Plus Soap-Type Thickeners

This group consists basically of the older type metal soap greases where the gelling agent (thickener) is a soap, e.g. Na-stearate, K-stearate, etc. The physical and chemical properties of these greases can be improved by using other alkali metal soaps, e.g. Li-stearate or alkaline earth soaps as for example Al-stearate or Ca-stearate.

In the case of metal soaps as gelling agents, the colloidal structure of the grease is different than in the case of the brush structure from platelet type gelling agents. The metal soap under the solvation power of the admixed base-oil forms micelles by solvation and orientation of the soap molecules into a three-dimensional network (see Figure 2). The excess solvent is trapped in the voids of the gel network thus forming the heterogeneous system of the grease. Such gelling agents which form a three-dimensional micellar structure are usually called thickeners in distinction to the platelet-shaped gelling agents.

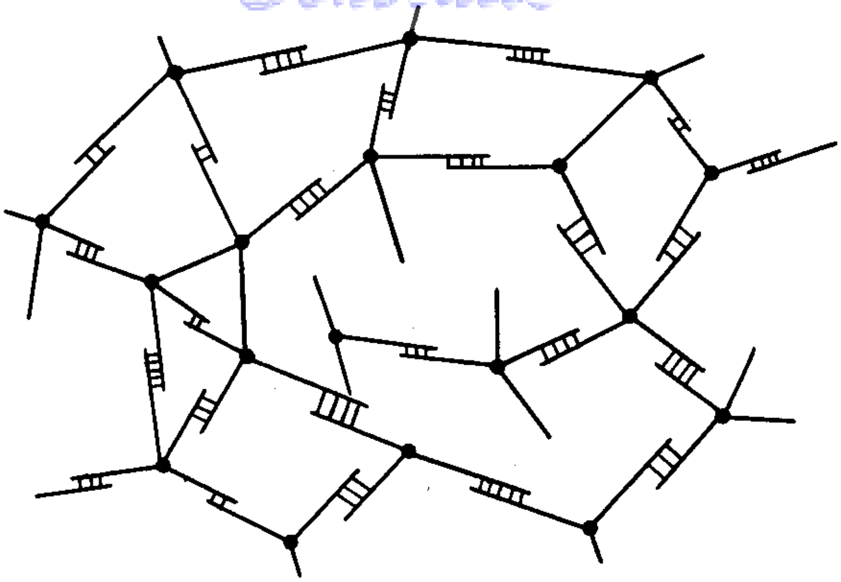


Figure 2. Micellar Structure of Metal-Soap Molecules (Schematic).

1.1.4 Greases With Mineral and/or Synthetic Base-Oils Plus Urea - Type Thickeners

The thickening agents in these greases are N-substituted urea compounds. These compounds, which provide a strong final stability in greases, form colloidal structures which are not yet completely understood, but which probably are very much related to the structure of the soap type colloids.

It is very likely that the urea derivatives form organic complexes of a three-dimensional character which function as a matrix similar to the metal soap micelles. Urea compounds may, therefore, be classified as organic thickeners.

1.2 OTHER COMPONENTS IN GREASES

Other components in greases may be additional fillers, as for example graphite, powdered lead, etc., although it is very unlikely that such fillers would be encountered in greases with present Air Force specifications.

Further components may include additives such as antioxidants and/or rust inhibitors. There are also greases, of course, in which a combination of gelling agents and thickeners of various types are used.

Figure 3 schematicizes the different groups of possible combinations and components of modern greases:

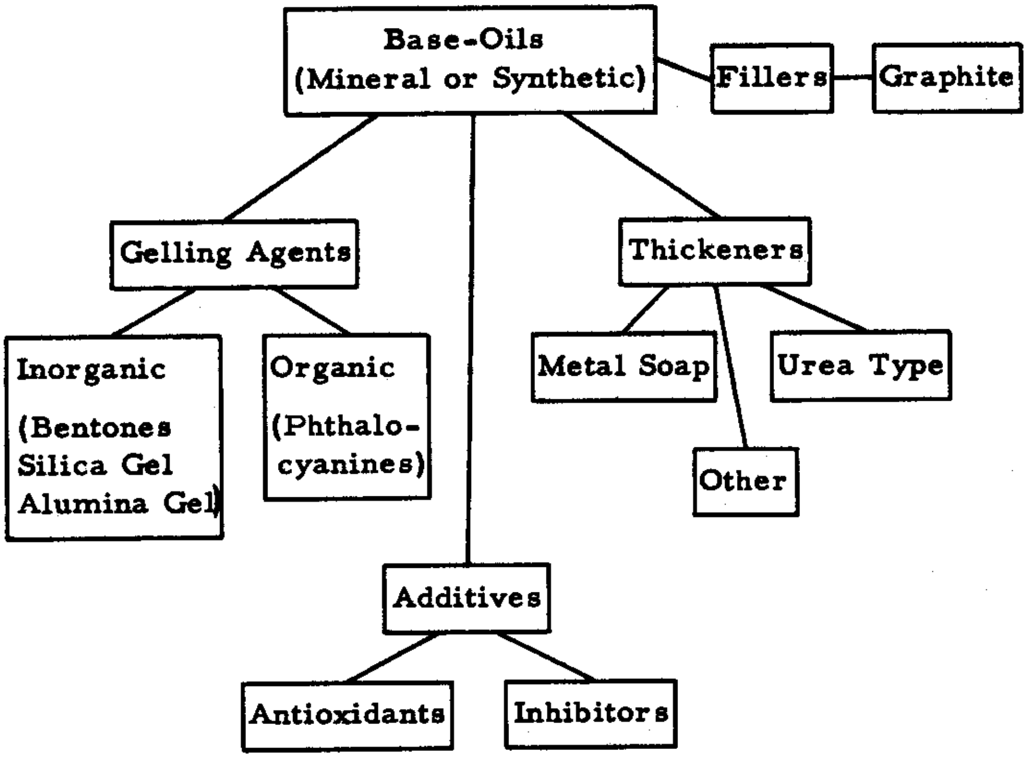


Figure 3. Components of Modern Greases.

2.0 SCHEMATIC CLASSIFICATION OF MODERN GREASES

In order to facilitate the denomination of a grease type referred to in this report, a general schematic classification system which will include greases of any composition has been established in this Institute. This classification is based on the colloidal characteristics discussed in Paragraph 1.1 above. This scheme consists of a series of numbers and letters designed to indicate the exact qualitative composition of the grease. It is a flexible system, in that it may be expanded or contracted at will, according to the needs of the operator to meet the ever-changing variety of commercially available greases. The scheme may be presented simply as follows:

1. The first digit is a Roman numeral indicating the base-oil in the grease:

I - Mineral oil.
II - Dibasic acid ester.
III - Silicate ester.
IV - Polysiloxane.
V - Glycol or polyalkalene glycol.
VI - Polyester.
VII - Polyisobutylene.
VIII- Other base-oil type, e.g., polyether.

2. The second digit is a capital letter, indicating the type of thickener or soap in the grease:

0 - None.
A - Na or K Soap.
B - Li-stearate.
B' - Li-hydroxystearate.
C - Ca, Ba, or Sr Soap.
D - Al-stearate.
E - Urea type thickener.
F - Metal sulfide (Cu, Ni, Fe)
G - Other.

3. The third digit is a small number, indicating the gelling agent in the grease:

0 - None.
1 - Silica gel.
2 - Alumina gel.
3 - Bentone.
4 - Bentone and silica gel.
5 - Bentone and alumina gel.
6 - Bentone, silica gel, and alumina gel.
7 - Phthalocyanine.
8 - Phthalocyanine and other gelling agent.
9 - Other.

4. The fourth digit is a small letter, designating the type of antioxidant in the grease:

0 - None.
a - Phenothiazine.
b - N-Phenyl-1-naphthylamine.
c - 2,6-ditertiarybutyl-4-methylphenol.
d - 2,4-dimethyl-6-tertiarybutylphenol.
e - Organic selenides.
f - Other.

5. The fifth digit is again a small number, designating the type of corrosion-preventive in the grease:

0 - None.
1 - Synthetic sulfonate.
2 - Petroleum sulfonate.
3 - Sorbitan-mono-oleate.
4 - Other.

In the event that such fillers as graphite, carbon black, magnesium carbonate, talcum, or mica are encountered in a grease, a further classification digit may be added to the scheme as needed. As an example of how the classification system would be employed, a grease with a classification of IID3a0 would contain a dibasic acid ester, Al-stearate, bentone, phenothiazine as antioxidant, and no corrosion preventive compounds. An IVE0b0 grease would be a polysiloxane with urea thickener, no gelling agent, N-phenyl-1-naphthylamine, and no corrosion-preventive compound.

Table I illustrates the use of this method of abbreviations for classifying greases. In order to classify an unknown grease for analysis, qualitative tests must necessarily be performed to determine the type of grease.

3.0 GENERAL APPROACH FOR THE ANALYSIS OF SYNTHETIC GREASES

The fact that most of the inorganic and organic gelling agents as well as some thickeners are insoluble in organic solvents and are very difficult to hydrolyze restricts, of course, the methods used in routine petrochemical grease analysis to such cases where the thickeners are of the Na-K-soap type and the base-oil is of the mineral oil type.

TABLE I

Examples of the Classification of Synthetic Greases With Different Base-Oils and Additives

Type	Base-Oil	Thickener or Soap	Gelling Agents	Antioxidants	Corrosion Preventives
I0000	I-Mineral Oil	0-None	0-None	0-None	0-None
IA1a1	I-Mineral Oil	A-Na- or K-stearate	1-Silica Gel	a-Phenothiazine(PT)	1-Synthetic sulfonate
IIB2b2	II-Dibasic acid ester	B-Li-stearate	2-Alumina gel	b-N-Phenyl-1-naphthyl-amine (NPNA)	2-Petroleum sulfonate
IIB'3c3	II-Dibasic acid ester	B'-Li-hydroxy-stearate	3-Bentone	c-2, 6-ditertiarybutyl-4-methylphenol(2, 6Ph)	3-Sorbitan-mono-oleate
IIIC4d4	III-Silicate ester	C-Ca-, Ba-, or Sr-stearate	4-Bentone and silica gel	d-2, 4-dimethyl-6-terti-arybutylphenol(2, 4Ph)	4-Other agent
IIID5e1	III-Silicate ester	D-Al-stearate	5-Bentone and alumina gel	e-Organic selenide	1-Synthetic sulfonate
IVE6f2	IV-Polysiloxane	E-Urea compound	6-Bentone, silica gel, alumina gel	f-Other antioxidant	2-Petroleum sulfonate
IVF703	IV-Polysiloxane	F-Metal sulfide (Cu, Ni, Mo)	7-Phthalocyanine	0-None	3-Sorbitan-mono-oleate
VG8a0	V-Polyalkylene glycol	G-Other thickener	8-Phthalocyanine and gelling agent	a-PT	0-None
V09b1	V-Polyalkylene glycol	0-None	9-Other gelling agent	b-NPNA	1-Synthetic sulfonate
VIA0c2	VI-Polyester	A-Na- or K-stearate	0-None	c-2, 6Ph	2-Petroleum sulfonate
VIB1d3	VI-Polyester	B-Li-stearate	1-Silica gel	d-2, 4Ph	3-Sorbitan-mono-oleate
VIIC2e4	VII-Polyiso-butylene	C-Ca-, Ba-, or Sr-stearate	2-Alumina gel	e-Organic selenide	4-Other agent
VIIID3f0	VIII-Other base-oil	D-Al-stearate	3-Bentone	f-Other antioxidant	0-None

For greases which are based on the gelling agents and thickeners mentioned above, a new method of approach had to be developed. The sequence of analysis therefore will be the following:

1. Separation of base-oils from the gelling agents, thickeners, and fillers respectively.
2. Separation of different type of gelling agents, thickeners, and fillers.
3. Identification of the individual gelling agents, thickeners, etc.
4. Identification and determination of other additives in the base-oil, as e.g. antioxidants and inhibitors.
5. Separation and identification of different componenets in the base-oil and their determination.

Step No. 5 will be discussed in detail in Part II of this report, since it amounts essentially to the separation of lubricants per se.

In the following sections methods for identification and determination of specific components will be discussed first, followed by discussion of separation methods from the base-oils and other additives. Consequently, Part I of this report is subdivided into the following Sections:

Section A: Gelling Agents.
Section B: Thickeners.
Section C: Separation Methods.
Section D: Antioxidants and Inhibitors.

SECTION A

GELLING AGENTS

In accordance with the definitions given under Paragraph 3.0 of the preceding chapter, gelling agents encountered in different greases may be subdivided into two groups, depending upon whether they are essentially of inorganic or organic nature:

I. Inorganic gelling agents. These are of predominantly inorganic nature.
II. Organic gelling agents of predominantly organic nature.

1.0 INORGANIC GELLING AGENTS

Inorganic gelling agents are platelet-shaped particles of essentially mineral nature used for the preparation of greases. In certain commercial agents the particles are combined with organic compounds in order to achieve a high degree of water repellency and affinity to the base-oils. The most feasible materials for inorganic gelling agents are:

1. Bentones.
2. Nitrated clays.
3. Clay minerals of the swelling type.

Among these, however, only the bentones have practical interest, especially in greases with excellent operational requirements.

1.1 BENTONES

In the majority of greases gelled with inorganic gelling agents, the gelling agents are bentones.

1.1.1 Constitution of Bentones

Bentone is a trade name applied to a class of products resulting from cation exchange reactions between organic bases and bentonite or its clay mineral component montmorillonite. The mechanism of the formation of these products is simply that sodium bentonite undergoes an equilibrium reaction with an organic quaternary ammonium salt (onium salt), to form an organic onium bentonite plus a salt. The complex formed is called bentone. The striking effect of the equilibrium reaction is to change the hydrophilic character of the inorganic bentonite to a lipophilic behavior, which enables the bentones to swell in organic liquids and to reject water.

The chemical and physical changes involved can be summarized as follows: clays of the swelling bentonite type (and only such clays can be used for preparation of bentones) consist essentially of montmorillonite minerals, which are responsible for the plastic and gelling properties of the clay. These minerals, particularly montmorillonite itself, are hydrous substituted aluminum silicates with a micaceous structure and exceptionally small ultimate size. The structure of montmorillonite is presented schematically in Figure 4.

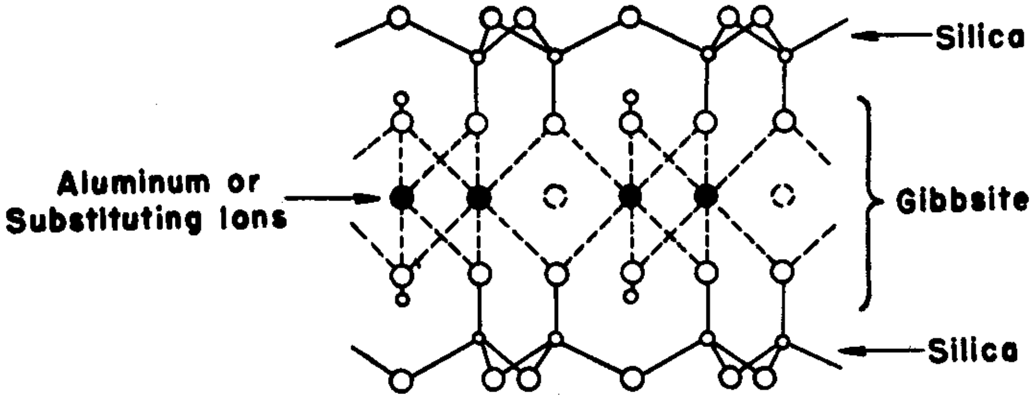


Figure 4. Structure of Montmorillonite.

Montmorillonite is noted for its ability to swell in water. Varying proportions of Ca, Mg, or Na are found in the cation exchange positions of montmorillonite, depending upon the source of the material.

In properly selected montmorillonite a high portion of the surface cations are Na-ions. It has been shown that about 80% of the total exchange positions are on the basal plane surface with the remainder on the edges of the platelets. The swelling properties of the bentonite are due to the presence of these cations which in turn can be exchanged with other positively charged cations.

1.1.2 Formation of Bentones

On the basis of a great deal of structural analysis the general formula for montmorillonite as assigned by Ross and Hendricks (176) is the following:

$$Al_4Si_8(OH)\cdot xH_20 \qquad (1)$$

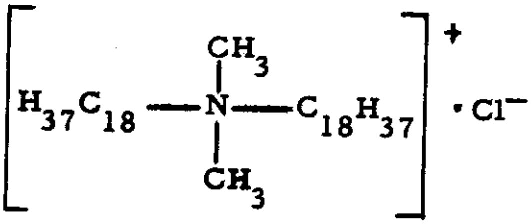
In this formulation the ratio of Al:Si is 1:2. In swelling montmorillonite a part of the Al is substituted by Mg corresponding to the formula

$$(Al_{1.67}Mg_{0.33})Si_40_{10}(OH)_2 \qquad (2)$$

The Mg in this mineral can in turn be exchanged with another cation such as Na, resulting in a mineral with the formula:

$$(Al_{1.67}Na_{0.33})Si_40_{10}(OH)_2 \qquad (3)$$

In this type of montmorillonite the cation Na can be exchanged by an organic compound, as for example the cationic part of a quarternary ammonium salt. Typical long chain aliphatic ammonium salts used have a chain length of C_{12}, C_{18}, C_{34}, C_{36} carbon atoms (according to the number of carbon atoms, commercial bentones in this country are denominated as Bentone-18, Bentone-34, etc.). A typical C_{38}-salt is dimethyldioctadecyl ammonium chloride:



$$\left[H_{37}C_{18}-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N}}-C_{18}H_{37}\right]^+\cdot Cl^- \qquad (4)$$

or in abbreviated form: $Q^+\cdot Cl^-$ (5)

where Q^+ represents the cation of the quaternary salt.

Exchange of the Na ion of montmorillonite with the organic cation of the Q-salt occurs with salt formation according to the reaction equation (Mt = montmorillonite):

$$Mt\cdot Na + Q\cdot Cl \longrightarrow Mt\text{-}Q + NaCl \qquad (6)$$

Because of the low solubility of the onium salt the reaction is shifted to the right side of the equation. The onium salt complex Mt•Q is called bentone (170, 174).

1.1.3 Composition of Theoretical Bentone

From the discussion of the formation of bentone (Par. 1.1.2, p.12) it is obvious that only those bentonites can form bentones which consist in their major part of montmorillonites with exchangeable Na cations:

$$(Al_{1.67}Na_{0.33})Si_4O_{10}(OH)_2$$

In bentone 95-100% of these Na atoms are exchanged with the Q-cation and hence the ideal formula for such a bentone would be

$$(Al_{1.67}Q_{0.33})Si_4O_{10}(OH)_2 \qquad (7)$$

However, in montmorillonites from swelling bentonites a part of the Al atoms are replaced by Fe atoms. The amount of Fe varies, depending on the source of the montmorillonite, within narrow limits. According to Ross and Henricks (176) the theoretical formula for such a montmorillonite with an average Fe content of about 4-5% would be:

$$(Al_{1.47}Fe_{0.20}Na_{0.33})Si_4O_{10}(OH)_2 \qquad (8)$$

and hence the formula for an ideal bentone would be the following:

$$(Al_{1.47}Fe_{0.20}Q_{0.33})Si_4O_{10}(OH)_2 \qquad (9)$$

According to this formula the chemical analysis of such a theoretical bentone will show a variation in the amount of organic matter (and consequently in the ash content) depending on the nature of the Q-cation involved; however, the relative amounts of inorganic ions in the ash, e.g. Al(as Al_2O_3), Fe (as Fe_2O_3), and Si (as SiO_2) will be constant even if the relation of Fe:Al varies in different samples of montmorillonite. The most feasible quaternary ammonium salts for bentone formation have proven to be the following:

Bentone-12 (with C_{12})....dimethyldipentylammonium ion

Bentone-18 (with C_{18})....dimethyldioctylammonium ion

Bentone-26 (with C_{26})....dimethyldidodecylammonium ion

Bentone-30 (with C_{30})... dimethyldodecylhexadecylammonium ion

Bentone-34 (with C_{34})....dimethyldihexadecylammonium ion

Bentone-36 (with C_{36})....dimethylhexadecyloctadecylammonium ion

Bentone-38(with C_{38}).....dimethyldioctadecylammonium ion

The chemical analysis of such a theoretical bentone with an average value for the organic matter, e.g. Bentone-34, would give therefore the following values, based on formula (9):

Organic matter	31.26%
Ash	63.75%
Al_2O_3 (in ash)	22.64%
Fe_2O_3 (in ash)	4.82%
Me_2O_3 (in ash) *	27.46%
SiO_2 (in ash)	72.55%
Nitrogen (in bentone)	0.89%

The theoretical composition for the various bentones used as gelling agents, from Bentone-12 to Bentone-38, is given in Table III. From these data it can be seen that the values for the Me_2O_3 oxides and SiO_2 in the ash are constant in all bentones. This fact can be used as a means for their analysis, as will be shown below.

1.2 METHODS OF APPROACH FOR THE ANALYSIS OF BENTONES

1.2.1 Introduction

The analysis of bentone as a raw material or after separation from the base-oils in greases could be achieved generally by:

(a) Separation and determination of the organic part of bentone (Q-cation) and identification of the Q-cation by N determination.

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* Sum of Al_2O_3 and Fe_2O_3.

(b) Determination of the inorganic part of bentone (montmorillonite) by silicate analysis; identification of the organic part by N determination, or from the ratio of ash content:volatile matter.

(c) Total analysis: determination of inorganic compounds as well as organic analysis for N, C, H content.

For the practical estimation of the amount of bentone-type gelling agent present in a grease, it is not necessary to carry out a total analysis, which is time-consuming. This leaves the choice between (a) and (b). Separation of the Q-cation from the inorganic part by hydrolysis on the other hand encounters difficulties. Even extensive extraction of bentones with acids or alkalies of different concentrations separates the organic part (the Q-cation) only partially (about 91%) (see Par. 1.3.2.4, p.27), and in many cases with alteration of the compound. Thus, such a method is not sufficiently accurate, and in addition is quite time-consuming.

By far the most efficient method for determination of bentones would, therefore, be determination of the inorganic part in the bentones (Si, Al, Fe,) and use of the relation between the volatiles and the ash compounds for the estimation of bentone-types. The inorganic elements are present quantitatively in the ash, and their determination is a well-known routine analysis.

1.2.2 Principle of the Bentone Determination

The principle of the quantitative determination of bentone is based on the fact that in a specific bentone derived from montmorillonite clays, the inorganic elements from the ash analysis and the organic components in the bentone have a specific ratio. This ratio is constant in narrow limits. It will, therefore, suffice to determine one or two elements quantitatively in the ash and the ratio of the ash compounds to total volatiles, to be able to estimate the amount and type of bentone in the grease. According to the general formula (1) for montmorillonite

$$Al_4Si_8(OH)\cdot xH_20$$

the relation Al:Si in this mineral is 1:2, and the relation of the oxides $Al_2O_3:SiO_2$ is 1:1.2. This oxide relation is very characteristic for the montmorillonite type minerals and can, therefore, be used for their characterization. Other clay minerals have different Al:Si or $Al_2O_3:SiO_2$ ratios as shown in Table II.

TABLE II

Al:Si and $Al_2O_3:SiO_2$ Ratios in Different Clay Minerals

Mineral	Al:Si	$Al_2O_3:SiO_2$
Montmorillonite	1:2	1:2.27
Muscovite	1:1.5	1:1.70
Kaolinite	1:4	1:4.53
Dickite	1:4	1:4.53
Halloysite	1:4	1:4.53
Narcite	1:4	1:4.53

Since only swelling clays of the montmorillonite type form bentones, the oxide relation of the montmorillonite will also be characteristic for the bentones.

In the case of bentones of the general formula:

$$(Al_{1.47}Fe_{0.20}Q_{0.33})Si_4O_{10}(OH)_2$$

in which part of the Al atoms are replaced by Fe and Q-cations, the ratios Al:Si and $Al_2O_3:SiO_2$ will, of course, exceed 1:2. In this type of compound there will be, however, a constant relation between $Al_2O_3:Fe_2O_3$ and also a relation between the sum of $Al_2O_3 + Fe_2O_3$ to SiO_2, which will be summarized as $Me_2O_3:SiO_2$. Thus the determination of Al_2O_3 or SiO_2 in the ash is sufficient to calculate that part of the ash which belongs to bentone.

The ratio Ash(in bentone):Total Volatiles(in bentone) will, of course, vary, depending on the Q-cation combined with the montmorillonite, and, therefore, is a characteristic for identification of the specific bentone. As a control determination, the N content in bentone is a linear function of the Q-cation used and its ratio to Al_2O_3 and SiO_2 in bentone is constant (Table III).

For the determination of bentone <u>per se</u> as raw material or in greases, the following ratios can be used for calculation:

(a) $Me_2O_3:SiO_2$; this ratio is for the ideal bentone 1:2.64.

(b) Ash_{Bt}*/Total $Volatiles_{Bt}$; this ratio varies with the type of bentone.

(c) $N_{Bt}:SiO_{2Bt}$; this ratio is 1:52.

These values are calculated for the ideal bentones of the formula (9) and are presented in Table III and graphically in Figures 5 and 6. A combination of two of these ratios (usually (a) and (b)) is sufficient to determine bentones in greases even when they are admixed with other inorganic gelling agents such as silica gel or alumina gel or in certain cases a mixture of all three.

For determination of these ratios the following analyses must be performed on a grease:

(1) Determination of hexane insolubles.

(2) Ash of the hexane insolubles.

(3) Ash analysis for Al_2O_3, SiO_2, and Fe_2O_3.

(4) Nitrogen in hexane insolubles or organic matter in hexane insolubles.

Determination (4) above is not mandatory unless the results of the first three determinations are such that the nitrogen-content is needed to clarify interpretation of the previous results. The feasibility of these methods could be shown by the practical analysis of different types of bentone commercially available, and also by the analysis of bentone-based greases in which bentone or bentone and other gelling agents are present. It can be expected, of course, that in such commercial products the ratios mentioned for calculations may actually be different from the theoretical value because of montmorillonites in which the metal oxide ratios may vary, or

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* The symbol Bt refers to Bentone.

TABLE III

Theoretical Analysis of Bentones

Bentone Type	Total Volatiles % (Vol_{Bt})	Organic Matter %	Organic Matter by Hydrolysis* %	Nitrogen in Bentone %	Ash in Bentone % (Ash_{Bt})	Ratio: $\frac{Ash_{Bt}}{Vol_{Bt}}$	Bentone Factor: $\frac{100}{\% Ash}$
C_{12}	20.86	14.67	13.20	1.10	79.14	3.79	1.264
C_{18}	25.77	20.00	18.00	1.04	74.23	2.88	1.347
C_{26}	31.37	26.01	23.41	0.96	68.63	2.19	1.457
C_{30}	33.90	28.72	25.85	0.92	66.10	1.95	1.513
C_{34}	36.25	31.26	28.13	0.89	63.75	1.76	1.569
C_{36}	37.35	32.36	29.21	0.87	62.65	1.68	1.596
C_{38}	38.53	33.73	30.30	0.85	61.47	1.60	1.627

TABLE III (Continued)

Bentone Type	Bentone Ash Components (%)				Ratios (Ash)		Ratios (Bentone)	
	Al_2O_3	Fe_2O_3	Me_2O_3	SiO_2	$\frac{Al_2O_3}{Fe_2O_3}$	$\frac{SiO_2}{Me_2O_3}$	$\frac{Al_2O_3}{N}$	$\frac{SiO_2}{N}$
C_{12}	22.63	4.82	27.45	72.54	4.7	2.64	16.2	52
C_{18}	22.63	4.83	27.46	72.54	4.7	2.64	16.2	52
C_{26}	22.63	4.82	27.45	72.55	4.7	2.64	16.2	52
C_{30}	22.64	4.83	27.47	72.55	4.7	2.64	16.2	52
C_{34}	22.63	4.82	27.45	72.56	4.7	2.64	16.2	52
C_{36}	22.63	4.82	27.45	72.55	4.7	2.64	16.2	52
C_{38}	22.63	4.82	27.45	72.55	4.7	2.64	16.2	52

* Hydrolysis with mineral acid results in 90% recovery of total organic matter present in bentones.

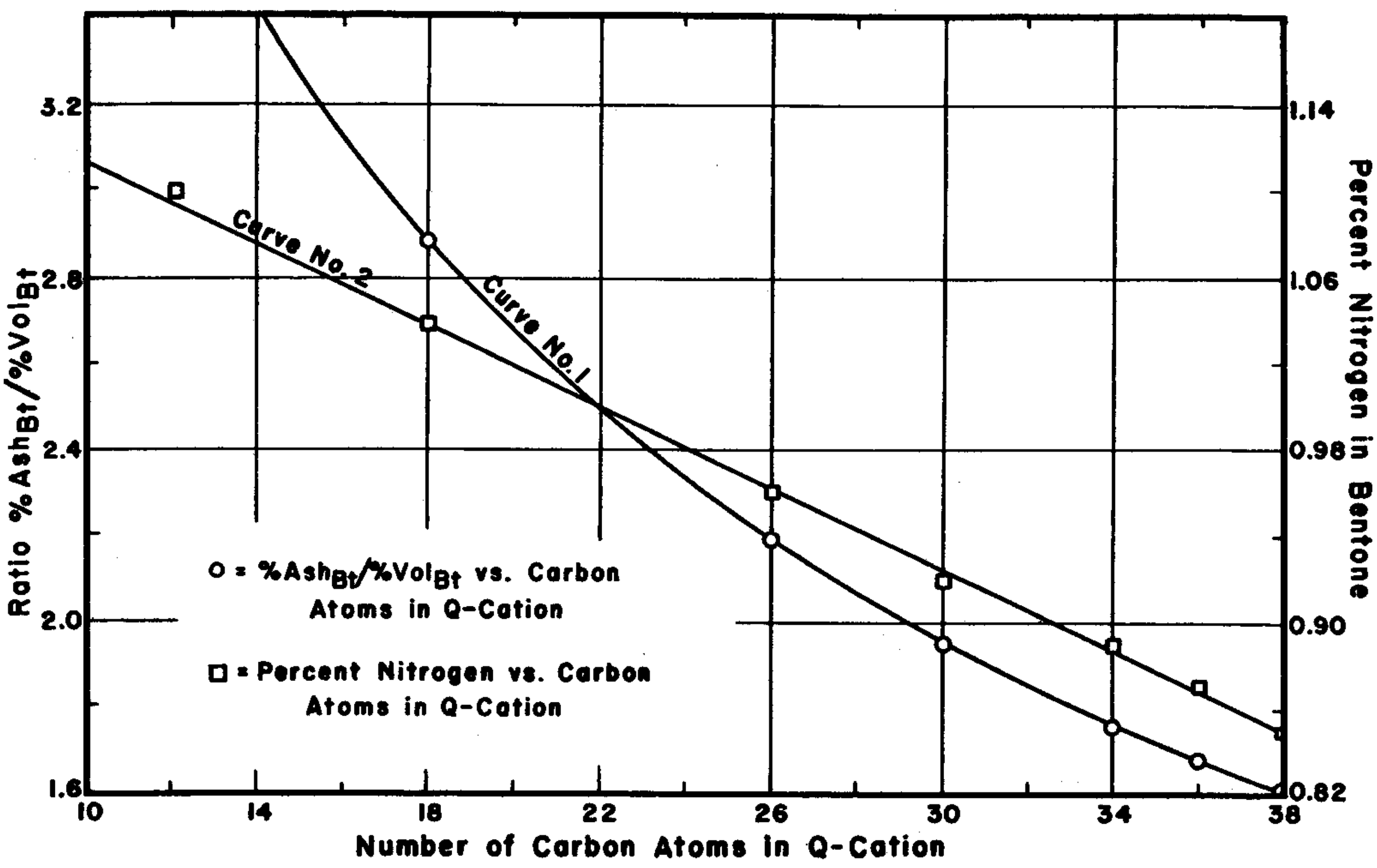

Figure 5. Nitrogen Content and Ratio Ash$_{Bt}$/Vol$_{Bt}$ in Theoretical Bentones.

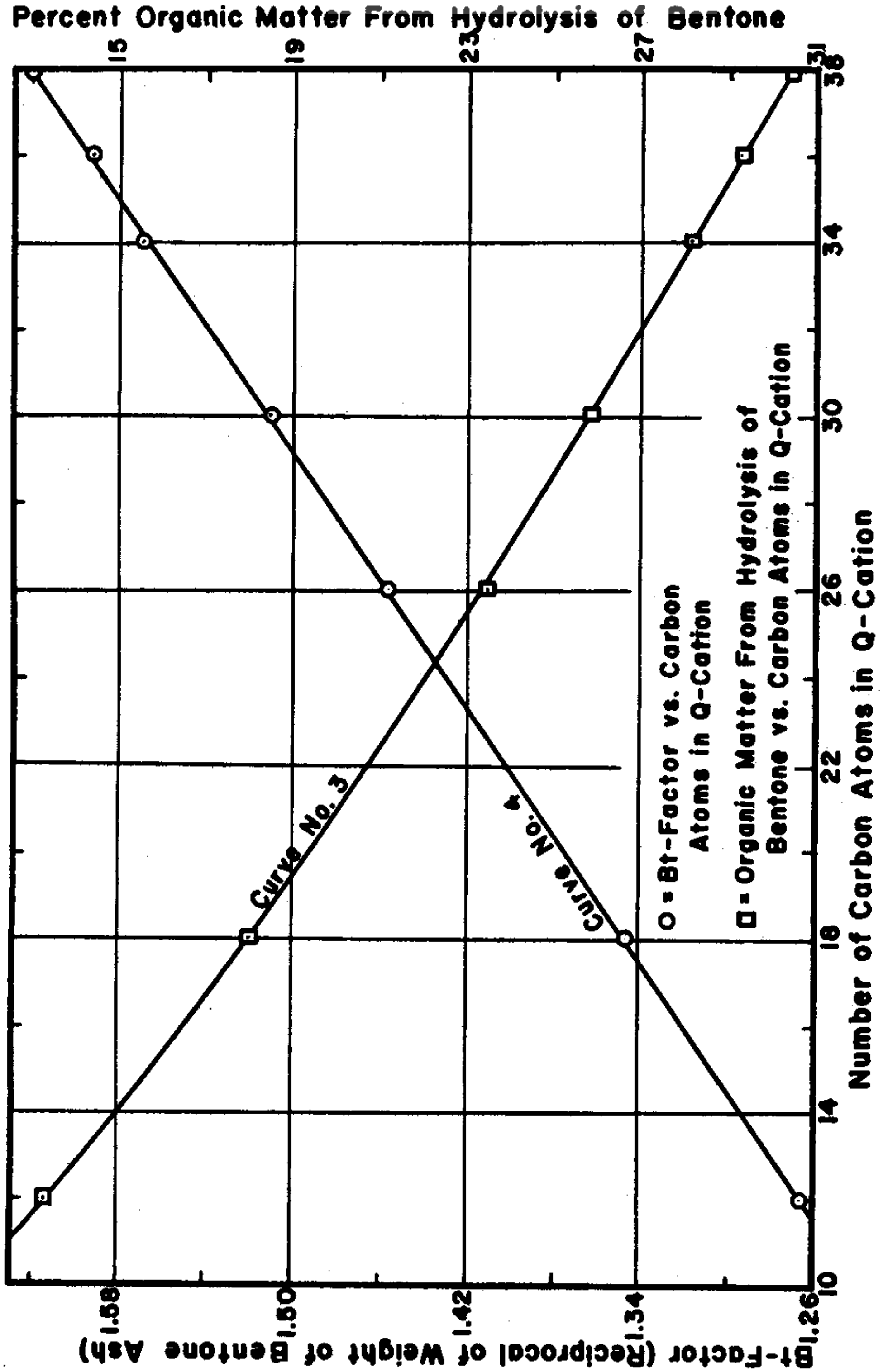

Figure 6. Bentone Factor and Organic Matter in Theoretical Bentones.

because the Na atoms are not completely exchanged with Q-cations, or in other cases when more Q-cations than normal are adsorbed to the montmorillonite. Thus, the ratio $Me_2O_3:SiO_2$ may vary slightly from the theoretical value of 1:2.64. However, it will not exceed 1:2.8 or be lower than 1:2.2

1.2.3 Practical Analysis of Bentones

According to the general ideas outlined above, the practical analysis of bentones will, therefore, be based principally on determination of the inorganic part of the montmorillonite and on the relation of the sum of the oxides in the ash* to the volatile matter in the bentones. In certain cases it will be additionally necessary to determine total nitrogen or the amount of organic matter in the bentone as a control. In the following paragraphs qualitative and quantitative determination of bentones as raw material and in greases, also in the presence of other inorganic gelling agents, will be presented.

1.3 BENTONES AS RAW MATERIAL

1.3.1 Qualitative Identification

Dry bentones have the appearance of a beige-colored light powder, insoluble in and not wettable with water. Between the fingers the bentone feels fatty, and smears. Bentones are insoluble in most organic solvents, but swell and disperse in hydrocarbons or oils, forming gelatinous mixtures if polar organic compounds, e.g. alcohols, ketones, and some esters, are present. Bentones do not give the blue benzidine reaction, which is characteristic for the bentonite-type clays. Treatment with con. NaOH hydrolyzes the bentone and the product becomes hydrophilic.

The Q-cation can be detected by qualitative identification of N after Na fusion. Ashing of the sample on a Pt sheet indicates the organic matter involved: the sample starts to burn and develop inflammable gases, leaving a carbonaceous residue which turns gray-white after prolonged heating. In the ash Al and Si can be determined after fusion with Na_2CO_3 by routine

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* In the case of montmorillonite the sum of the oxides in the ash is practically identical with the actual weight of the ash.

inorganic qualitative reactions(phosphomolybdic acid, Aluminon, etc.). The type of Q-cation cannot be identified qualitatively. This, however, is not necessary because it can be identified during the quantitative determination.

1.3.2 Quantitative Analysis of Bentones

The quantitative analysis of bentones proper would normally consist in determination of:

(1) Moisture.

(2) Volatile matter.

(3) Organic matter.

(4) Ash.

(5) Ash components.

(6) Identification of Q-cations (type of bentone).

1.3.2.1 Moisture in Bentones

The moisture determination in bentones is carried out in the usual routine way, drying the sample one hour at 105-10°C. and cooling in a desiccator. Too extensive drying should be avoided, since some of the volatile matter can be driven off. It is advantageous to dry in a vacuum oven or drying pistol at a pressure of about 20mm Hg and 50°C. for about one hour to constant weight. Bentones are not hygroscopic so that weighing can be done in an open container. The average moisture content found in the bentones used in these investigations was 0.63% on a dry weight basis.

1.3.2.2 Bentone Ash

The ash content of bentones will depend upon the type of Q-cation used for the formation of the gelling agent. This ash from bentones will be called bentone-ash to distinguish it from total ash, which may contain other oxides than those resulting from the inorganic part of the bentone. The ash content of different theoretical bentones can be seen in Table III. It varies in these theoretical cases from about 80% down to 61%; hence the total volatiles varies from 20% up to 39%.

The ash analysis of bentones is carried out in the usual routine procedure by ashing at 800-900°C. in a Pt crucible to constant weight. The average ash value from five runs each of two different bentone-types, which are at the present time commercially available, showed the following ash values (on dry weight basis):

Bentone-18	74.16%
Bentone-34	62.95%

These values show fair agreement with the theoretical values in Table III.

The difference of the ash values to 100% gives the percentage of volatile matter in bentone. The ratio between the ash content and the total volatile matter in a bentone, represented by the following symbols,

$$Ash_{Bt}/Vol_{Bt}$$

is a characteristic value for the different bentone-types and thus a means for their estimation. For the analyzed bentones this ratio was as follows:

Bentone Type	Ash_{Bt}%	Vol_{Bt}%	Ash_{Bt}/Vol_{Bt}
C_{18}	74.16	25.84	2.87
C_{34}	62.95	37.05	1.70

Curve No. 1, Figure 5 is a plot from data in Table III of Ash_{Bt}/Vol_{Bt} for the theoretical bentones against the number of C atoms of the Q-cation. Using this curve the empirically found Ash_{Bt}/Vol_{Bt} ratio can be used to estimate the type of bentone analyzed, without determinations of C, H, or N. If for instance, the ratio is 1.70, from Curve No. 1 it can be estimated that the Q-cation will have 34 or 36 carbon atoms (an uneven number of carbon atoms in a long chain compound is very unusual and is practically excluded). This estimated value is in most cases sufficient for calculation of the bentone in greases, since a difference of two carbon atoms causes errors less than 0.02% in calculating the bentone in greases. If, however, a closer determination is desirable, then an additional N determination can be used, providing that such a determination is feasible under the circumstances, i.e. that no other

N compounds are adsorbed on the bentone after separation from the base-oil.

1.3.2.3 Analysis of Bentone Ash Components

For more accurate bentone analysis the determination of the components of the ash will be necessary. In the ash of bentone the following compounds must be determined:

(1) Al as Al_2O_3.
(2) Fe as Fe_2O_3.
(3) Si as SiO_2.

The experimental determination of these elements can be made gravimetrically or colorimetrically. Since in certain cases only small amounts of grease samples may be available, we have adapted the semi-micro method of Corey and Jackson (150) for the silicate analysis, which employs colorimetric methods for the determination of Al, Si, and Fe; however, this method can easily be modified for a gravimetric determination of these elements. The colorimetric method is also feasible for the use of a Duboscq colorimeter and even Nessler tubes if necessary. The detailed procedure is explained in the experimental part (Par. 5.0, p.48) and in Appendix A of this report.

The analysis of several bentone types shows good coincidence with the theoretical values calculated in Table III, as is shown in Table IV below.

TABLE IV

Ash Analysis of Commercial Bentones

(Average of Five Parallel Runs)

Bentone-Type	Ash %	Al_2O_3 %	Fe_2O_3 %	Me_2O_3 %	SiO_2 %	$\frac{SiO_2}{Me_2O_3}$
Bentone-18	74.33	22.46	4.98	27.44	71.75	2.61
Bentone-34	62.87	22.30	5.41	27.71	70.16	2.53

The $Si0_2$:Me_20_3 ratio is also in fair agreement with the theoretical values.

The ash values and oxides in bentone ashes have been calculated for the series of theoretical bentones. These values all show the same ratio of Al_20_3:Fe_20_3 as 1:0.21 and Me_20_3:$Si0_2$ being 1:2.64. These ratios are useful for control of the analysis and also for interpretation of ash analysis in greases as is shown in the following examples:

Example 1. In bentones as raw material or in greases which contain only bentone as gelling agent, the ash analysis can be calculated from a single determination in the ash (Al_20_3 or $Si0_2$). Supposing in the above analysis (Table IV) of the Bentone-18 ash, only the Al was determined as Al_20_3. Then the other components could be computed from the theoretical ratios in Table III as follows:

Al_20_3 . . . . 22.46% by actual analysis.
$Fe_20_3 = Al_20_3/4.7=$ 4.72%
$Me_20_3 = Al_20_3 + Fe_20_3 =$ 27.18%
$Si0_2 = Me_20_3 \times 2.64 =$ 71.76%

The actually found values and the calculated values for Bentone-18 are thus:

	Found	Calculated
Al_20_3%	22.46	-
Fe_20_3 %	4.98	4.72
$Si0_2$ %	71.75	71.76

These figures show good agreement. Usually all three compounds will be determined in ash from a bentone, and the ratio should be used as a control measure.

Example 2. In ash analysis from a grease the oxide ratios can eventually be very important in determining whether the gelling agent consists only of bentone or of a mixture of bentone and other inorganic gelling agents, such as silica gel or alumina gel. For example, the ash from a grease shows the following actual analysis:

Al_2O_3%	12.37
Fe_2O_3%	6.54
SiO_2%	81.97

The ratio $Me_2O_3:SiO_2$ of 1:4.3 exceeds by far the theoretical value of 1:2.64, as does the ratio of $Al_2O_3:Fe_2O_3$ of 1:0.53 the theoretical value of 1:0.21. This means that there is an excess of Fe_2O_3 and SiO_2 in the ash which does not belong to or stem from the bentone. The oxides which stem from bentone can in this case be calculated from the Al_2O_3 value, which is the lower of the two and will be taken as the calculation base. Thus,

Oxide		Calculated Oxide from Bentone(%)
Fe_2O_3	=	$12.37 \times 0.21 = 2.60$
Me_2O_3	=	$12.37 + 2.60 = 14.97$
SiO_2	=	$14.97 \times 2.64 = 39.52$

From these values the excess Fe_2O_3 and SiO_2 in the total ash of the grease can be calculated as the difference between total Fe_2O_3 and total SiO_2 and the respective oxides belonging to the bentone portion of the ash. Thus,

Oxide	Bentone Ash Oxides in Total Ash (%)	Excess Oxides in Total Ash (%)
Al_2O_3	12.37	-----
Fe_2O_3	2.60	3.94
SiO_2	39.52	41.59
	54.49	45.53

Total Ash Oxides = 100.02%

Thus 54.49% of the total oxides in the grease ash belong to the original bentone, whereas the excess SiO_2 probably belongs to silica gel originally added to the grease. The excess Fe_2O_3 must be attributed to impurities from the manufacturing processes.

In the case of a mixture of bentone plus alumina gel, an analogous calculation can be made to determine the amount of total ash oxides which belong to the alumina gel. The oxide ratios in the bentone ash can thus be used advantageously in the analysis of greases with either bentone or mixtures of bentone and silica gel or alumina gel. If, however, the mixture consists of bentone, silica gel, <u>and</u> alumina gel, the ash analysis is insufficient and the additional determination of organic matter will be necessary (see Par. 2.3, p.37).

1.3.2.4 Organic Matter in Bentones

In general determination of the organic matter in bentones would consist in quantitative separation of the Q-cation from the montmorillonite part of the bentone. Separation of the organic part by treating bentone with mineral acids is, however, incomplete, and can be achieved only up to 90% of the total organic matter present. A series of extractions of Bentone-34 with HCl-ethanol mixtures of different concentrations was carried out for various lengths of time. The degree of separation was found by Kjeldahl N determination on the extracted filtrate and on the residue. The values are presented in Table V.

TABLE V

Separation of Organic Matter in Bentone-34 With HCl-Ethanol Mixtures

(Total N in Bentone = 0.91%)

	Extraction Mixture			Nitrogen %			
Run Number	EtOH %*	HCl %**	Hours	Residue	Filtrate	Total Nitrogen Recovered %	Q-cation Recovered %
1	95	5	1	0.43	0.48	0.91	44.8
2	85	15	1	0.18	0.74	0.92	80.4
3	95	5	3	0.12	0.80	0.92	87.0
4	85	15	3	0.14	0.77	0.91	84.6
5	80	20	5	0.18	0.72	0.90	80.0
6	50	50	5	0.24	0.59	0.83	71.1

* Absolute EtOH by volume.

** Con. HCl by volume.

From these results it seemed that reflux with a mixture of 95% abs. EtOH and 5% con. HCl, v/v, would be most promising if the extraction time were increased. From a series of tests with this mixture on the bentones available the following average values were obtained:

Bentone Type	Number of Runs	Q-Cation Recovered %	
		By N-Determination	Gravimetric
Bentone-18	5	89.2	90
Bentone-34	6	90.1	90.2

Other mineral acids yield similar results.

The organic matter separated from the bentone can be determined either by N determination on the filtrate and residue (if such a method is feasible under the circumstances) or by gravimetric determination of the difference in residue weight. In the latter case, the residue must be washed three times with 50% EtOH and three times with abs. EtOH and dried in the vacuum oven at 50°C. Although the separation of total organic matter from bentone by this method is incomplete, determination of the 90% value of the total organic matter can be useful, and in fact is the only practical way for the estimation of bentone in a grease which contains bentones admixed with silica gel <u>and</u> alumina gel or other silicates. Such combinations are quite improbable, but to check the feasibility of the method a test grease of this type was prepared. The method of attack for analysis of such a oombination is shown in (Par. 2.3, p.37).

1.4 OTHER INORGANIC GELLING AGENTS

Besides bentones or in mixture with bentones several other inorganic gelling agents may be added to synthetic lubricants for gelation. The most common of these compounds are silica gel and alumina gel. In certain cases instead of bentones, so-called "nitrated clays" may be present. The term "nitrated clays," however, is misleading. In this type of clay, analogous to the formation of the bentones, the Na cation of the montmorillonite is exchanged with ammonium cations of inorganic or organic nature, such as the ammonium ion of certain amines with very short carbon chains, e.g., ethylamine. This type of compound, however, is very rarely used in high quality performance greases.

1.4.1 Silica Gel

1.4.1.1 Qualitative Identification

Silica gel is a colloidal modification of SiO_2 with high adsorptive power. It is a light powder of white or slightly gray color, and is insoluble in water, organic solvents, and in mineral acids. It is soluble in NaOH when fused or boiled, and from alkaline solution Si can be identified with phosphomolybdic acid.

1.4.1.2 Quantitative Determination

The quantitative determination of silica gel as raw material consists in the determination of moisture and SiO_2 content.

Moisture is determined in the routine manner by drying at 105°C. to constant weight. The silica gel used in our preparations (Santocel ARD, Monsanto Chemical Corp.) showed an average moisture content of 0.72%.

SiO_2 in silica gel is determined by routine wet chemical analysis gravimetrically or colorimetrically (see Par. 5.0, p.48, and APPENDIX A.) The average SiO_2 content from five runs on Santocel ARD samples was 88.7% SiO_2 on a dry weight basis. The difference of 11.3% is volatile matter from colloidal-bound H_2O. This volatile part of silica gel must be kept in mind when the amount of silica gel in a grease is to be calculated from the ash analysis.

1.4.1.3 Silica Gel In Greases

If a grease is gelled with silica gel possibly in combination with a soap, the silica will be essentially based on the ash content of the grease, after separating out all the base-oil and soap before ashing. The ash consists in such a case primarily of SiO_2 and possibly some Fe_2O_3. If the grease contains for example Santocel-type silica gel, the percent ash must be multiplied by 1.13 to give the amount of silica gel added to the grease. In case silica gel is present together with bentone or bentone and alumina gel, the determination can be done only by difference as will be shown in Par. 2.1, below, and Par. 3.3, p. 37. In such cases the total volatiles in silica gels can be assumed to be approximately 15%.

1.4.2 Alumina Gel

In certain cases alumina gel is used instead of silica gel in admixtures with bentones. The analysis of alumina gel per se is done in the routine way by determining Al as Al_2O_3. In greases with alumina gel and bentone, alumina gel is determined like silica gel by difference from the bentone determination as shown in Par. 2.2, p.34, only using silica content as a base for calculations of the bentone content of the grease. In the case of alumina gel it must be kept in mind that approximately only 60% of the original alumina gel added to the grease is found in the ash as Al_2O_3, because there is an average of 40% volatile matter in alumina gel.

2.0 ANALYSIS OF MIXTURES OF INORGANIC GELLING AGENTS

2.1 BENTONE-SILICA GEL

2.1.1 Qualitative Identification

Although the presence of bentone in grease can be estimated by reactions for identification of bentone (Par. 1.3.1, p. 21), the presence of a mixture of bentone and silica gel cannot be determined qualitatively. The presence of silica gel in addition to bentone can be estimated and determined in the course of the quantitative analysis.

2.1.2 Quantitative Determination

The quantitative determination of bentone and silica gel mixtures as gelling agents in a grease applies the use of the different oxide ratios from the ash and the determination of volatile matter (Par. 1.3.2.4, p.27) for the calculation of the bentone content. Silica is calculated as the difference. Determination of these gelling agents employs the following steps:

(1) Separation of the base-oils and the soap thickener (if present) from the gelling agents.

(2) Determination of the organic insolubles (hexane insolubles or cuff).

(3) Total ash content in grease (so-called total ash).

(4) Total volatiles in hexane insolubles.

(5) Ash analysis for Al_2O_3, Fe_2O_3, and SiO_2.

(6) Calculation of so-called "bentone ash."

(7) Calculation of percent silica gel in grease.

(8) Calculation of "bentone-type."

(9) Percent bentone in grease.

(10) Percent of impurities in grease (e.g., Fe as Fe_2O_3).

A brief explanation of each of the above ten steps is presented below:

(1) The separation of base-oils and soap thickeners from gelling agents is accomplished by methods presented in Section C, p. 97.

(2) The difference in weight between the sum of base-oils plus soap thickeners (if present) and the grease sample gives the total amount of inorganic gelling agents in the grease. Usually these gelling agents are separated as a cuff which is insoluble in hexane or a combination of hexane with other organic solvents. This cuff is not merely determined by difference from the base-oil determination, but is actually weighed after washing and drying. The accuracy with which this separation is carried out is of great importance for the bentone determination. Therefore, much care must be placed on this separation and determination.

(3) The ash content of the separated cuff (hexane insolubles) is determined as presented in Par. 1.3.2.2, p. 22.

(4) Total volatiles are determined as the difference between total ash and total hexane insolubles.

(5) The analysis of ash components is carried out according to the methods described in Par. 1.3.2.3, p. 24.

(6) Steps (6)-(10) are made by calculation from the data in steps (1)-(5) and by using Table III and the curves in Figures 5 and 6.

2.1.3 Example for Analysis of a Grease With a Bentone-Silica Gel Mixture

Separation of the base-oil and analysis of the ash in the example grease gave the following figures:

Base-oil	91.41%
Hexane insolubles	8.52%
Total ash in grease	6.41%
Ash analysis:	
Al_2O_3	6.79%
Fe_2O_3	9.22%
SiO_2	84.05%

With these figures the individual steps (1)-(10) (Par. 2.1.2, p.30) will have the following values:

(1)	Base-oils	91.41%
(2)	Hexane insolubles	8.52%
(3)	Total ash	6.41%
(4)	Total volatile matter	2.11%
(5)	Ash analysis:	
	Al_2O_3	6.79%
	Fe_2O_3	9.22%
	SiO_2	84.05%

(6) "Bentone ash": determination of that part of the total ash in grease which belongs or stems from the original bentone present in the grease can be calculated fairly accurately from the ash analysis. Using the ratios Al_2O_3:Fe_2O_3 and Me_2O_3:SiO_2 for the theoretical bentone from Table III (which are constant and independent of the type of Q-cation in the bentone), the sum of the oxides can be calculated which correspond to the bentone part of the ash. The sum of these oxides corresponds very closely to the actual ash weight from the original bentone in the grease. (It must be kept in mind, however, that the sum of the oxides is not identical with the ash, since in the ash Al, Si, Fe, and oxygen are still present as silicates and not merely as a mixture of oxides. In the case of bentones this difference is, however, practically negligible).

From the ash values it can be immediately seen that the percent of SiO_2 is much higher than would be the case if all this SiO_2 were a part of the bentone. Therefore, there is an excess of SiO_2 and also of Fe_2O_3 beyond the values which would correspond if the gelling agent consisted only of bentone. Using, therefore, the Al_2O_3 value as a calculation base (assuming that all the Al stems from the bentone), calculations of the bentone-ash will be as follows (see also Par. 1.3.2.3, p. 24):

Percent Oxides Belonging to the Bentone Part of Total Ash

Al_2O_3	6.78%	$Me_2O_3 = 8.20\%$
$Fe_2O_3 = Al_2O_3/4.7 =$	1.42%	
$SiO_2 = Me_2O_3 \times 2.64 =$	21.65%	21.65%
		29.85%

The sum of the oxides in the ash from bentone is 29.85%. The amount of total ash belonging to the original bentone is, therefore:

$$\frac{\text{Total ash x Bentone ash}}{100} = \frac{6.41 \times 29.85}{100} = 1.91\%$$

Thus, 1.91% of the total ash in the grease originates from the bentone.

(7) Silica gel in grease: calculation of silica gel in the grease is based on the excess SiO_2 in the total ash. The amount of excess SiO_2 in total ash originates from the original silica gel present in the grease:

$$\text{Excess } SiO_2 = \text{Silica in total ash} - \text{Silica in bentone ash}$$

$$SiO_2 = 84.05\% - 21.65\% = 62.40\%$$

Amount of ash in total grease which originates from silica gel in the grease:

$$\frac{62.40\% \times 6.41\%}{100} = 4.00\%$$

Since on the average silica gel contains about 80% SiO_2, the amount of silica gel in the original grease would be:

$$\%\text{ Silica gel in grease} = \frac{4.00\% \times 100}{80\%} = 5.00\%$$

(8) Determination of the bentone-type: the total volatiles in the cuff (hexane insolubles) originate from the bentone and silica gel originally present in the grease. Since 5.00% silica gel is present in the grease and about 15-20% of the silica gel volatilizes during the ashing process, the amount of volatiles belonging to the original bentone will be:

$$\text{Volatile}_{Bt} = \text{Volatile}_{Total} - \text{Volatile}_{Silica\ gel}$$

$$\text{Volatile}_{Bt} = 2.09 - 1.00 = 1.09\%$$

From this value and the bentone ash value, the ratio Ash_{Bt}: Vol_{Bt} can be calculated:

$$Ash_{Bt}/Vol_{Bt} = 1.91/1.09 = 1.75$$

From Curve No. 1 in Figure 5, the type of bentone can be determined. The value 1.75 corresponds to a bentone with 34 carbon atoms; therefore, the bentone present in the grease is most probably Bentone-34.

(9) Percent bentone in grease: to obtain the percent Bentone-34 in the grease the percent bentone ash is multiplied with a factor for Bentone-34. The conversion factor (Bt factor) can be read from Curve No. 4 in Figure 6. For Bentone-34 this factor is 1.57. Thus,

$$\text{Bentone-34 in grease} = 1.91 \times 1.57 = 2.99\%$$

(10) Impurities: because only 1.4 x 2% of the Fe_2O_3 in the ash can be attributed to bentone, there is an excess of Fe_2O_3 present, which probably stems from the manufacturing process.

$$\text{Excess } Fe_2O_3 = 9.22 - 1.42 = 7.80\%$$

$$Fe_2O_3 \text{ in grease} = \frac{7.80 \times 6.41}{100} = 0.5\%$$

The final analysis of the grease would therefore be as follows:

Base-oils.	91.41%
Gelling agents	8.52%
Bentone-34.	3.00%
Silica gel.	5.00%
Fe as Fe_2O_3.	0.50%
Ash.	6.41%

2.2 BENTONE-ALUMINA GEL

2.2.1 Approach

In the cases where alumina gel is mixed with bentones, an analogous procedure can be applied to the mixture as in the case of bentone-silica gel mixtures. The presence of alumina gel in addition to bentone can be seen from the excess aluminum oxides present in the ash. In certain instances, however, it is not possible to determine from the ash analysis alone either bentone or the type of mixture present. In such cases a few trial calculations and comparisons using the volatile matter data will be necessary to determine the most probable mixture. An example of this situation will be shown in Par. 2.3.2, p.38.

2.2.2 Analysis of a Grease With a Bentone-Alumina Gel Mixture

Practical analysis of a grease with inorganic gelling agents has shown the following values:

Base-oils.	88.9%
Hexane insolubles	10.98%
Total ash.	7.83%
Ash analysis:	
Al_2O_3.	40.13%
Fe_2O_3	4.95%
SiO_2	54.94%
	100.03%

From these values the following calculations are carried out in the same manner as shown in the example in Par. 2.1.3, p. 31, for bentone-silica gel mixtures:

$$\text{Total volatiles} = 10.98 - 7.83 = 3.15\%$$

From the ash analysis it can be estimated that Al_2O_3 must be present in excess, since the SiO_2 value would be too low if all the aluminum oxide were derived from bentone. Therefore, it can be assumed that in this analysis the SiO_2 value must originate entirely from the bentone ash, and is, therefore, chosen as the calculation base. The procedure is as follows:

To obtain the percent of Al_2O_3 in the bentone ash, use the value of SiO_2 in the ash (54.95%), after first establishing the Me_2O_3 content of the ash in terms of Al_2O_3:

$$Me_2O_3 = Al_2O_3 + Fe_2O_3$$

$$Fe_2O_3 = Al_2O_3 \times 0.21$$

$$Me_2O_3 = Al_2O_3(1 + 0.21)$$

$$Me_2O_3 = 1.21 \ Al_2O_3$$

Since

$$SiO_2 = Me_2O_3 \times 2.64$$

then substituting for the Me_2O_3,

$$SiO_2 = Al_2O_3 \times 1.21 \times 2.64$$

Rearranging to find Al_2O_3,

$$Al_2O_3 = SiO_2 \div 3.194$$

Substituting the actual value of SiO_2,

$$Al_2O_3 = 54.94 \div 3.194 = 17.20\%$$

To find Fe_2O_3, simply multiply the Al_2O_3 value by the factor 0.21:

$$Fe_2O_3 = 17.20 \times 0.21 = 1.35\%$$

Therefore, the bentone ash oxides are as follows:

Al_2O_3	17.20%
Fe_2O_3	1.35%
SiO_2	54.94%
Bentone oxides in total ash =	73.49%

The amount of alumina gel in the grease is calculated from the excess of aluminum oxide in the ash:

Excess aluminum oxides = Total Al_2O_3 - Bentone Al_2O_3

Thus excess $Al_2O_3 = 40.13 - 17.20 = 22.93\%$

Alumina gel in grease: $22.93 \times \frac{100}{60} \times 7.83 = 2.99\%$

$$Fe_2O_3 \text{ in grease} = \frac{(4.96 - 1.35)7.83}{100} = 0.28\%$$

Bentone volatiles:

$$Vol_{Bt} = Vol_{Tot} - Vol_{Al\ gel} = 3.15 - 1.2 = 1.95\%$$

From this value the ratio ash/volatile in bentone can be calculated:

$$Ash_{Bt}/Vol_{Bt} = 5.75/1.95 = 2.95$$

This value roughly corresponds to a bentone with 18 carbon atoms (from Curve No. 1, Figure 5.). Therefore, the bentone in the grease is very probably Bentone-18. To calculate the percent of Bentone-18 in the grease, obtain the bentone factor (Bt-factor) from Curve No. 4, Figure 6. For Bentone-18 the factor is 1.35; therefore, the percent of Bentone-18 in the grease is

$$5.75 \times 1.35 = 7.76\%$$

Thus, the final analysis of the grease is as follows:

Base-oil.	88.90%
Hexane insolubles.	10.98%
Bentone-18	7.76%
Alumina gel.	3.00%
Fe_2O_3.	0.28%
Ash	7.83%

2.3 BENTONE-SILICA GEL-ALUMINA GEL

2.3.1 Approach

It is not likely that in a grease there would be a combination of inorganic gelling agents such as silica gel, alumina gel, and bentone at the same time. However, in order to check the feasibility of the methods developed, a sample of grease containing both silica and alumina gel mixed with bentone has been prepared and analyzed. With such a combination, calculations cannot start by using the components of the ash (Al_2O_3 or SiO_2) as the calculation base because there is an excess of both of these oxides in the ash. The method of approach in this case must be to determine the amount of organic matter which is associated with the bentone in the mixture, and from this quantity to calculate the amount of bentone in the mixture. Knowing the bentone content of the grease, the amount of bentone oxides can be calculated. From these oxide values and the total oxide values in the ash the excess Al_2O_3 and SiO_2 can be calculated which pertain to the silica and alumina gel, respectively, and thus the amount of gels themselves in the bentone. The difficulty in this approach lies in the fact that determination of the organic matter cannot be achieved with simple methods which would avoid determination of C, H, and N in the hexane insolubles. If laboratory conditions permit making such determinations, the method gives results comparable with those when only bentone or bentone and one of the gels is present. If, however, the organic matter can be determined only by extraction with alcohol-acid mixtures, as discussed in Par. 1.3.2.4, p. 27, then this method is only approximate, because (1) the determination is not accurate and (2) because only an average type of bentone can be calculated from the organic matter.

Nevertheless, for quick orientation these estimated values may be adequate if the combination should occur. Subsequently, a more accurate determination may be carried out, if necessary.

2.3.2 Analysis of a Grease With a Mixture of Bentone, Silica Gel, and Alumina Gel as Gelling Agents.

Practical analysis of a grease has shown the following values:

Base-oil	86.8%
Hexane insolubles	13.2%
Total ash	9.2%
Total volatiles	4.0%
Ash analysis:	
SiO_2	68.70%
Al_2O_3	27.44%
Fe_2O_3	3.85%
	99.99%

From the ash analysis no definite conclusions on the possible type of mixture can be drawn. This means that it is impossible to calculate whether Al_2O_3 or SiO_2 is in excess:

(a) Assuming Al_2O_3 as the base for calculations, the SiO_2 value is too low:

$27.44 \times 2.64 = 87.65\%$ SiO_2 (vs. 68.70% actually present)

(b) Assuming SiO_2 as the base for calculations, the Al_2O_3 value is too high:

$68.70 \div 3.194 = 21.5\%$ Al_2O_3 (vs. 27.44% actually present)

The conclusion from these figures is that in all probability the gelling agents are a mixture of bentone, silica gel, and alumina gel. In order to determine the approximate amount of ash which derives from bentone, determination of organic matter in the hexane insolubles is necessary. This can be done using the technique described in Par. 1.3.2.4, p. 27, extracting with a mixture of 95% abs. ethanol and 5% con. HCl for 5 hours. By this treatment about 90% of the total organic matter present can be extracted, as measured by the difference in weight of the hexane insolubles before and after extraction.

From Curve No. 3, Figure 6, which is the plot of 90% of total organic matter in different bentones against the number of carbon atoms in the Q-cation, the organic matter in a bentone may be estimated. For the purposes of calculation, an average bentone (about 26 carbon atoms in the Q-cation) may be assumed, or it may be assumed that a specific bentone (Bentone-34, for example) is present. Under the extraction conditions used, an average bentone with 26 carbon atoms in the Q-cation would yield about 23.5% organic matter. If such an extraction gave a value of 1.41% organic matter in the hexane insolubles, the percent bentone in the grease (assuming a 26 carbon bentone) may be calculated as follows:

$$\begin{array}{c}\text{\% Bentone-26}\\ \text{in grease}\end{array} = \frac{\text{\%Organic Matter in hexane insolubles} \times 100}{\text{\%Organic Matter in Bentone-26}}$$

thus

$$\begin{array}{c}\text{\% Bentone-26}\\ \text{in grease}\end{array} = \frac{1.41 \times 100}{23.5} = 6\%$$

If Bentone-34 had been assumed, the value would be about 5%; for Bentone-18, 7%. It can, therefore, be assumed as an approximation that there is 6% bentone present in the grease.

In order to estimate the amount of silica gel or alumina gel present with the bentone, the excess SiO_2 and Al_2O_3 in the total ash must be calculated. First one must determine the percent of bentone ash oxides in the total ash by use of the bentone-factor (Bt-factor), as plotted in Curve No. 4, Figure 6. For a 26 carbon bentone, the bentone factor is about 1.46. Therefore, a grease with 6% bentone corresponds to $\frac{6}{1.46} = 4.11\%$ bentone oxides in the ash. Since the total ash content is 9.2%, the difference of 5.09% is the sum of those oxides belonging to the silica and alumina gel. The 4.11% bentone oxides in the grease correspond to 44.67% of the total ash. The oxides from the bentone ash must be subtracted from the oxides in the total ash to obtain the excess of SiO_2 and Al_2O_3 in the total ash. Thus,

Oxide	In Bentone Ash	In Total Ash	Excess Oxide
Al_2O_3	$\frac{44.67 \times 22.63}{100} = 10.01\%$	27.44%	17.43%
Fe_2O_3	$\frac{44.67 \times 72.55}{100} = 32.40\%$	68.70%	36.30%
SiO_2	$\frac{44.67 \times 4.8}{100} = 2.14\%$	3.85%	1.71%

From the excess oxides the percent silica gel, alumina gel, and Fe_2O_3 in the grease can be calculated as in Par. 2.3.2, p.38:

$$\text{Silica gel} = \frac{36.30 \times 9.2}{80} = 4.17\%$$

$$\text{Alumina gel} = \frac{17.43 \times 9.2}{60} = 2.7\%$$

$$Fe_2O_3 = \frac{1.71 \times 9.2}{100} = 0.16\%$$

Thus the total analysis of such a grease would be as follows:

Base-oils	86.8%
Hexane insolubles.	13.2%
Bentone(as Bentone-26).	6.00%
Silica gel.	4.17%
Alumina gel.	2.17%
Fe_2O_3.	0.16%

It is, of course, possible to check the calculation with N determination on the hexane insolubles, providing that all other nitrogen-containing compounds (for example many antioxidants) have been completely removed from the insoluble residue.

3.0 IDENTIFICATION OF MIXTURES OF INORGANIC GELLING AGENTS IN GREASES

Since there is no qualitative means for identifying mixtures of bentones with silica gel and/or alumina gel, the only criteria for determining whether these mixtures are present must be based on evaluation of the ash. From the relation between the Al_2O_3 and the SiO_2 in the ash it can usually be deduced whether the ash oxides stem only from bentone or whether one of the oxides is in excess. If the $Al_2O_3 : SiO_2$ ratio is approximately 1:2.6, then the total ash originates very probably from bentone. If the ratio is larger than 2.6, then SiO_2 is in excess and very probably silica gel was present in the original grease. If the ratio is smaller than 2.6, then alumina is in excess and probably alumina gel is present in the grease.

However, in a few cases the oxide ratio may indicate a mixture which is not actually present in the grease. Assume the following ash analysis:

Al_2O_3	59.68%
SiO_2	34.25%
Fe_2O_3	6.06%

Evaluation of this analysis would lead to a first impression that this is a mixture of bentone and alumina gel, since there is an excess of Al_2O_3 present in the ash. But the possibility exists that this could be a mixture of bentone, alumina gel, and silica gel. In order to determine which evaluation is correct the analysis must be checked against the experimentally determined total volatiles value. Let us assume that the total 34.25% SiO_2 belongs to the bentone and that there is an excess of alumina. Using the assumed analysis values and carrying the calculations through as in Par. 2.1.3, p. 31, for the mixture bentone-silica gel, the experimentally-found volatiles are compared with the total volatiles calculated with these assumed values. If the assumption of a bentone-silica gel mixture was correct, then the two volatiles values should coincide within the limits of experimental error. If the assumption was wrong, i.e., if there was less bentone present than calculated, then the two values will be markedly different from each other. An additional N determination is in such cases indicated.

3.1 FEASIBILITY OF THE METHODS PRESENTED

The feasibility of the methods presented in the previous paragraphs was checked by analysis of test greases with known contents of different inorganic gelling agent mixtures. In the majority of cases the values found were in good agreement with

TABLE VI

Analysis of Inorganic Gelling Agents in Greases

(Average of the Number of Runs)

Grease Type	USAF Spec. or Ident.	No. of Runs	%Base-Oils		% Bentone		%Silica Gel		%Alumina Gel		%Fe_2O_3		% Ash	
			Pre-sent	Found	Pre-sent	Found	Pre-sent	Found	Pre-sent	Found	Pre-sent	Found	Pre-sent	Found
I0400*		4	93	92.9	2	1.96	5	5.05	-	----	0.5	0.43	7.0	7.02
I0400		3	92	91.1	3	2.9	4.5	4.6	-	----	0.2	0.25	8.5	8.3
I0300		4	90	89.4	10	9.7	---	---	-	----	0.3	0.25	6.0	5.83
I0300		3	95	95.5	5	4.7	---	---	-	----	0.5	0.46	3.2	3.18
I04a0		3	94	94.0	3	2.96	2	2.1	-	----	---	0.23	3.52	3.56
II0400		3	93	93.0	5	4.96	2	2	-	----	---	----	4.78	5.01
IV0300	MLG 53-185	3	78	77.8	20	21.2	---	---	-	----	---	----	12.74	13.0
I0500		3	89	88.8	8	7.7	---	---	3	2.86	0.5	0.44	7.83	7.80
I0600		2	86	86.8	5	6.0	5	4.7	3	2.7	0.2	0.16	9.0	9.2

* DRI classification as explained in Par. 2.0, p. 5.

the actual values; in the case of bentone, silica gel, and alumina gel mixtures, the values could of course represent only an approximation of the actual values. See Table VI for a summary of analyses of inorganic gelling agents in actual greases performed in these laboratories.

3.2 SEPARATION OF INORGANIC GELLING AGENT MIXTURES FROM BASE-OILS

The principle and general discussion of the methods of separation of base-oils from the gelling agents and thickeners will be presented in Section C, p. 97. In connection with analysis and separation of inorganic gelling agents, only those cases are of interest which involve greases in which inorganic gelling agents of bentone and silica gel or alumina gel are present with base-oils of different types, such as the dibasic acid ester-mineral oil type or the polyglycol type.

Separation of inorganic gelling agents from the base-oil can best be accomplished, if no soap thickener is present, by extraction with hexane. The grease sample is dispersed in hexane by vigorous shaking in a special centrifuge tube (see experimental part, Par. 5.0, p. 48). After dispersion, the mixture is centrifuged and the hexane layer is transferred to a separatory funnel by means of a suction apparatus (described and illustrated in the experimental part, Par. 5.6.1, p. 54). Fresh hexane is added, the separated cuff is again dispersed, and after 10 minutes shaking the tube is centrifuged. This washing procedure is repeated three times. After the last wash the hexane is drawn off, the tube is placed in a vacuum oven and dried at 50°C. to constant weight. Precautions must be taken in drying in vacuum, since all of the hexane must be removed from the cuff before the vacuum is applied; otherwise, some of the insolubles might sputter out of the tube.

This method is faster and more exact than extraction in a Soxhlet apparatus, because in the latter case the fine bentone particles are likely to pass through the thimble. If alundum thimbles are used, the thimble will plug up quickly and cannot be reused. The case of gooch crucibles with their porous bottom is analogous, where the filtration is very slow and time-consuming. It appears that the use of hexane is preferential to that of pentane, which has been used by other investigators. Recovery of the base-oil and the insolubles with hexane is not so difficult as seems to be the case with pentane, and evaporation of the solvent while manipulating the solutions is less serious. The feasibility of the method can be seen from results of the separation of different grease types presented in Table VI.

4.0 ORGANIC GELLING AGENTS

4.1 CHARACTERIZATION OF ORGANIC GELLING AGENTS

Organic gelling agents are large organic molecules with a poly-ring structure which usually possesses chelating properties. The shape of the molecule is usually flat and sometimes long side-chains can be attached to the basic flat-shaped body of the molecule. The most frequently used compounds for gelation of lube-oils to form greases are organic pigments which have been made lipophilic by the chemical or physico-chemical attachment of long chain aliphatic compounds, such as quaternary ammonium salts. The most commonly used pigments of this type are phthalocyanines.

Phthalocyanines are heterocyclic compounds related to the porphyrins with strongly resonating molecular structures, and are also strongly chelating compounds. Their general chemical structure is represented in the formula, Figure 7.

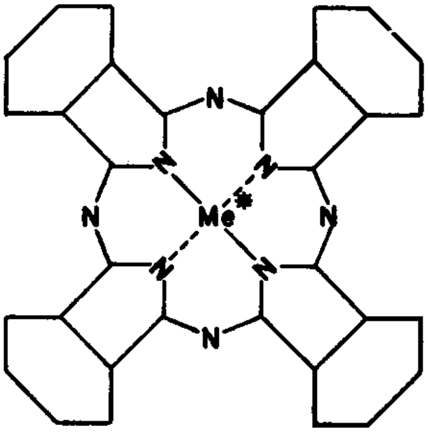


Figure 7. Structure of Phthalocyanine Molecule (*Me=Metal Atom)

Most phthalocyanines are chelated with copper, and this gives the compounds an intense blue, bluish-violet, or green color, which is very stable and light proof. The strongly chelating and resonating properties of the molecule permit it to bind the above-mentioned quaternary ammonium salts by additional Van der Waal forces, thus creating a brush-type structure similar to bentone platelets, although these pigment platelets with a diameter of 10-20 Angstroms are much smaller than bentone platelets. Because of their brush platelet shape they are not only good color pigments but also excellent gelling agents. Since the molecule consists primarily of organic matter, these pigments may be considered as organic gelling agents.

4.2 ANALYSIS OF THE PHTHALOCYANINES

Identification and determination of phthalocyanine gelling agents is relatively simple because of (1) the distinctive color of these compounds, (2) their chelation with some characteristic metal, and (3) their solubility in concentrated mineral acids. The quantitative determination can be based on this solubility; however, for a more accurate determination of the type of phthalocyanine, elementary analysis will, of course, be necessary.

4.2.1 Qualitative Identification

Phthalocyanines are characterized as organic pigments by an intensive blue, blue-violet, or green-colored light powder, insoluble in water and organic solvents, insoluble in most mineral acids and bases. Only concentrated sulfuric acid or chlorosulfonic acid dissolve phthalocyanines, yielding a brownish-colored solution. From this solution the phthalocyanines can be reprecipitated nearly quantitatively by dilution with water. Since most of the phthalocyanines are chelated with Cu or Zn, the qualitative Cu reaction of Beilstein as Cu-chloride or a Zn determination in the ash is specific and an easy qualitative reaction. Most gelling agents are either creamy white or slightly pinkish (some urea type thickeners), while phthalocyanines give intensely blue-colored greases, which, when smeared in a thin film on a porcelain dish, will show a blue or green coloration.

4.2.2 Quantitative Determination of Phthalocyanines

The quantitative determination of phthalocyanines as a raw material consists in the determination of (1) moisture, (2) ash content, and (3) organic matter. In the analysis of greases the determination of C, H, N, and thus the possible structure of the phthalocyanine is not required, since in most cases it will be adequate to determine simply the amount of phthalocyanine gelling agent present.

For the quantitative determination of phthalocyanines, the most likely approach would seem to be determination of nitrogen or the chelated metal atom. However, investigations in this direction have shown that these methods cannot be used because the metal content of the commercial products is not constant, but is lower than predicted in the theoretically pure compound. On the other hand the nitrogen value of the phthalocyanines cannot be used because the compounds are combined with quaternary ammonium bases as wetting agents to make the pigment more lipophilic. Therefore, the nitrogen value would be very inaccurate. The practical methods for determining phthalocyanines in greases must, therefore, be those which are based on separation of the pigment from the base-oil and from other gelling agents when present.

4.2.3 Analysis in Absence of Other Gelling Agents

If no other gelling agent is present in a grease than phthalocyanine, the determination is made in a manner similar to the determination of bentone in grease, as discussed in detail in Par. 1.3, p. 21. The grease is dispersed in hexane, centrifuged, and the hexane solubles separated by suction. The insolubles are washed three times with fresh hexane and dried in vacuum. The drying temperature should not exceed 100°C., since part of the phthalocyanine begins to sublime at this temperature.

4.3 SEPARATION OF INORGANIC FROM ORGANIC GELLING AGENTS

In case inorganic and organic gelling agents are both present in the grease, separation of the two types of gelling agents is accomplished in the same way as separation of inorganic gelling agents from each other. After separation of the hexane insolubles from solubles, the organic gelling agents (phthalocyanines) are dissolved in concentrated sulfuric acid or chlorosulfonic acid, filtered by centrifuging, separated by suction, and washed with the acid about three times. After the separation the filtrate is very carefully diluted with distilled water and the reprecipitated phthalocyanines centrifuged, washed repeatedly with distilled water, dried in a vacuum oven, and weighed. With chlorosulfonic acid 98-99% separation can be achieved.

In the separated phthalocyanines ash and volatiles are determined. These values must be subtracted from the total volatiles in the mixture in order that the calculation of the bentone and/or silica gel present can be carried out correctly as described in Par. 1.3, p. 21, and Par. 2.1, p. 30. The results of a triplicate separation of one bentone-phthalocyanine mixture are presented in Table VII:

TABLE VII

Separation of Bentone and Phthalocyanine Mixture

Mixture	Number of Runs	Known%	Found%
Phthalocyanine-Blue	3	60	58.7
Bentone-34		40	39.65

4.4 SEPARATION OF INORGANIC AND ORGANIC GELLING AGENTS FROM BASE-OILS

The separation of mixtures of inorganic and organic gelling agents from base-oils is accomplished in the same way as the separation of the individual gelling agents from base-oils, by extraction of the oils with hexane or hexane-IPA mixtures (see Par. 3.2, p. 43). Results of separation and analysis of two phthalocyanine greases are shown in Table VIII:

TABLE VIII

Analysis of Phthalocyanine Greases

Grease Type	No. of Runs	Base-Oil %		Phthalocyanine%		Bentone-34%		Silica-gel%		Ash%
		Present	Found	Present	Found	Present	Found	Present	Found	Found
I03.7a0	4	87	86.5	3	2.7	10	9.5	---	---	6.53
I01.7c0	3	60	59.1	30	28.96	--	---	10	9.5	22.24

In the presence of mineral oils or dibasic acid esters, it is possible that very small amounts of phthalocyanines are carried along with base-oils, giving it a slight greenish caste. Although these amounts are in the range of experimental error, this fact must be kept in mind in later steps for the separation and identification of the base-oils.

4.5 SCHEMATIC PRESENTATION OF IDENTIFICATION AND SEPARATION METHODS FOR GELLING AGENTS

Table IX is a schematic representation of the methods for identification and separation of inorganic and organic gelling agents from base-oils and from each other. Details of the methods are given in the experimental section, Par. 5.0, below, in APPENDIX A, and are discussed throughout Section A, p. 10.

5.0 EXPERIMENTAL SECTION ON GELLING AGENTS

In the following paragraphs brief descriptions of the experimental determination of inorganic and organic gelling agents and their separation from base-oils are given. Part of the more detailed procedure for silicate analysis will also be found in APPENDIX A. For these analyses greases were chosen which did not contain alkaline or alkaline-earth soaps to avoid complications at this stage of the investigation.

5.1 DETERMINATION OF Si AS SiO_2 OR COLORIMETRICALLY

The silicon content of certain gelling agents was determined either gravimetrically as SiO_2 or colorimetrically as the yellow-colored heteropoly acid $H_8(Si_2(Mo_2O_7)_6)$:

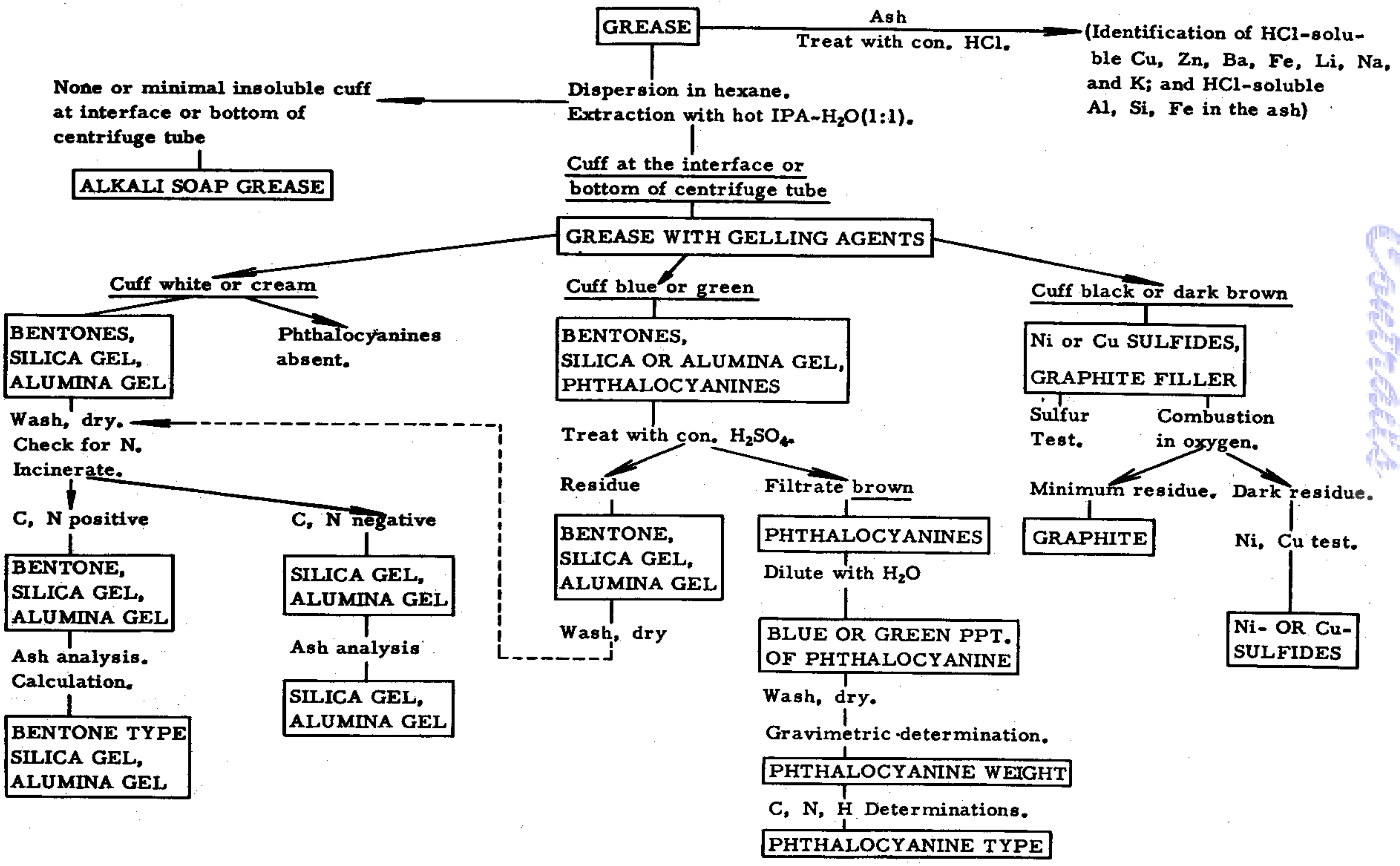
5.1.1 Gravimetric Method

Reagents - Na_2CO_3, anhydrous, reagent grade.
HCl, con. and dil., reagent grade.
H_2SO_4, 1:2, reagent grade.
HF, reagent grade.

Procedure - Determination of silica by the gravimetric method is a standard procedure, and may be found in a number of texts (151, 367, etc.).

TABLE IX

Schematic Identification and Separation of Gelling Agents



Results - Silicon analyses by the standard method on Santocel ARD (Monsanto Chemical Co.) gave an average SiO_2 content of 88.7% on oven-dried samples (moisture content was 0.72%).

5.1.2 Colorimetric Method

Complete details for colorimetric determination of SiO_2 by the method of Corey and Jackson (150) are reproduced in their entirety in APPENDIX A. The method can be applied to Nessler tubes or a Duboscq colorimeter.

Figure 8 shows the calibration curve obtained with the Beckman spectrophotometer for standard silicon solutions. Beer's Law holds for the range of concentration tested, and unknown silicon solutions may be read directly from the curve in gammas of silicon per 50 ml. of solution. Calculating back through the various dilutions will give the percent silicon or silica in the sample.

Results of analyses employing this technique are presented in the discussion.

5.2 DETERMINATION OF Al WITH ALUMINON

While aluminum could be determined gravimetrically, it was much more convenient to employ the colorimetric method of Corey and Jackson (for details of method, see APPENDIX A), to determine aluminum simultaneously with the determination of silicon.

Figure 9 shows the calibration curve obtained with the Beckman spectrophotometer for standard aluminum solutions. Beer's Law holds for the range of concentration tested, and unknown aluminum solutions may be read directly from the curve in gammas of aluminum per 50 ml. of solution. Calculating back through the various dilutions gives the percent of aluminum or alumina in the sample.

Results of analyses employing this technique are given in the discussion section.

5.3 ANALYSIS OF BENTONE

Moisture content of Bentone-34 (National Lead Co.) was determined by heating in a drying oven one hour at 105-110°C. Six

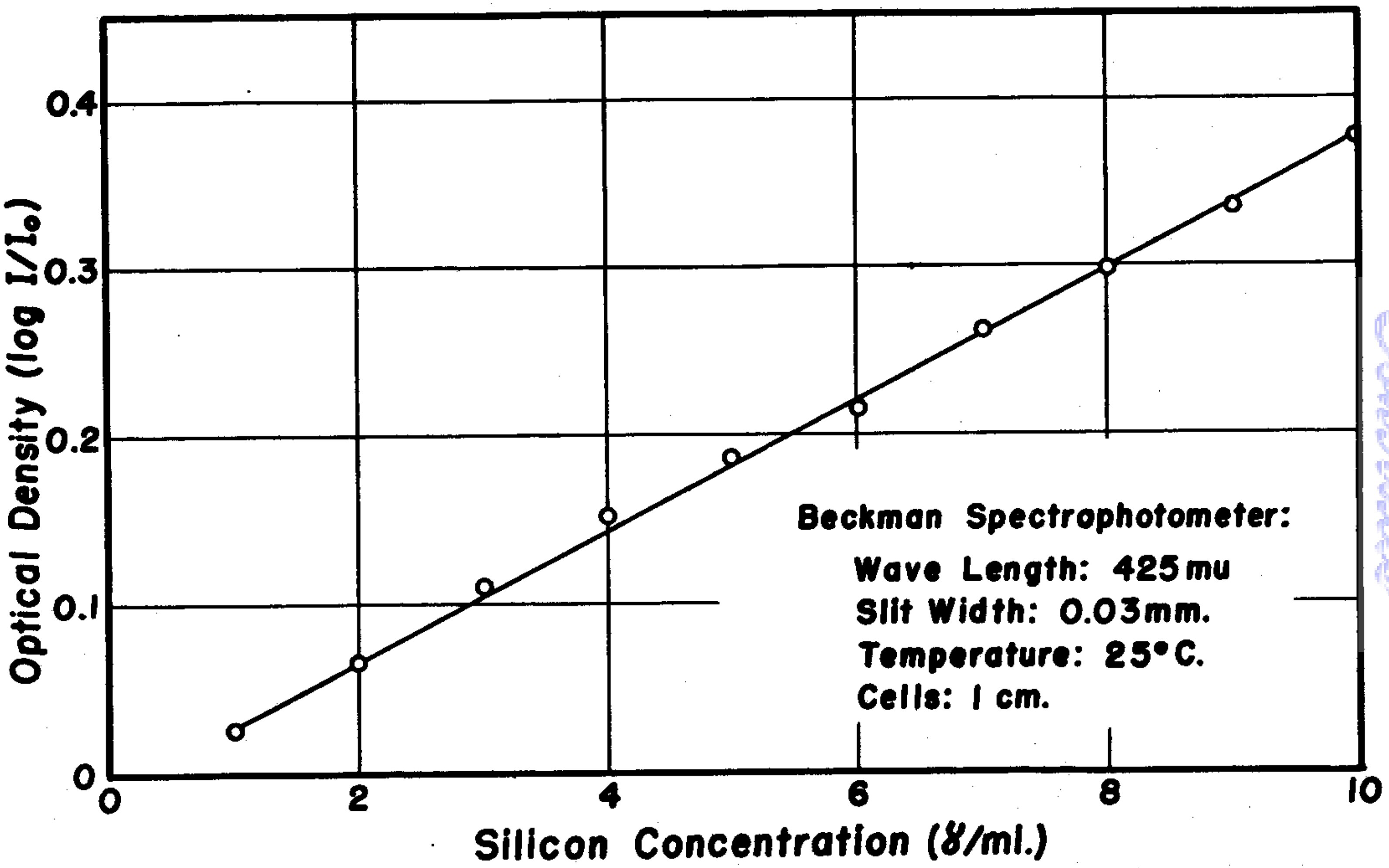
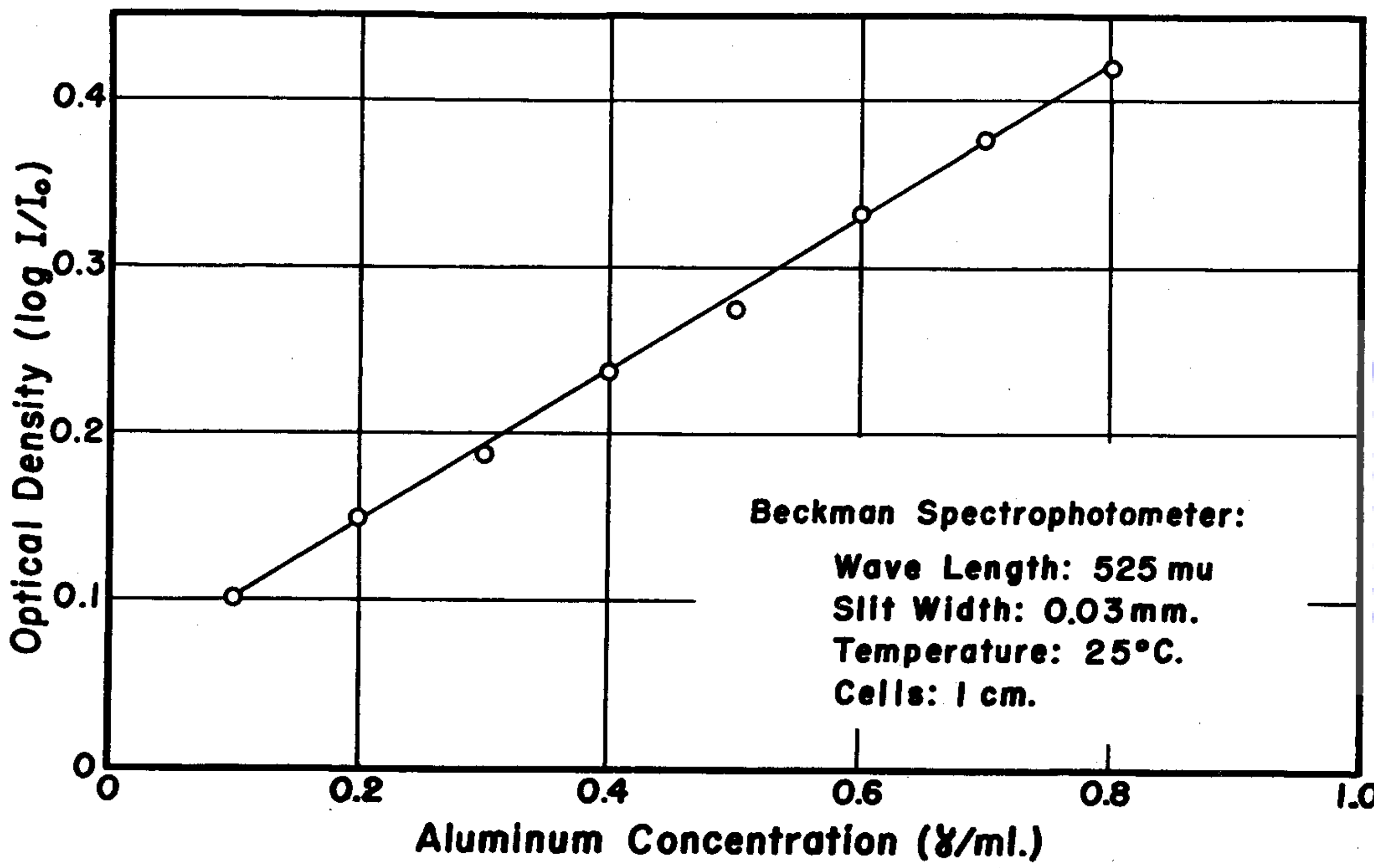


Figure 8. Silicon Calibration Curve - Analysis For Silica in Greases.



Beckman Spectrophotometer:

Wave Length: 525 mu
Slit Width: 0.03 mm.
Temperature: 25°C.
Cells: 1 cm.

Figure 9. Aluminum Calibration Curve - Analysis For Alumina in Greases.

samples were tested, yielding an average moisture content of 0.63% on a dry weight basis.

Ash content of Bentone-34 was determined by heating to constant weight in a platinum crucible. Three samples gave an average ash content of 62.87% on a dry weight basis. By difference the amount of organic matter was 37.13%. Bentone-18 had an average ash content of 74.33%.

Nitrogen content of Bentone-34 was determined by Kjeldahl digestion and distillation. Five samples gave an average nitrogen content of 0.91%.

Iron content was determined by the method of Corey and Jackson (see APPENDIX A) to the point where the iron was obtained as the hydroxide precipitate. Instead of continuing the method colorimetrically, the hydroxide was filtered and ashed for one hour at 950°C. in a porcelain crucible. The results of three analyses gave an iron content of 5.41% on a dry weight basis for Bentone-34, and 4.98% for Bentone-18.

Silica and alumina content of Bentone-34 were determined colorimetrically on the ash. Five samples gave an average silica content of 70.16%. Three samples gave an alumina content in the ash of 22.3% corresponding to an alumina content in the Bentone-34 of 14.9% on a dry weight basis. Bentone-18 had an average silica content of 71.75% and an alumina content of 22.46%.

A number of attempts were made to extract quaternary ammonium salt from the bentone under strong hydrolyzing conditions. Kjeldahl nitrogen was used as a measure of the amount of Q-salt removed from the bentone. Table V, p. 27, is a summary of these runs.

5.4 ANALYSIS OF BENTONE-SILICA GEL AND/OR ALUMINA GEL

Several actual greases were prepared and analyzed containing various mixtures of mineral oil, bentone, silica, and alumina. The analyses included ash, organic matter (by difference), silica, alumina, and nitrogen. The amount of bentone present was calculated by use of the ratios discussed in Par. 2.0, p. 30.

5.5 DETERMINATION OF PHTHALOCYANINE

5.5.1 Ash Content

Ash content of phthalocyanines was determined in the following manner: three samples with different types of phthalocyanines (Numbers P-4603, Pb-4753, and P-4653 of the Standard Ultrmarine Co.) were weighed into 30 ml. crucibles. Two of the samples of one gram were placed in a muffle furnace and incinerated at 300-400°C. Strong acidic fumes developed and examination of the crucibles showed that a large quantity of the material was subliming. Therefore, this method was abandoned. The third and subsequent samples were digested on a hotplate and sand bath with ten ml. HNO_3 and two ml. con. H_2SO_4 for eight hours to dryness, then ashed at 900°C. In this way a smooth ashing with no sublimation was achieved.

The digestion characteristics of different phthalocyanines varies considerably. Some digest quite easily with con. HNO_3 without foaming or creeping, while others give considerable trouble. The foaming types require very slow heating with con. HNO_3 and perchloric acid to obtain a clear solution. This is accomplished in about two days. The use of a sealed-tube digestion (Carius tube) is much faster, digesting the sample completely in a few hours. This latter method is recommended, if the laboratory is equipped to perform such operations.

5.5.2 Determination of Copper in Phthalocyanines

Solutions prepared from digestion of the samples in con. HNO_3 were evaported several times with H_2SO_4 to dryness, brought into solution with distilled water, acidified with one ml. dil. H_2SO_4, and the Cu content determined either electrolytically or iodometrically after treatment with ammonium fluoride and HF.

5.6 SEPARATION OF GELLING AGENTS FROM BASE-OILS

5.6.1 Separation of Bentone, Silica Gel, and Base-Oils

Approximately two grams of petroleum-base grease containing bentone and silica gel as gelling agents were transferred to a 100 ml.

ASTM oil centrifuge tube (see Figures 10 and 12) and 50 ml. hexane added. The bottle was closed with a rubber stopper and shaken vigorously for about five minutes (a shaking apparatus is recommended) or until the grease was completely dispersed. Then 70 ml. of hot (60-65°C.) isopropyl alcohol-water mixture (1:1 v/v) were added and the tube was again shaken vigorously for about 5 minutes. The tube was then centrifuged for ten minutes at 1800 r.p.m. Two liquid phases separated, on the top being the colorless IPA layer. At the interface the creamy white cuff of the gelling agents was concentrated. The hexane layer was then drawn off with the suction apparatus shown in Figures 10 and 12, by immersing the capillary tip near the cuff and applying a light suction. This technique is faster than paper filtration, and is based on filtration techniques used in microchemistry. With proper technique and care none of the precipitate in the cuff is lost.

The cuff was then washed by adding 30 ml. of hexane to the centrifuge tube, again shaking vigorously, and centrifuging. This wash hexane was drawn off into the separatory funnel containing the original hexane solution. The washing was repeated once more with 25 ml. of hexane, adding the hexane to the separatory funnel. The collected hexane was washed twice with 25 ml. portions of hot isopropyl alcohol-water mixture, separating the two phases after each washing. The bulk of the hexane was distilled off (about 75-85%) from a 500-ml. round bottom flask, the concentrate transferred to a 125 ml. Erlenmeyer, and the remainder of the hexane driven off by heating first on a water bath and then with aspirator vacuum at 50°C. until all the hexane had evaporated. After cooling the sample was transferred to a vacuum oven and heated to 50°C. at 23 inches vacuum until constant weight was achieved.

In the centrifuge tube the IPA-$H_2$0 layer was removed by immersing the capillary tip under the cuff until most of the liquid was removed. The remaining cuff was washed three times with fresh IPA-$H_2$0 mixture, centrifuged after each wash, and the liquid layer removed by suction. The cuff settled to the bottom after one wash, and the wash IPA-$H_2$0 could be removed nearly completely. After this washing procedure, the centrifuge tube was dried in vacuum at 50°C. for one hour, cooled and weighed. In this manner the cuff was not removed from the centrifuge tube and material loss was restricted to a minimum.

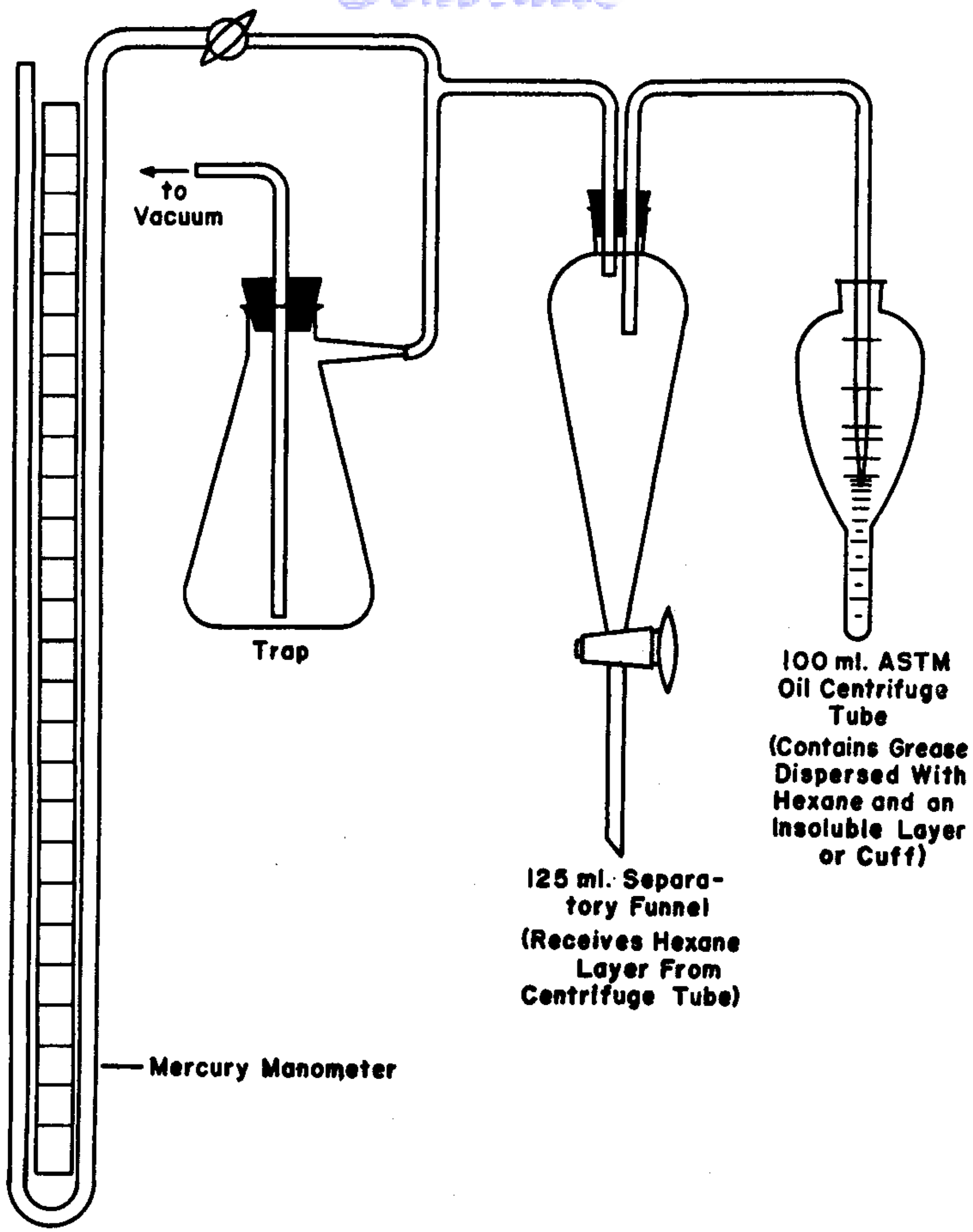


Figure 10. Schematic Diagram of Suction Apparatus For Separation of Gelling Agents From Base-Oils.

An aliquot part of the cuff was then removed from the centrifuge tube for the determination of ash, SiO_2, Al_2O_3, Fe_2O_3, etc. Nitrogen was determined directly on another aliquot of this cuff.

5.6.2 Separation of Bentone-Silica Gel-Phthalocyanine-Base-Oil

About ten grams of a grease containing dibasic ester-mineral oil as base-oil and bentone, silica gel, and Phthalocyanine-Blue as gelling agents (test grease prepared in this laboratory) were separated into base-oils and gelling agents according to the method described in the preceding Par. 5.6.1. The separated hexane insoluble part was divided into two weighed aliquot parts:

(a) One part was used to determine the total ash content and hence also the total volatile content. The ash was analyzed for Al, Si, and Fe.

(b) The second part (about three g.) was placed in a 250 ml. beaker to which 100 ml. conc. H_2SO_4 were added at room temperature and stirred with a glass stirrer (in a parallel experiment chlorosulfonic acid was used instead of sulfuric acid). A brown solution was formed. The well-stirred solution was then divided between two 100 ml. centrifuge bottles and centrifuged for 10 minutes at 2000 r.p.m. After centrifugation the bulk of each solution (approximately 30 ml.) was drawn off into a 250 ml. Erlenmeyer flask. The residue in the centrifuge bottles was washed and centrifuged three times with conc. H_2SO_4 until the acid was clear. Each time the acid was drawn off and added to the previously collected acid. The collected fractions of the filtrate were then very carefully poured into a 500 ml. beaker containing 200 ml. of distilled water. The phthalocyanines precipitated, settled out, and the diluted acid was decanted. After washing the precipitate with dilute ammonia and decanting, the precipitate was filtered through an asbestos gooch crucible, dried, and weighed.

Occasionally some of the phthalocyanine pigment adheres to the walls of the beaker. In order to remove the pigment, the beaker is washed with a detergent of the quaternary ammonium type and $Na_2S_2O_3$ at 60°C. After washing and drying, the phthalocyanine was weighed. From an aliquot part of the phthalocyanine the ash was determined, as described in Par. 5.5.1, p.54.

SECTION B

THICKENERS

1.0 INTRODUCTION

The characteristic of thickeners which distinguishes them from gelling agents is the fact that thickeners are organic compounds which by intermolecular forces form three-dimensional networks (matrix) in which the solvent (base-oil) molecules are trapped and entangled, forming a colloidal structure, a so-called grease. Compounds which are able to form such micell structures can be metal salts of long chain aliphatic acids and are called soap thickeners.

Another type of compound classed as thickeners are urea derivatives. These compounds form organic complexes with the base-oil, similar to the three-dimensional micelles of the metal soaps. The urea compound complexes are much more thermostable than the soap micelles, thus allowing the preparation of greases with better thermal stability.

2.0 SOAP-TYPE THICKENERS

Soaps are the metal salts of long chain aliphatic carboxylic acids which are prepared by the alkaline hydrolysis of a glyceride fat. The traditional soaps were either the Na or K salts of stearic acid. These alkaline soaps were combined with the traditional petroleum base-oils to form greases.

In greases with synthetic lubricants as base-oils, new types of soaps are being employed; soaps with other alkali metals or alkaline-earth metals are replacing the older Na and K soaps, and soaps with epoxy-and hydroxy-stearic acids are used instead of stearic acid. These new soaps form greases possessing better performance qualities, stability to oxidation processes, higher shearing properties, etc.

The classification of soap-type thickeners used in greases can be based on the type of metal salt of the monocarboxylic acid as well as on the type of monocarboxylic acid itself. Thus the following classes of soap thickeners can be distinguished:

(a) Alkaline soaps.
(b) Alkaline-earth soaps.
(c) Hydroxy-and epoxystearate soaps.

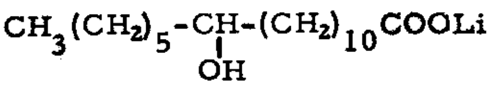
The individual determination and identification of these monobasic acid salts and their separation from the base-oils shall be discussed in the following paragraphs.

3.0 ALKALINE SOAP THICKENERS

Alkaline soap thickeners are the alkali salts of monobasic acids, usually stearic acid. The alkali metals used in the formation of the soap are Na, K, and Li. Among these the most commonly used in modern greases is Li-stearate. Since the chemical behavior and the method of analysis of all the alkaline soaps **are very similar, the analysis of Li-stearate soaps shall** be discussed in more detail.

Li-soaps are either Li-stearate or Li-hydroxystearate with the formulas:

$(C_{17}H_{35})COOLi$ Li-stearate



$CH_3(CH_2)_5\text{-}\underset{\displaystyle OH}{\underset{|}{CH}}\text{-}(CH_2)_{10}COOLi$ 12-Hydroxy-Li-stearate.

Lithium soaps have been used in the formulation of synthetic and multipurpose greases because Li-stearate yields a grease with excellent shear stability, high dropping point, low volatility, and high water resistance. Li-hydroxystearate shows in addition a very high oxidation stability. Because of these superior characteristics the older type thickeners have been nearly completely replaced by Li-stearate in grease with high performance requirements.

As far as the analysis of Li-stearate <u>per se</u> or in grease is concerned, the methods are very much the same as those used for determination of the traditional Na and K soaps. The ASTM methods for the latter can also be applied to the analysis of Li-stearate soaps and greases.

3.1 QUALITATIVE IDENTIFICATION

Li-stearate or hydroxystearate is a white powder with a softening point of approximately 200°C. and a specific gravity of about 1.01. It smears when rubbed between the fingers and has a "soapy" feeling. It is very slightly soluble in cold water and forms colloidal solutions in hot water. It is soluble in warm EtOH and isopropyl alcohol as well as in a mixture of isopropyl alcohol-water (1:1). This latter property is the basis for the separation method of Li-soaps from base-oils. The Li metal in Li-stearate can be identified by a flame test: after separation of the metal from stearic acid by treatment with HCl and extraction of the stearic acid with ether, lithium chloride (LiCl) can be detected in the acidic aqueous phase. The flame test shows a carmine-red color. The presence of Na masks the reaction; however, the red color can be seen through a cobalt glass. The presence of K interferes with the flame test, even with the cobalt glass. Li can also be identified by its reaction with 1-amino-4-hydroxy-anthraquinone, yielding a yellow color characteristic for Li.

Stearic acid in the ether extract from the hydrolysis can be identified after evaporation of the ether (a) by its melting point, (b) by formation of the hydroxamate, and/or (c) by formation of a complex compound with urea. Both of the latter compounds have characteristic melting points.

For the formation of the hydroxamates, the monobasic acid is esterified first with MeOH, using 1-2 ml. conc. H_2SO_4 as catalyst, and refluxing for about one hour. The esterification can be attained more rapidly with diazomethane; however, this reagent must be prepared fresh shortly before using in the reaction. The methyl ester is then treated with hydroxylamine. The hydroxamates so formed are white crystalline compounds with specific melting points for the individual monobasic acids (e.g. stearic acid hydroxamate = 107°C.). These compounds give characteristic color reactions: with alcoholic ferric perchlorate a stable red ferric hydroxamate is formed which can be used not only for their qualitative identification but also for quantitative determination of the monobasic aliphatic and also aromatic acids by colorimetric or chromatographic methods. The simultaneous presence of different monobasic acids in addition to stearic acid (e.g. hydroxystearic, palmitic, oleic, or dibasic acids) can be detected by partition chromatography of the hydroxamates of these acids on acetylated paper and detection of the spot on the paper by spraying with ferric perchlorate. (See also Section D of Part I - ANTIOXIDANTS and Section A of Part II - MONOBASIC AND DIBASIC ESTERS).

3.2 QUANTITATIVE DETERMINATION

Quantitative determination of Li-stearate as a raw material consists of:

(a) Moisture.
(b) Softening point.
(c) Li content.
(d) Free fatty acids.
(e) Total stearic acids.
(f) Hydroxystearic acid.

These six determinations are made as follows:

(a) The moisture determination is done in the routine manner according to ASTM methods or by drying the sample in vacuum at 50°C. to constant weight.

(b) Softening point is also done according to ASTM methods for greases.

(c) After hydrolysis of the soap with HCl and extraction of the stearic acid and free fatty acids, Li content is determined in the aqueous residue as Li_2SO_4 if Li is present by itself. If, however, Na, K, or Ba are present, the Li must first be separated from these elements. This separation is achieved quantitatively by treatment with anhydrous or 90% pyridine. LiCl is quantitatively soluble in the pyridine, whereas the other compounds are insoluble. After removal of the pyridine, the LiCl is treated with H_2SO_4 and evaporated to dryness. The determination is analogous to that of the K or Na metals as sulfates.

(d) Free fatty acids are determined by titration with alcoholic KOH.

(e) Total stearic acids are determined from the ether extract (c) by evaporation of the ether and weighing, or after transforming the monobasic acids into their hydroxamates. From the values of total stearic acid, free stearic acids, and Li content, the amount of Li-stearate can be calculated in the usual way.

(f) The determination of hydroxystearate soap is based upon determination of the OH-group on the 12-carbon atom. This is done using acetyl chloride for the determination of the OH-number.

A typical analysis of a commercial Li-stearate used in this Institute for the preparation of test greases showed the following analysis:

Moisture	0.5%
Softening Point.	204°C.
Li content	2.5%
Free fatty acids	0.4%
Total stearic acids	96.2%

4.0 SEPARATION OF ALKALI SOAP THICKENERS FROM BASE-OILS

The separation of soap thickeners from base-oils is in general more complicated than the separation of gelling agents, because most soaps form colloidal emulsions when the grease is dispersed in hexane. This emulsion cannot be separated by filtration or centrifugation. For the separation and determination of the older type greases with alkaline soaps as thickeners and petroleum base-oils, the routine standard method ASTM D128-47 Method I was fully adequate and gave good results. However, with the introduction of synthetic lubricants as base-oils these methods could not be applied in their original form.

4.1 FEASIBILITY OF ASTM METHODS FOR THE ANALYSIS OF SYNTHETIC GREASES

Due to the use of synthetic lubricants like dibasic acid esters, poly-glycols, and polysiloxanes as base-oils in greases and the use of inorganic gelling agents like bentones in addition to the metal soaps or metal hydroxy-acid soaps, it could be expected that considerable difficulties would be encountered if traditional standard methods for grease analysis were applied. This fact was confirmed by experimental tests, applying the ASTM D128-47 Method I in an attempt to investigate the feasibility of this method for the analysis of modern greases. This method involves decomposition of the grease by digestion with mineral acid followed by solvent extraction and partition of the various components.

The consequence of the application of a strong hydrolyzing agent such as hot 10% HCl is:

(a) The partial hydrolysis of the oil-base constituents, like dibasic-esters or polyesters and polyglycols, and the decomposition of fatty acids.

(b) If bentones or polysiloxanes are present in the hot digestion step, highly colloidal gelatinous mixtures are formed, which are very difficult to separate by the ASTM method.

(c) If hydroxy-acid soaps are present, the digestion requires hot and relatively concentrated mineral acid, which is undesirable because of the reasons mentioned under (a) and (b).

Furthermore, hydroxy acids have a very low partition coefficient between the solvents used in the ASTM D128-47 Method I (petroleum ether and alcohol). The hydroxy acids are rejected in the hexane-oil phase in which they are difficult to saponify. Consequently, this method is not applicable in its present form for the analysis of greases containing other components than the usual mineral base-oils and metal-soaps.

4.2 REQUIREMENTS FOR A MODIFIED ANALYTICAL METHOD FOR SYNTHETIC GREASES

A modified analytical method for synthetic greases must fulfill the following requirements:

(a) Mild hydrolysis must be employed to achieve metathesis of the alkali and alkaline-earth soaps, but must avoid hydrolysis of the base-oils and gel-formation.

(b) The polar and non-polar solvents should have such distribution coefficients that a sufficiently fast and satisfactory partition of base-oils and soaps may be achieved.

(c) The gelling agents should be separated in solid but not colloidal form.

(d) The method should be simple and fast.

(e) The method should be applicable for most synthetic base-oils and additives.

4.3 DEVELOPMENT OF A NEW METHOD FOR GREASE ANALYSIS

Based upon previous experiences in the field of partition paper chromatography in this Institute, a possible new method was visualized for the metathesis and separation of modern greases, which seemed to be adequate to meet the conditions mentioned above. Preliminary experimental tests have confirmed the feasibility as well as the accuracy and the precision of the method.

While investigating the reversed-phase partition paper chromatography of water-insoluble fatty-acids with C-chains longer than C_8 and their esters, it was noticed that low R_f values could be achieved by using iso-butanol:water:acetic acid (1:1:1) mixtures as the polar phase and n-hexane as the non-polar phase. This fact indicated a fairly good partition coefficient of the organic acids between these two phases. In recognition of this fact, application of this solvent combination for separation of soaps in greases was visualized. Experimental investigations of the hydrolysis and partition of alkali and alkaline-earth soaps in the systems hexane:isobutyl alcohol:acetic acid or hexane:isopropyl-alcohol: dil. HCl (or formic acid) proved to be feasible.

It could be demonstrated that in the case of a grease with a mixture of mineral oil and dibasic acid esters as base-oils, Li-stearate as thickener, and bentone-silica gel as gelling agents:

(a) The base-oils are concentrated in the hexane phase.

(b) The separation of the Li-stearate is accomplished by the acetic acid or cold HCl without affecting the dibasic esters.

(c) The metal part of the soap is concentrated in the polar phase.

(d) The gelling agents form a cuff at the interface between the two phases and can easily be separated by filtration with a suction apparatus (Figures 10 and 12). Separation of the two phases is quantitative if the grease is first dispersed in the hexane and the polar phase is added hot.

(e) If only alkali soaps are present in the grease, the separation can be achieved between the hexane and isobutyl-alcohol:water phase (or isopropyl alcohol:water phase), without the use of acid.

The feasibility of this approach was demonstrated by analysis of a series of alkaline-soap thickened greases with mineral oil and dibasic acid esters as base-oils. The results of these analyses are shown in Table X on the following page. From these results it can be concluded that the method is feasible for the separation of alkaline-soap thickeners (K, Na, Li) from the base-oils. Hydroxy-stearate soaps can also be separated, providing that during the separation the temperatures are kept at 65°C. (see also experimental part, Par. 9.0, p.84). The presence of free fatty acid is detected and measured by a separate titration with alcoholic KOH in the hexane dispersion of the grease.

5.0 ALUMINUM AND ALKALINE-EARTH SOAPS

Synthetic greases may contain not only Li-stearates as gelling agents but also aluminum and alkaline-earth soaps like Al-stearate or Ba- and Ca-stearates. Because of the specific properties of greases prepared with these thickeners, they have been used in increasing quantities in addition to the multipurpose Li-stearate greases. Since the methods of analysis for all of these thickeners are very similar, the Al-stearate and its analysis as a raw material and in greases will be presented in more detail.

5.1 ALUMINUM STEARATE

5.1.1 Chemical Composition

Aluminum stearate is the Al salt of stearic acid, or in certain special soaps it can also be the Al salt of stearic acid combined with dimerized linoleic acid. Aluminum stearate is manufactured commercially by reacting a water solution of the Na soap of a commercial fatty acid (e.g., Na-stearate) with an aluminum salt solution, generally $Al_2(SO_4)_3$. Since Al is trivalent, it is theoretically possible that a tri-stearate as well as a di- or mono-stearate could be formed. However, it is inconclusive whether each of these stearates exists as a separate compound. In different commercial grades of aluminum stearates the relation of Al to

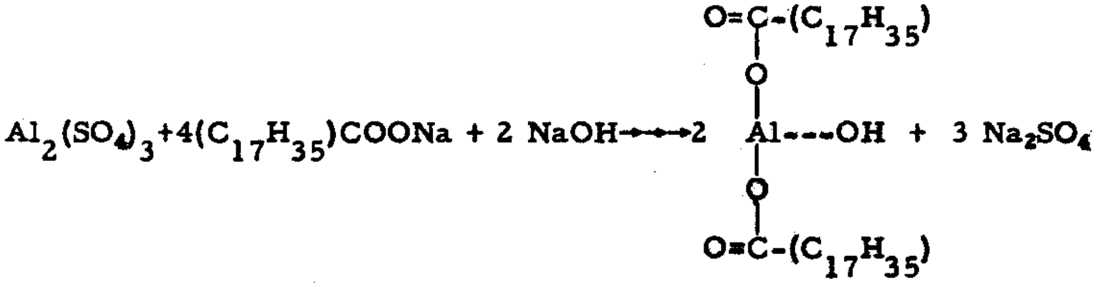
TABLE X

Separation of Alkaline Soaps From Base-Oils in Greases With IPA-$H_2$0 Mixtures

Grease Type	Mineral Oil%		Dibasic Acid Esters%		Na-Stearate%		Li-Stearate%		Li-Hydroxy-Stearate%		Free Fatty Acids%	
	Present	Found	Present	Found	Present	Found	Present	Found	Present	Found	Present	Found
IA0a.0*	85	84.6	--	----	15	14.5	--	----	--	----	0.5	0.3
IB0c0	90	90.5	--	----	--	----	10	9.7	--	----	0.3	0.23
IIB'0a0	--	----	85	84.2	--	----	--	----	15	14.8	0.3	0.31
I, IIB'0a0	50	47.3	30	30.2	--	----	--	----	20	19.56	0.4	0.42
IB100	80	80.6	--	----	--	----	15	14.8	--	----	---	----

* DRI Classification

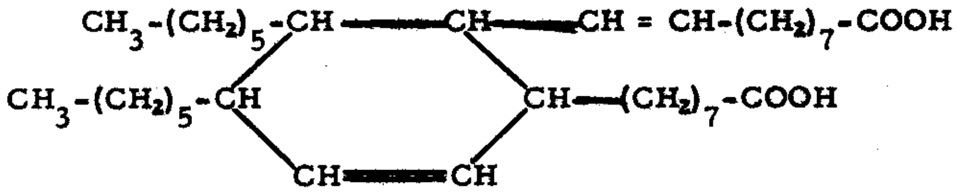
fatty acids correspond to any of these mono-, di-, or tri-stearates as well as any intermediates. Therefore, in these cases the Al content of the soap does not allow conclusive calculation of the Al-stearate present. In general, stearates with Al:fatty acids ratios corresponding to a di-stearate are used in the manufacture of greases because they have proved most effective in synthetic lubricating greases. In the manufacturing of the di-stearates it is possible that the $Al_2(SO_4)_3$ and sodium soap combine in water solution in the following manner:



$$Al_2(SO_4)_3+4(C_{17}H_{35})COONa + 2\ NaOH \longrightarrow 2\ \begin{array}{c} O=C-(C_{17}H_{35}) \\ | \\ O \\ | \\ Al---OH \\ | \\ O \\ | \\ O=C-(C_{17}H_{35}) \end{array} + 3\ Na_2SO_4$$

The third OH-group of the Al-stearate is so weak that it will not remain combined with the weak and insoluble stearic acid in the presence of water. Thus, even if all the NaOH in the equation above were replaced by addition of more Na soap, it is very probable that Al-stearate would remain as the di-compound and the excess soap would form Na_2SO_4 and free fatty acid. This explains why in such Al-stearates the amount of free fatty acid is quite high and also the presence of residual Na soap which is evident from the large amount of water soluble ash.

In recent years other fatty acids have been used in combination with stearic acid in soap formation. Such a fatty acid is, e.g., dimerized linoleic acid (American Cyanamid Co.), which has the formula:



This type of compound resembles in its structure cyclic dibasic acids. These fatty acids can, of course, also be combined with alkaline-earth metals like Ba or Ca, yielding in this way the so-called alkaline-earth soaps.

5.1.2 General Properties of Greases With Al or Alkaline-Earth Soap Thickeners

Greases prepared with these thickeners are, compared with the older type greases, more water-proof, tacky, and adhesive in nature. Usually they have a brilliant clarity like a gelatin gel and possess superior lubricating characteristics. They can carry higher loads than the oils from which they are made and respond very satisfactorily under difficult working conditions imposed by low speed and rapid shifting load, etc. These greases also have a much lower metallic residue than other soap base greases.

5.1.3 Qualitative Identification

Al-stearate is a yellow-white powder which when rubbed between the fingers does not have the typical soapy feeling. Al-stearate is insoluble in cold and warm water and insoluble or only slightly soluble in many common organic solvents. A very good solvent for Al-stearate, however, is amyl acetate in which it is quantitatively soluble.

Cold glacial acetic acid, 50% acetic acid, or cold dilute HCl (1:1) hydrolizes Al-stearate, and the Al ion can be detected and determined after neutralization in the aqueous layer with diphenyl carbazide (forming a light green precipitate). Another identification reaction for Al ion can be carried out with aluminon (aurintricarboxylic acid) which can also be used for a quantitative colorimetric determination, the ion forming a wine-red color with the reagent. The fatty acids can be extracted with ether from the hydrolyzate and after evaporation of the ether identified either by their melting point or transformed into their hydroxamates. The hydroxamates have very definite melting points and react with alcoholic ferric perchlorate to form a stable characteristic red color. If mixtures of fatty acids are present they can be separated and detected with partition paper chromatography (see Part II, Section A, MONOBASIC AND DIBASIC ACID ESTERS).

5.1.4 Quantitative Determination

The quantitative determination of Al-stearate as a raw material will in general follow techniques similar to the determination of alkaline soaps, namely: (a) determination of moisture, (b) dropping point, (c) aluminum oxide, (d) water soluble ash, (e) free fatty acids, and (f) total fatty acids.

Aluminum oxide can be determined in the ash sample, after having ashed the sample in the usual routine manner in a Pt crucible. The ash is then extracted with hot H_2O in the crucible several times, and the residue is transferred quantitatively to a filter, washed, and again ashed in the Pt crucible. The residue is Al_2O_3, and the difference is the water-soluble ash which consists primarily of the alkaline oxides from the residual Na soap.

Because of the chemical reactions involved in the formation al Al-stearate (see Par. 5.1.1, p.65) there is a large amount of free fatty acid present in these soaps. The determination of these free fatty acids is carried out as with alkaline soaps. After hydrolysis and extraction with ether, the total amount of fatty acid can be determined either gravimetrically or by titration with alcoholic KOH. If a quantitative separation of the different fatty acids present is desired, either standard methods or partition chromatography of the methyl esters may be used.

The analysis of three Al-stearates from three different commercial sources gave the following values (average of four determinations each):

	Sample 1	Sample 2	Sample 3
Moisture at 105°C., %.	0.5	0.6	0.5
Al_2O_3 %	8.5	9.5	9.8
Water soluble salts %.	0.5	0.5	0.6
Free fatty acids (as stearic)% .	7.5	5.0	6.0
Total fatty acids(as stearic)% .	82.6	82.1	81.9
Dropping point, °C.	155°	152°	153°

5.2 ALKALINE-EARTH SOAPS

Alkaline-earth soaps of the Ba- and Ca-stearate type have properties similar to those of Al-stearate, and their analysis is also similar. The identification of Ba ion (which is the more commonly used alkaline-earth soap) can be carried out in the aqueous solution after hydrolysis of the stearate with HCl or acetic acid, as $BaSO_4$ or with cupferon. Analagous to the Al soaps the amount of Ba or Ca in Ba- and Ca-stearates is of no direct value in the quantitative determination of the alkaline-earth soap, because the ratio of the Ba or Ca to the fatty acids is not a stoichiometric one. The determination of free and total fatty acid contents is, therefore, necessary.

In order to determine the amount of Na soap in Al or Ba soap, the soap can be dispersed in hexane, followed by extraction of the Na soap with a mixture of IPA-water (1:1) in which the Al- and Ba-stearate are insoluble while the Na-stearates are soluble. This is also a possible method for separation of a mixture of alkaline and alkaline-earth soaps in a grease.

6.0 SEPARATION OF ALUMINUM AND ALKALINE-EARTH SOAP FROM BASE-OILS

For the separation of Al-stearate and alkaline-earth soap thickeners from base-oils, it appeared promising to investigate the feasibility of the IPA-hexane separation method developed for the separation of alkaline soaps (see Par. 4.3, p.64). However, since neither Al-stearate nor Ba- or Ca-stearates are soluble in the IPA-water mixture, it was necessary first to transform these insoluble stearates into soluble alkaline soaps (metathesis) and then to treat these soluble soap-base-oil mixtures in the same manner as an alkaline soap thickened grease with the IPA-H_20-hexane mixture.

The metathesis can be achieved using routine ASTM methods, hydrolyzing the Al- and alkaline-earth soaps with hot conc. HCl. The fatty acids formed thereby together with the base-oils are then separated by ether extraction. In the extract the fatty acids are resaponified by neutralization with alcoholic KOH to the respective K soaps, which can then be extracted with the alcohol-water mixture and thus separated from the base-oils.

In the case of synthetic greases, however, the base-oils consist in many cases of a mixture of dibasic acid esters or polyesters with corrosion inhibitors of an ester type. The application of hot conc. HCl for the metathesis of the soaps would not be feasible in such cases because the treatment would hydrolyze to a large extent the esters of the base-oils. It was demonstrated, however, that by using cold acetic acid or cold dilute HCl the metathesis could be accomplished quantitatively without hydrolyzing the ester components of the base-oils.

6.1 METHODS OF APPROACH FOR THE SEPARATION OF Al AND ALKALINE-EARTH SOAPS FROM BASE-OILS

Using cold HCl (1:1) for the hydrolysis, separation of the Al and alkaline-earth soaps from the base-oils is carried out in the following steps in analogy to the methods used in the separation of alkaline soaps (Par. 4.3, p.64).

(a) Dispersion of the grease in hexane.

(b) Addition of cold HCl (1:1) and shaking until the flock of Al- and Ba-stearate disappears.

(c) Wash of hexane phase until free of acid.

(d) Determination of Al, Ba, and Ca in the aqueous phase.

(e) Neutralization of the hexane phase with alcoholic KOH (metathesis of the alkaline soap).

(f) Extraction of alkaline soaps with IPA:H_2O mixture, followed by the standard procedure for alkaline soaps.

6.2 PRACTICAL RESULTS OF THE METHOD AND SOURCES OF ERROR

In most cases the recovery of the base-oil and the thickener was quantitative within the limits of error. However, in the case of greases with alkaline-earth soaps as thickeners, irregularities in the results occurred. This fact led to an investigation for sources of errors which may have entered in the course of the metathesis and separation. Two major possible sources of error were found to be responsible for variations in the results:

(a) In the case of alkali soap thickeners, there was a possibility that small amounts of soap were dissolved when the separated polar phase was washed several times with hexane to remove residual base-oil. It was found that the amount of base-oil actually present in the polar phase was very small and could be removed almost completely by washing only once with hexane. When the washing was repeated too often with hexane, values for the quantitative recovery of the base-oils were always slightly high, due to the presence of small amounts of soap in the oil. In such cases the recovered oil had a cloudy appearance and occasionally even became solid. The viscosity of these oils differed considerably from that of the original base-oil. The soap present in the oil could be removed simply by re-extracting the soap with aqueous isopropyl alcohol. This was done by re-dissolving the cloudy oil-soap mixture in hexane and extracting with IPA-water mixture, separating, washing the separated phases once or twice with hexane and IPA respectively, and evaporating the solvent. However, this error can be avoided from the beginning, if, as pointed out above, washing of the aqueous phase is restricted to a minimum.

(b) Another source of error can occur if alkaline-earth soaps are present as thickeners and acetic acid is used for their hydrolysis. In this case the hexane phase must be washed thoroughly several times with distilled water by vigorous shaking in order to dissolve the excess acetic acid and alkaline-earth acetates. If this procedure is neglected, the residual acetic acid is carried along in each step; and, since acetic acid is very soluble in ether, it will partition in the ether extract which finally contains the stearic acid from the soap, thus influencing the quantitative results. The acetic acid present is difficult to remove even by heating in the vaccum oven.

6.3 FEASIBILITY OF THE METHOD

Feasibility of the separation method for different types of aluminum and alkaline-earth soap greases was investigated by analysis of soaps and greases which contained Al- and Ba-stearates as thickeners. Hydrolysis of the aluminum and alkaline-earth soap with cold HCl was in all cases quantitative. If the soaps used were pure Al- or Ba-stearates, determination of the amount of soap could be made by determination of the metal ion which remained in the aqueous phase after hydrolysis. This could, however, not be done because the alkaline-earth soap used in the manufacture of the grease was technical grade with only an approximate and not constant composition. A typical technical grade alkaline-earth soap as shown in Par. 5.1.4, p.68, might have an Al_2O_3 content of about 8.5-9.8%, free fatty acids from 5-6%, and unsaponifiables of about 6%. Therefore, the value of the alumina is not adequate for determining the Al soap present, and determination of the total amount of stearic acid (organic acid) and free fatty acid is necessary.

Due to the sources of error mentioned in the preceding paragraph, the values for the first greases analyzed varied. After elimination of errors good results were achieved. By re-extracting the soaps from the base-oils of the first analysis, the corrected values were within the limits of experimental error.

In order to avoid possible errors introduced by the use of acetic acid, the hydrolysis was carried out with cold HCl (1:1). The results showed that use of cold HCl is preferable to use of acetic acid and gives better results. Hence HCl was used for the hydrolysis of Al- and alkaline-earth stearates after the first unsuccessful runs with acetic acid. The results of the analyses of different test greases are summarized in Table XI. These results show that in case only Al and alkaline-earth soaps are present in the grease, metathesis of these thickeners with cold HCl is feasible for the quantitative separation of the thickeners from the base-oils. Similar results have been achieved with Ca-stearate greases.

TABLE XI

Separation of Al- And Alkaline-Earth Soaps From Base-Oils by Metathesis

Grease Type	No. of Runs	Base-Oil%		Total Fatty Acid % (as stearic)		Free Fatty Acid % (as stearic)	
		Pre-sent	Found	Pre-sent	Found	Pre-sent	Found
ID0c0*	3	91	90.8	8.5	8.1	5	4.2
IID000	3	89	89.1	11.5	11.3	6	5.5
IIC000	2	85	84.3	11.5	10.9	6	5.6
IID003	3	85	84.7	11.5	11.3	5	5.4

TABLE XI (Continued)

Grease Type	No. of Runs	Al %		Ba %		Soap % (by calculation)	
		Pre-sent	Found	Pre-sent	Found	Pre-sent	Found
ID0c0*	3	0.27	0.25	----	----	9	8.5
IID000	3	0.36	0.30	----	----	12	11.2
IIC000	2	----	----	0.63	0.60	12	10.8
IID003	3	0.42	0.40	----	----	12	11.7

* DRI Classification

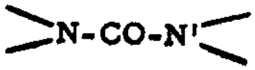
7.0 UREA TYPE THICKENERS

7.1 GENERAL CHARACTERIZATION OF UREA TYPE THICKENERS

In certain synthetic greases which are used at higher temperature ranges the thickening agent used may consist of an N, N'-substituted urea derivative. These urea compounds have a high thermal stability and can, therefore, be used in such greases where this property is a requirement, e.g. for military purposes where temperature problems are particularly severe as in jet-prop engines, high speed operation, or size reduction of accessory equipment. At the same time the operating temperature range may necessarily be extended to the low and cold region as in high altitude or arctic operations. Under such conditions traditional greases may fail because of deficiencies in either the base-oil or the thickener.

The best base-oil for greases of such requirements appears to be certain silicone fluids, as for example methylphenylsiloxanes. As for the thickener, the inorganic gelling agents are not suitable, because of the high speed and their instability above 300°F. Organic gelling agents like Cu phthalocyanines are more suitable but do not give satisfactory performance in high speed ball bearings at 450°F.

N, N'-substituted ureas of the general formula



with their high thermal stability appear to be most satisfactory in this respect. Aryl substituted ureas in particular are quite stable at high temperatures, most of them having a melting temperature above 600°F. These aryl urea compounds are, therefore, the most commonly used urea thickeners in synthetic greases.

7.1.1 Formation of N, N'-Substituted Ureas

There are several methods for the synthesis of N, N'-substituted ureas:

(a) Reaction of an amine with an isocyanate:

$$R\text{-}NH_2 + O{=}C{=}N\text{-}R' \longrightarrow R\text{-}NH\text{-}CO\text{-}NH\text{-}R'$$

(b) Reaction of an amine with an acid azide:

$$R\text{-}NH_2 + N_3\text{-}OC\text{-}R' \longrightarrow R\text{-}NH\text{-}CO\text{-}NH\text{-}R' + N_2$$

(c) Reaction of an amine with carbonyl chloride:

$$\mathrm{R{-}NH_2 + Cl{-}CO{-}NH{-}R' \longrightarrow R{-}NH{-}CO{-}NH{-}R' + HCl}$$

(d) Reaction of an amine with urea or monosubstituted urea:

$$\mathrm{R{-}NH_2 + H_2N{-}CO{-}NH{-}R' \longrightarrow R{-}NH{-}CO{-}NH{-}R' + NH_3}$$

The last method was used in this laboratory to synthesize test compounds, such as, N,N'-diphenyl urea:

$$\mathrm{C_6H_5{-}NH{-}CO{-}NH{-}C_6H_5}$$

7.1.2 Types of Substituted Urea Thickeners

Depending upon the substituted radicals and the number of urea groups (-NH-CO-NH-) involved in the molecule, several general types of urea derivatives can be conceived as possible thickeners, as listed in Table XII. Among these compounds the symmetrical diaryl urea compounds are the more commonly used.

7.2 GENERAL APPROACH FOR THE ANALYSIS OF UREA THICKENERS

Since urea type thickeners are used for the gelation of greases designed for high temperature ranges, their presence in a grease will very probably exclude the simultaneous presence of inorganic gelling agents of soap type thickeners. The simultaneous presence of Cu phthalocyanine type of organic gelling agents is also very unlikely; if, however, such gelling agents should be present, they could be easily detected by their distinct color in the grease.

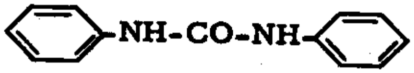
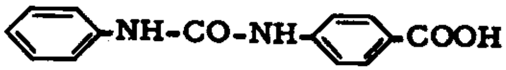
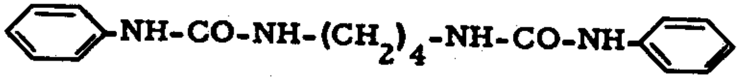
Furthermore, the presence of a urea type thickener would exclude the presence of certain base-oil components such as dibasic acid esters, petroleum fractions, polyesters, polyglycols, etc., and would indicate that the most probable base-oil components would be of the polysiloxane type. Thus, the positive identification of a urea type thickener would already exclude many combinations and indicate the method of approach for the quantitative separation and analysis of the grease.

7.3 IDENTIFICATION AND DETERMINATION OF UREA TYPE THICKENERS

The fact that there is a wide variety of substituted urea compounds, (as shown in Par. 7.1.2, above, and Table XII) and the particular physical behavior of such compounds, contributes to the fact that the

TABLE XII

Types of Substituted Ureas

Class	Example
Alkylmonourea	$CH_3-(CH_2)_7-NH-CO-NH-(CH_2)_7-CH_3$
Alkyldiurea	$CH_3-(CH_2)_7-NH-CO-NH-(CH_2)_4-NH-CO-NH-(CH_2)_7-CH_3$
Alkylarylmonourea	
Arylmonourea	 
Aryldiurea	
Alkylaryldiurea	
Polyurea unit.	$-[-CO-NH-(CH_2)_4-NH-]_n-$

identification, differentiation, and determination of the different alkyl-, aryl-, and poly-ureas offers great difficulties and is very laborious. There are no simple reactions or determination methods for the identification and quantitative determination of specific urea derivatives available at the present time. However, N, N'-substituted ureas or polyureas as a group can be detected relatively easily, and the quantitative determination as a group can also be achieved in a fairly satisfactory way. For the investigation of these reactions, several N, N'-substituted urea compounds (starting with N, N'-diphenyl urea) were synthesized and compared with the reactions of urea thickeners isolated from commercial greases (1, 4-bis-3-(para-diphenylyl)-ureido benzene).

7.3.1 Qualitative Identification

Alkyl and aryl substituted urea compounds as well as polyureas are white or sometimes pale pink powders, the melting point of which lies between 450° and 600° F. These compounds are insoluble in cold or hot water, insoluble in most inorganic acids, excepting con. H_2SO_4, insoluble in most organic solvents, but slightly soluble in pyridine. Like phthalocyanines, alkyl and aryl ureas are soluble in con. H_2SO_4 without decomposition, and from these solutions the ureas can be reprecipitated by dilution. Since polysiloxanes are also soluble in con. H_2SO_4, it can be considered as a characteristic of urea thickened greases to be completely soluble in this acid, yielding a clear and nearly colorless solution without decomposition. Any other organic compound containing grease would give some carbonization products.

Another solvent for urea derivatives is 90% phenol. This solvent will probably be used in a possible paper partition chromatographic identification and separation method for different substituted urea types. Another possible solvent is a mixture of 75% chloroform and 25% MeOH.

Qualitative identification of substituted ureas as a group will make use of a reaction giving a brilliant red color from urea compounds in the presence of oxidants. For example, a solution of N, N'-diphenyl urea in con. H_2SO_4 with potassium bichromate or lead dioxide gives a stable, wine-red color. This reaction is most sensitive if a layer of con. HNO_3 is carefully placed on top of the sulfuric acid solution. In this case the red color appears at the interface even in the absence of the other oxidizing agents. Other urea compounds show a more reddish-brown color reaction.

7.3.2 Quantitative Determination

The quantitative determination of urea type thickeners is relatively simple as long as no other type of gelling agent or soap thickener is present in the grease. This is fortunately the case in most of the commonly used urea thickened greases because of the circumstances discussed in Par. 7.2, p.75. If no other gelling agent is present, quantitative determination of the urea thickener consists simply in the quantitative separation of the urea compound from the base-oil by methods discussed below. In case urea thickeners should be mixed with other gelling agents or soap thickeners, the mixture of these gelling agents must be separated from each other. This can be accomplished on the basis of the markedly different solubility of the components involved. Thus urea thickeners can be separated from bentones and silica or alumina gels by their insolubility in con. H_2SO_4 or in 90% phenol; from soap-type thickeners by their insolubility in IPA-H_2O mixtures or in ether; and from phthalocyanines by their solubility in 90% phenol. If identification of a specific class of urea compound is desired, the quantitative estimation can be accomplished using (a) determination of the CO_2 developed by hydrolysis with strong acids and (b) the Kjeldahl nitrogen determination. These two values permit an approximate estimation of the type of unknown urea thickener at least to the extent to determine whether a mono-, di-, or poly-urea is present in the grease.

It is obvious that the common characteristic group for the determination of the different compounds is the -CO-NH-R-NH- group or a single block of the urea compound skeleton. The number of -CO-groups indicates the degree of polymerization of the compound (mono-, di-, and poly-urea). From each block one mole of CO_2 and one mole of N_2 (Kjeldahl) is liberated. Quantitative determination of the urea compound can, therefore, be based partially on determination of the amount of CO_2 liberated from the compound by strong hydrolysis with acids. Determination of the aliphatic and aromatic amines which are split off at the same time allows not only quantitative determination of the urea-type thickener but also permits identification of the class of urea compound. However, hydrolysis of this type of urea compound is sometimes rather difficult to carry out quantitatively. Therefore, the Kjeldahl nitrogen method is usually used for the approximate estimation of the number of blocks.

The hydrolysis can be carried out either with acid or alkali. It could be shown that hydrolysis with H_2SO_4 is the most effective. Determination of the CO_2 developed during the hydrolysis in connection with the determination of the aliphatic and aromatic amines can, therefore, be used to determine and characterize the urea-type compounds (for details see Experimental Part, Par. 9.3, p.90).

In order to investigate the feasibility of the proposed hydrolysis method, different types of urea compounds have been synthesized, as for example, symmetric N-N'-diphenylurea, 1-phenyl-3-methylurea, etc. If N-N'-diphenylurea is refluxed with 15% H_2SO_4 at 115°C. for 48 hours, 98.5% of the urea compound is hydrolyzed to aniline and CO_2.

From the results of these tests it appeared that hydrolytic decomposition with 29/N H_2SO_4 at 150°C. was feasible for determination of the N,N'-diphenyl urea compound which was synthesized as test substance. The amount of CO_2 developed and the amount of aniline formed could be used for the quantitative estimation of the urea compound. Using the synthesized N,N'-diphenyl urea, a series of test runs were made to check the feasibility of such a determination. The compound was submitted to hydrolysis with 78.8% sulfuric acid, and the CO_2 developed was determined volumetrically(by the method described in the Experimental Part, Par. 9.3, p. 90).

The results of these test experiments (Table XIII) show that hydrolysis in the case of N,N'-diphenyl urea and determination of the CO_2 could be used for the quantitative estimation of this urea compound. In addition, the determination of amino nitrogen and aniline formed by the Kjeldahl method is another means for determining the urea type compound. In poly-ureas the ratio between nitrogen from the amino nitrogen determination and carbon from the CO_2 determination is always 2.3. The additional determination of aniline formed during hydrolysis can be used as a more precise determination of the urea type thickener.

8.0 SEPARATION OF UREA THICKENERS FROM BASE-OILS

Separation of urea thickeners from the base-oils is relatively simple as long as only urea type thickeners are present in the grease. The grease can be separated into its thickener and base-oil components by leaching or extracting the oil with a low-boiling organic liquid, such as, benzene, hexane, dioxane, acetone, alcohol, etc., followed by removal of the solvent by evaporation under reduced presure from both

TABLE XIII

Determination of N, N'-Diphenyl Urea by Hydrolysis With 78.8% H_2SO_4 (CO_2 Volumetric; N Kjeldahl)

Compound	Run Number	Carbon Dioxide %	Nitrogen %	Compound Calculated
N, N'-diphenyl urea	1	20.12	12.8	98.4
	2	19.75	12.6	97.1
	3	20.43	12.65	98.78
	4	19.85	12.43	98.57

the fluid and the thickener. Such a method is feasible because the substituted urea compounds used in making these greases are practically insoluble in most of the common solvents. For complete removal of the base-oil from the thickener it is very important that the extraction solvent be miscible with the base-oil components in all proportions. After the grease is separated into its two components, the determination of the thickener can be accomplished as discussed in Par. 7.0, p. 74.

8.1 FEASIBILITY OF THE IPA METHOD FOR THE SEPARATION OF UREA THICKENERS FROM BASE-OILS

In the case of greases with urea-type thickeners separation methods developed for the separation of gelling agents and soap thickeners with IPA-H_2O-hexane mixture are available if silicone fluid or polysiloxanes as base-oils are absent. For mineral oil or dibasic acid ester greases, the aryl-urea thickeners, which are insoluble in most of the common solvents, remain as a cuff at the interface of the solvents, and the mineral oils or dibasic acid esters enter into the hexane phase. However, if silicone oils are used as base-oils or viscosity improvers, the silicone swells upon contact with the aqueous phase and builds up a gel of considerable volume and consistency, which occludes most of the urea thickener and also other base-oils present. These gels as well as colloidal solutions sometimes found, are practically impossible to separate. For the analysis of such greases, another approach has been investigated as is shown below in Par. 8.2, p.82.

This experience indicates that probably in all cases in which polysiloxanes are involved, the IPA phase may cause difficulties in separation. Therefore, for such greases another method of separation must be developed. If only mineral oils or dibasic acid esters are present as base-oils, the grease can be treated by the IPA-water method. The base-oils will be removed in the hexane phase and the urea thickener remains as a cuff at the interface between the polar and non-polar phase. In case no other organic or inorganic gelling agent is present, the cuff can be easily separated, washed with hexane, dried, and weighed as urea compound. However, in case bentones are present at the same time, the urea component in the cuff will have to be determined separately by one of the tentative methods outlined below.

Similar experiences in other connections suggested the use of ethylene dichloride or simply hexane as a solvent for the polysiloxane fluid. The grease is submitted to an extraction process in a Soxhlet apparatus with ethylene dichloride or normal hexane. The silicone is extracted quantitatively in about eight hours, and the urea compound remains in the thimble as residue. After the extraction, the solvent is removed and the base-oil is determined. The urea thickener in the extraction thimble can be determined as such; or, if other gelling agents are present, can be determined in an aliquot part. Table XIV shows the results for separation using this extraction process:

TABLE XIV

Separation of Urea-Type Thickeners From Silicone Base-Oils
(Grease Batch 308041, supplied by Standard Oil Co.)

Grease Type	Run No.	Silicone Oil %		Urea Thickener %	
		Present	Found	Present	Found
IVE000	1	79	78.0	21	20.5
	2		78.6		20.7
	3		78.4		20.8

To investigate the feasibility of the separation method using hexane as solvent for the analysis of urea-type greases, a grease containing mineral oil and dibasic acid ester as base-oils and diphenyl urea as gelling agent was prepared and submitted to the same method of analysis as with ethylene chloride. Soxhlet extraction of this grease with hexane removed the base-oils quantitatively after 3 hours' extraction in three parallel runs at different time intervals. Prolonged extraction did not increase the amount of hexane-soluble extract. After removal of the hexane, the base-oil and the residue were dried and weighed (Table XV). The urea thickener was practically insoluble in hexane and, therefore, could be determined directly by the weight of residue in the extraction thimble after drying in vacuum at 50°C. for one hour, provided no other gelling agent was present.

TABLE XV

Separation of Urea-Type Thickener (N,N'-Diphenyl Urea)

From Base-Oils With Hexane

Run No.	Base-Oil %		Urea Thickener %	
	Present	Found	Present	Found
1	85.00	84.5	15.00	14.81
2		84.3		14.67
3		84.6		14.70

8.2 TENTATIVE IDENTIFICATION OF THE UREA COMPOUND IN WADC GREASE MLG-9301

Several runs with WADC urea-type grease, sample code number MLG-9301, were made to investigate the feasibility of the hexane extraction method. The results of these runs (Table XVI) showed that separation of the urea-type thickener from silicone fluid could be quantitatively accomplished. Extraction was done in three hours in a Soxhlet extractor, with a sidearm stopcock on the extraction chamber. From time to time a drop from the extraction chamber was withdrawn onto a watch glass. If there was no oily residue after evaporation of the hexane solvent, the extraction was completed. The solvent was then evaporated, the base-oil dried in vacuum at 50°C. for one hour and the thimble dried in vacuum and weighed.

TABLE XVI

Separation of Urea-Type Thickener From Base-Oil (Silicone DC-550) in WADC Grease MLG-9301

Run No.	Base-Oil % Present	Base-Oil % Found	Urea Thickener % Present	Urea Thickener % Found
1	86.00	85.35	14.00	13.71
2		85.6		13.54
3		85.41		13.62

Variation in the values in Table XVI may be due to the moisture content of the grease. In general, variations in determination of greases may occur from the loss of volatile organic compounds during weighing. Many gelling agents (as for example bentones) need small amounts (1-2%) of a polar organic compound for better colloidal dispersion and swelling. Such compounds are acetone, ethyl alcohol, etc., which are quite volatile at room temperature. Thus, during weighing of the sample noticeable loss of weight can take place, affecting the results adversely.

Consideration has been given to the possibility of determining in a simple way the type of urea thickener in WADC Grease MLG-9301 by hydrolysis with 78.8% H_2SO_4 followed by determination of the CO_2 and the amino nitrogen. The results of the hydrolysis are given in Table XVII. Attempts to determine aniline formed during the hydrolysis did not lead to definite conclusions about the exact type of urea compound involved. Only the additional determination of total C, H, N, and molecular weight by microanalysis could give an exact clue as to what type of urea compound was present. Therefore, to date there could not be developed a simple method to determine the specific urea compound, which would avoid routine determination of the elementary composition and functional groups. However, if only the amount of urea-type gelling agent is required, the determination of CO_2, N, and determination of the aniline formed by the hydrolysis can be used for the estimation of these compounds.

TABLE XVII

Hydrolysis of Urea Compound (1,4-bis-3-(p-biphenylyl) ureido-benzene) From WADC Grease MLG-9301 With 78.8% H_2SO_4

Run No.	Carbon Dioxide %	Nitrogen %	Hydrolysis %	Ratio N:C
1	17.4	11.21	97.0	2.3
2	16.97	10.86	96.3	2.3
3	17.45	11.05	98.2	2.3

9.0 EXPERIMENTAL SECTION ON THICKENERS

9.1 DETERMINATION OF SOAP TYPE THICKENERS

9.1.1 Determination of Alkali Soaps

As indicated in Par. 3.2, p. 61, quantitative determination of Li-stearates as raw material consists of six different steps;

(a) Moisture. Moisture on a commercial sample of Li-stearate (Witco Lithium Stearate #306), performed by drying a one gram sample in vacuum at 50°C. to constant weight, was 0.4%. Moisture on a sample of Witco Lithium Hydroxystearate was 0.44%.

(b) Softening Point. Softening point was determined by ASTM Method No. D-566-42. Li-stearate gave a value of 204°C; Li-hydroxy-stearate 203°C.

(c) Lithium Content. Lithium content of the soap can be determined in two ways, both of which have been tried in these laboratories and which give comparable results. First is an ashing method in which two grams of soap are ashed by burning off the organic matter over a burner followed by ignition in a muffle furnace at 800°C. After cooling, the ash is converted to the sulfate by addition of one ml. con. H_2SO_4. Re-ignite with a low burner flame, then ash in the muffle at 500°C. Lithium content can also be determined after hydrolysis of the soap with HCl either by converting the LiCl to the sulfate and ashing as above or by extracting with anhydrous or 90% pyridine. The latter method is necessary when contamination with Na or K is suspected, as the chlorides of these metals are insoluble in anhydrous or 90% pyridine. Samples of the Li-stearate and hydroxy-stearate gave a lithium content by both the ashing and the extraction methods of 2.5 and 2.1% respectively.

(d) Free Fatty Acids. One gram of the soap was dissolved in about 25 ml. of ethanol and titrated with 0.1N. alcoholic KOH with phenolphthalein indicator. Both Li-stearate and hydroxy-stearate showed a free acidity of 0.4%.

(e) Total Stearic Acids. A one gram sample of the dried soap was refluxed one-half hour with 100 ml. of a 25% solution of con. HCl in a 250 ml. round-bottom flask. The flask was then cooled, removed from the apparatus, and the solution transferred to a separatory funnel. 50 ml. of diethyl ether were added, and the funnel shaken vigorously. After separation of the two phases, the aqueous phase was drawn off and extracted twice more with 25 ml. portions of diethyl ether. The ether extracts were combined, the excess ether distilled off, and the concentrated extract transferred to a crystallizing dish, then dried on a steam bath, and finally in a vacuum oven at 50°C. to constant weight. The total stearic acids thereby obtained for Li-stearate and hydroxy-stearate (which of course, includes free fatty acids) were, respectively, 96.2 and 97.0%.

9.1.2 Determination of Alkaline-Earth Soap (Metathesis).

Analysis of alkaline-earth soaps involved the following steps:

(a) Moisture. Moisture was determined on three one-gram samples of a commercial aluminum stearate(Fisher Scientific Company, Technical Grade) by drying in vacuum at 60°C. for one hour, yielding an average value of 0.25% on a dry weight basis.

(b) Ash Content. Ash content was measured on two samples of dried aluminum stearate by heating in the muffle furnace, starting at 150°C. and slowly raising the temperature to 850°C. The samples must be brought to constant weight. Ash value for these samples was 8.94%.

(c) Organic Matter. This value was obtained by difference between ash value and 100%, or, in this case, 91.06%.

(d) Free Fatty Acids. A one-gram sample was dispersed in 25 ml. of a solvent such as hexane, benzene, or cyclohexane with 25 ml. of water added and titrated with 0.1N. alcoholic KOH, using phenolphthalein indicator, to obtain the free fatty acid content.

Three samples gave an average value of 5.6%.

(e) Dropping Point. Measured by ASTM Method No. D-566-42.

(f) Aluminum Content. A two gram sample was dispersed in 50 ml. of hexane in a separatory funnel. Twenty-five ml. of cold 25% HCl were added to the separatory, followed by five minutes' shaking. After separation of the two layers, the aqueous layer was drawn off, and hydrolysis of the aluminum stearate was repeated with two more acid washes of 15 ml. each. The hexane layer was then washed several times with 15 ml. portions of water to remove traces of acid and aluminum salts. All acid and water washes were combined in a beaker and slowly evaporated to dryness on a water bath to remove all traces of organic solvent from the aluminum salts. The residue was taken up with five ml. of 1:1 HCl and warmed; 40 ml. of water were added and warmed to dissolve the salts completely. The solution was transferred quantitatively to a 100 ml. volumetric flask, washing out the beaker with 25 ml. of water and transferring to the volumetric. The procedure was repeated, and the solution brought to volume with distilled water.

A ten ml. aliquot was removed from the volumetric, transferred to a 250 ml. volumetric flask and diluted to volume with distilled water. From this dilute solution aliquots (usually about 2-5 ml.) were removed for the colorimetric determination of aluminum with aluminon reagent, comparing the color in Nessler tubes or in a Duboscq colorimeter with standards prepared at the same time. In these laboratories the aluminum content was read on a Beckmann Spectrophotometer and compared to the standard curve (see Figure 9) to save time. The method for development of the aluminum color was that of Corey and Jackson (150), given in detail in APPENDIX A.

(g) Stearic Acid Content. The hexane layer from the metathesis of the aluminum stearate, described in part (f) above, contains all of the stearic acid from the hydrolysis of the soap, plus free fatty acids in the sample. To obtain the stearic acid, the hexane layer was treated with 10 ml. of water and enough alcoholic KOH to convert all of the acids into potassium soaps (using phenolphthalein to indicate the presence of sufficient KOH). To extract the soap from the hexane phase 20 ml. hot IPA-water (1:1) solution were added, and the funnel heated on a steam bath, shaken vigorously for about two minutes, let stand until the layers separated clearly, and the lower (alcohol-water) layer, which contained the soap, was drawn off. The process was repeated twice with 15 ml. of alcohol-water solution, adding the solution to the first soap solution. If any traces of soap appear at the interface, repeat washing.

Distilling off the excess IPA, the remainder of the soap solution was transferred to a large (6" diameter or larger) crystallizing dish and evaporated to dryness on a water bath (solution turned pink due to the presence of phenolphthalein. The soap was taken up in 20 ml. of water and transferred quantitatively to a 250 ml. separatory funnel, washing the dish out thoroughly with small portions of water. Enough HCl (1:1) was added to neutralize with 3-4 drops in excess. Twenty-five ml. diethyl ether were added, shaken and the phases separated. Two more extractions, first with 20, then 15 ml. of ether were performed to obtain all of the stearic acid from the aqueous phase. The ether layer was washed twice with 10 ml. portions of water, which was discarded. The ether layer was transferred to a weighed 125 ml. Erlenmeyer flask, evaporated on a water bath, and dried in a vacuum oven at 50° C. for one hour.

(h) Unsaponifiables. The hexane layer, from which the stearic acids were extracted in part (g) above, was distilled off to about 80% of the hexane. The remaining small volume of solvent was transferred to a weighed 125 ml. Erlenmeyer flask, and the remaining hexane evaporated on a water bath, dried in a vacuum oven at 50° C. for one hour, cooled in a desiccator, and weighed.

Results of these analyses are presented in Tables X and XI.

9.2 SEPARATION OF SOAP THICKENERS

9.2.1 Separation of Alkali Soaps from Base-Oil (Isopropyl Alcohol Method)

A 2.5 g. sample of grease was dispersed with vigorous shaking in 60 ml. of hexane in a 100 ml. ASTM oil centrifuge tube. Thirty-five ml. of hot IPA-H_2O (1:1) were added to the tube, and the tube stoppered and shaken for several minutes. Several times during the shaking the tube was immersed in a water bath to keep the contents hot. Brief centrifugation separated the two phases, and the hexane phase was drawn off with the suction apparatus illustrated in Figures 10 and 12 into a 125 ml. separatory funnel. The hexane phase was extracted twice with hot 25 ml. portions of IPA-H_2O(1:1), to remove final traces of soap from the hexane phase. After combining the alcoholic extracts in a separatory funnel, they were washed once with 10 ml. of hexane to remove residual oil from the solution. The alcoholic soap extract was transferred quantitatively to a 500 ml, round-bottom flask, using small portions of IPA to rinse out the separatory. About 75% of the alcohol was distilled off, and the concentrated extract again transferred quantitatively to a weighed crystallizing dish or Erlenmeyer flask, and evaporated to dryness, first on a water bath, followed by drying to constant weight in a vacuum oven at 50°C. The weight is that of the soap in the grease, plus any other IPA-H_2O solubles present in the grease.

This dried extract may now be subjected, if necessary, to the determinations discussed in Par. 9.1.1, p. 84, for lithium content and total stearic acids, from which determinations the exact amount of alkali soap may be calculated. Free fatty acids, of course, are determined on a sample of the grease by titration with alc. KOH.

The amount of base-oils (hexane-solubles) may be determined in the hexane phase simply by distillation of the excess hexane and drying in the vacuum oven at 50°C. to constant weight.

If the final analysis of the unknown grease has revealed that an alkali soap is the only thickener present, then ash analysis of the grease will reveal directly the amount of soap present in the grease. In the case of a Li-stearate thickened grease, a 10 g. sample was ashed by burning off excess organic matter over a burner, followed by ignition in a muffle furnace at 800°C. The cool ash was coverted to the sulfate with one ml. of con. H_2SO_4, and the ash was again ignited over a low flame, then ashed in the muffle at 500°C. The following calculations will give directly the amounts of lithium and of soap in the grease:

$$\%\ \text{Lithium} = \frac{\text{Wt. Ash} \times 0.1262}{\text{Wt. Grease Sample}}$$

$$\%\ \text{Li-soap} = \frac{\%\ \text{Lithium}}{0.25} \qquad \text{(as Li-stearate)}$$

$$\%\ \text{Li-soap} = \frac{\%\ \text{Lithium}}{0.22} \qquad \text{(as Li-hydroxystearate)}$$

9.2.2 Separation of Alkaline-earth and Aluminum Soaps from Base-Oils

The separation method is exactly the same as the method in Par. 9.1.2, p. 86, part (f), with the exception that a five gram sample of grease is dispersed in 75 ml. of hexane at the start of the procedure. It must be borne in mind that this procedure is useful only when inorganic and organic gelling agents are absent from the grease.

After the soap has been hydrolyzed by the acid treatment, all of the metal ion from the soap is in the aqueous phase, and the base-oils and stearic acids are present in the hexane phase. The stearic acids are recovered and determined exactly as outlined in Par. 9.1.2, p. 86, part (g). Free fatty acids are determined on a sample of the grease dispersed in hexane by titration with alc. KOH.

If the final analysis of the grease indicates that the only thickening agent or gelling agent present is the aluminum or alkaline-earth soap, then an ash analysis on the grease will assist materially in an exact determination of the soap by confirming the amount of metal ion associated with the soap found in the analysis after separation.

9.2.3 Separation of Mixtures of Alkali and Alkaline-Earth Soaps From Base-Oil

There are two procedures for analyzing greases with both kinds of soaps present as thickeners. After dispersing the grease in hexane, the alkali soap is extracted from the hexane with hot IPA-H_2O (1:1) in a separatory funnel, as described in detail in Par. 9.1.1, p.84, and 9.2.1, p.87. Aluminum or alkaline-earth soaps remain as a cuff or precipitate since they are insoluble in both solvents. With the alkali soap removed, the aluminum or alkaline-earth soaps are then hydrolyzed and separated, as explained in detail in Par. 9.1.2, p.85, and 9.2.2, p.88. This is rather difficult, and great care must be taken to secure complete separation of the alkali soap before starting hydrolysis of the remaining soap.

The second procedure is simply to hydrolyze with 25% HCl all soaps present after dispersion in hexane. All metal ions can be measured in the aqueous phase; fatty acids are re-converted to a K-soap with alc. KOH and extracted with IPA-H_2O mixture. Calculation will give the approximate amounts of each type of soap present in the grease.

9.2.4 Separation of Mixtures of Soap Thickeners With Inorganic Gelling Agents From Base-Oil

As will be indicated in the discussion of these mixtures (Par. 2.0, p.98), soaps cannot satisfactorily be separated from inorganic gelling agents by the previously described methods. Instead the soaps and base-oils must first be extracted from the bentone and other inorganic gelling agents in a Soxhlet apparatus with amyl acetate.

A grease containing mineral oil, 9% Al-stearate, 4.5% Bentone-34, and two antioxidants was prepared and separated in the following manner: a three g. sample of the grease was placed in a weighed single weight Soxhlet thimble (double weight is recommended for future use). A 250 ml. standard taper flat-bottom flask containing about 125 ml. of amyl acetate was attached to the apparatus. Extraction was continued until a drop of solvent withdrawn from a stopcock sidearm on the extraction chamber onto a watch crystal evaporated with no residue. This required about six hours. The thimble was withdrawn, partially dried in a drying oven at 105°C., and completely dried in a vacuum oven at 50°C. for one hour. Weighing must be done with the thimble in a light-weight glass container, both before and after the extraction. Bentone-34 recovered by this procedure was 4.45%.

The flask now contained all of the base-oil, Al-stearate, and amyl acetate. After distilling off the bulk of the amyl acetate under aspirator vacuum, the remainder of the solvent was removed by heating two hours in the vacuum oven at 50°C., leaving a base-oil, Al-stearate grease, free of inorganic gelling agents and solvent. This grease can then be dispersed in hexane and separated by the methods outlined in Par. 9.1.2, p.85 and 9.2.2, p.88.

9.3 DETERMINATION OF UREA TYPE THICKENERS

9.3.1 Synthesis of N,N'-Diphenyl Urea

For the investigation of urea-type greases it was necessary to synthesize at least one of the basic urea-derivatives used as thickening agents in such greases, because it was not possible to find such compounds commercially available. Since the urea compounds used in commercial greases are primarily of the aryl type, the simplest of this group of compounds, N,N'-diphenyl urea, was synthesized by the following procedure:

Sixty g. aniline and 20 g. urea in 150 ml. of benzene were refluxed at 150-170°C. with stirring. The reaction was exothermic at the beginning and careful control of the temperature was necessary. After three hours, heating was stopped and the reaction product allowed to cool. The crystallized N, N'-diphenyl urea was separated from the benzene by filtration through a Buchner funnel.

Recrystallization from hot ethyl alcohol yielded colorless rhombic prisms, m.p. 235°C. Microanalysis of the recrystallized product gave according to the formula $C_{13}H_{16}N_2O$:

	Theory %	Found %
C	72.35	71.97
H	7.97	7.21
N(Kjeldahl)	12.95	12.53

9.3.2 Hydrolysis of N, N'-Diphenyl Urea

In order to investigate the feasibility for hydrolysis of aryl urea compounds, N, N'-diphenyl urea was submitted to different types of hydrolysis with acids and alkalies:

(a) Heating with 78.8% H_2SO_4 for 2.5 hours at 150°C. yielded 99.1% aniline. At 170°C. the yield dropped to 98.3%. The time study indicated that after one hour at 150°C. the acid of 74.8% concentration gave 97% hydrolysis with further slow hydrolysis from that point on. No hydrolysis occurred with con. HCl at 100°C. in two hours, while 30% HCl at 150°C. gave 98.4% in two hours.

(b) Heating with 10% NaOH at 100°C. for two hours gave 1% hydrolysis, while at 125°C. it was 89%, and at 150°C. it was 98%. NaOH at 150°C. for four hours gave 99.1% hydrolysis. In a closed vessel at 140-150°C. N, N'-diphenyl urea and 5% NH_4OH gave aniline and urea in a yield of 56% of theory. Melting with NaOH yielded nearly quantitatively N, N', N"-triphenylguanidine and aniline.

The hydrolysis and CO_2 determination was carried out in the apparatus shown in Figures 11 and 13. Operation of the apparatus is as follows:

The sample is placed in container A which is connected to condenser C and with dropping funnel B which contains con. H_2SO_4. From funnel B the acid is added in small increments and the vessel A is heated gently. The developed CO_2 passes through the water-jacketed cooler C which removes H_2O and any residue of the H_2SO_4. The CO_2 is transferred through the capillary connection tubes and the three-way stopcocks D and E into a measuring burette F by lowering the leveling bulb S which contains a saturated aqueous solution of NaCl. The burette F together with the compensation burette G is surrounded by a water jacketed thermostat H. After having transferred the bulk of the gas into the burette, the container A including the connection tubes up to the stopcock D is filled with liquid by filling from the dropping-funnel with H_2O. Thus, the rest of the gas is driven through the stopcock D and E into the burette. The stopcock D is then closed and F is connected with E with the Hg manometer J. The opposite side of J is connected with the compensation burette G which shortly before the transfer was equilibrized with the atmosphere by the stopcock K.

Now bulb S is raised to the point where the Hg level in J indicates pressure equilibrium in F and G. The gas volume V_1 in burette F is noted and F is connected with the absorption tube M. The absorption tube consists of two connected tubes N and O filled with KOH solution. The gas enters the solution through the dispersion tube and the CO_2 is absorbed by the KOH. The tube O contains thermometer T and serves as a pressure equalizer which is closed to the atmosphere by the rubber gas expansion bag P. After the gas is transferred to M, stopcock L is closed and the gas washed thoroughly by pumping the rubber bag P, thus mixing the gas with the liquid. The gas is sucked back into the burette F, which is again connected with the manometer J. The pressure in both burettes is equalized with S and the volume V_2 in F noted. The difference $V_1 - V_2$ is the volume of CO_2 absorbed in the KOH. After correction for temperature and pressure the percent CO_2 can be calculated.

9.3.3 Separation of Urea Thickener From Base-Oil With Ethylene Chloride

A five g. sample of the grease was placed in a preweighed extraction thimble and extracted for eight hours with 250 ml. ethylene chloride in a Soxhlet apparatus. After removal of the solvent from the extract by distillation and from the thimble by heat, the oil and the residue were dried in vacuum at 50°C. to constant weight.

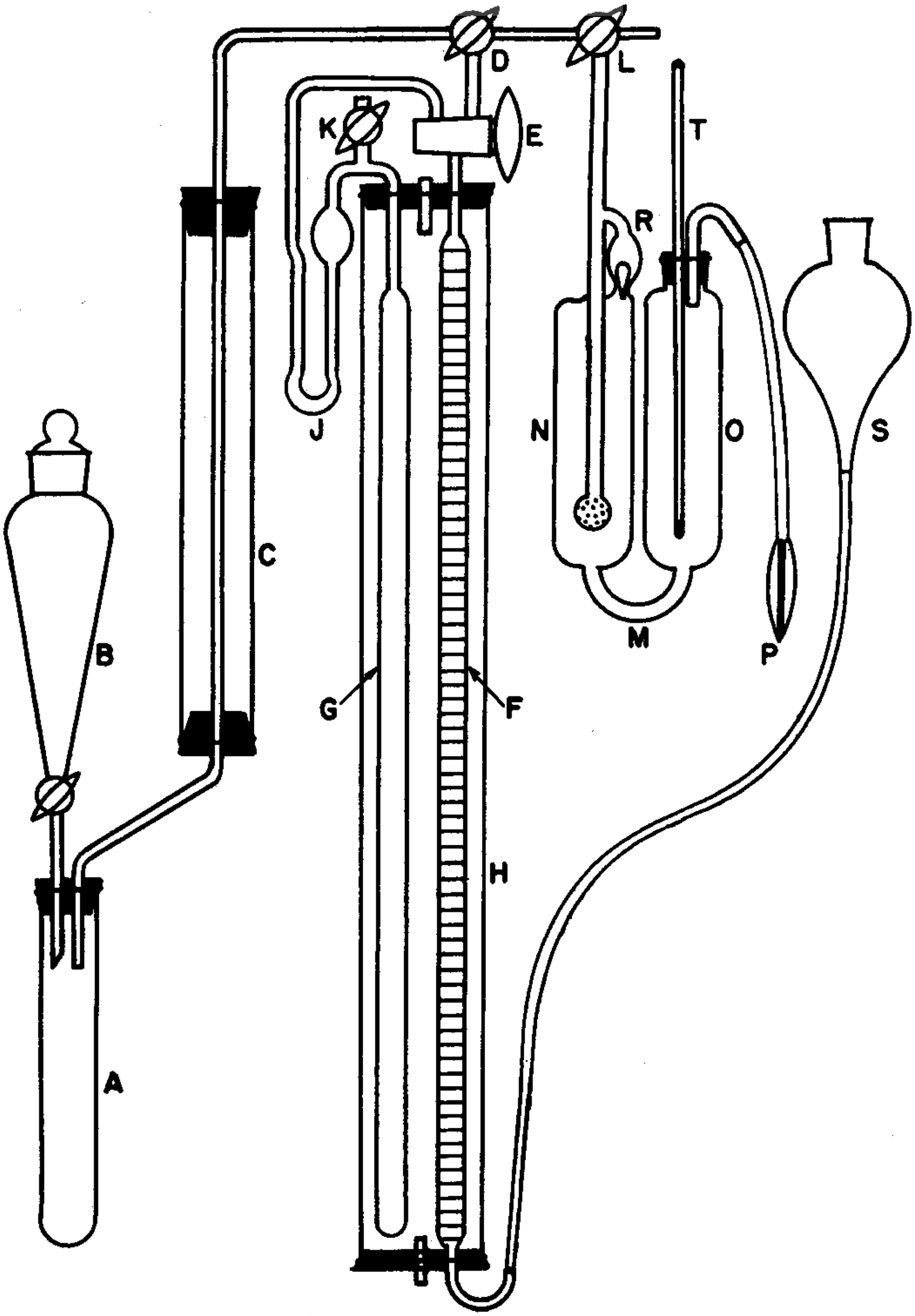


Figure 11. Schematic Diagram of CO_2—Determination Apparatus For Urea Thickeners.

9.3.4 Separation of Urea Thickeners From Base-Oils by Hexane Extraction

The same technique was used as in Paragraph 9.3.3, above. In this case, however, the Soxhlet was equipped with a side stopcock through which one drop of liquid was periodically withdrawn onto a watch crystal. When no oil residue was visible on the watch crystal, the extraction was considered completed, requiring about three hours. Further treatment was the same as above.

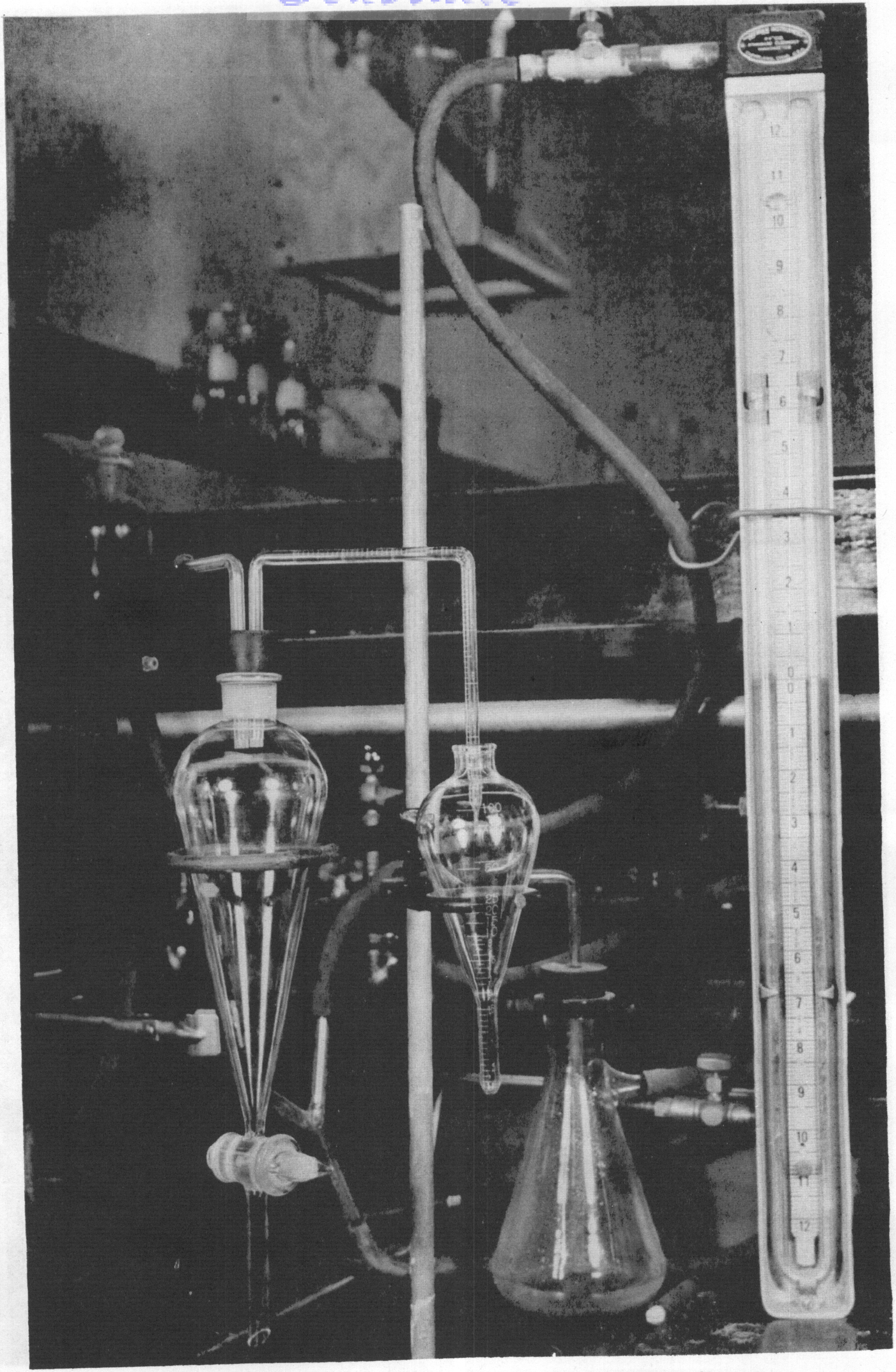


Figure 12. Suction Apparatus For Gelling Agents.

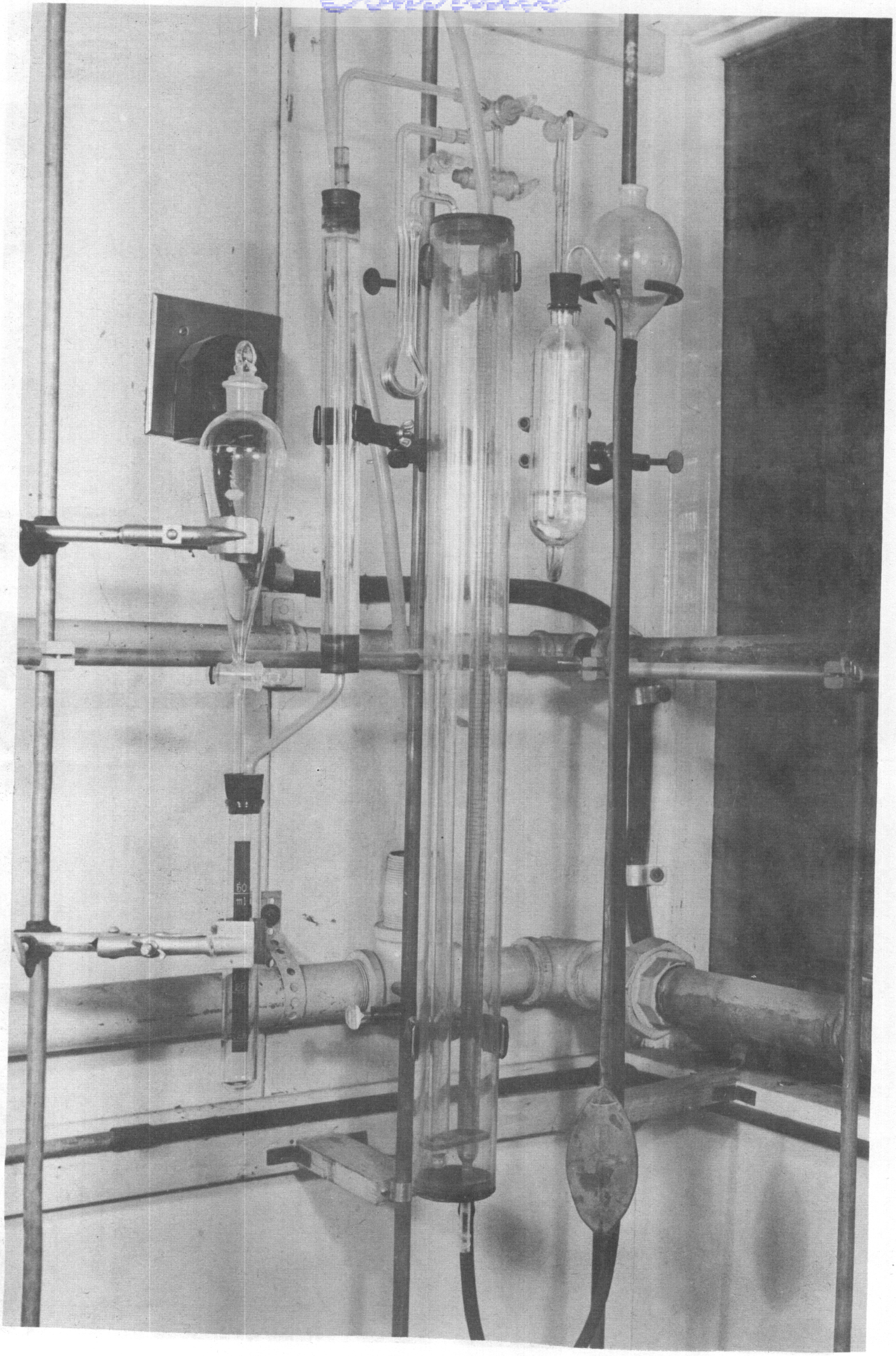


Figure 13. CO_2-Determination For Urea Thickeners.

SECTION C

SEPARATION OF GELLING AGENTS - THICKENERS - BASE-OILS

1.0 INTRODUCTION

Discussion of analytical methods for the separation of gelling agents and of thickeners in Sections A and B revealed that for the determination of certain combinations of gelling agents and/or thickeners with a mixture of base-oils there are different methods of approach for the most effective separation of grease-types into their components. There is, of course, the possibility that a grease contains a mixture of certain combinations of inorganic or organic gelling agents with thickeners and base-oils of different types. Depending on the nature of such combinations, the method of approach must be different. Since in a grease sample the type of combination is unknown, it is of primary interest for the analyst to determine the class of combination to which such a grease belongs before he begins to separate it into its components. In this section the methods of attack on such possible combinations shall be discussed, and a general schematic procedure for identification of the grease type will be presented. In general the following classes of possible combination types for greases can be visualized:

I. Gelling agents - alkaline soap thickeners-base-oil.

II. Gelling agents - aluminum or alkaline-earth soaps - base-oil.

III. Alkaline soaps - aluminum or alkaline-earth soaps - base-oils.

IV. Gelling agents - alkali soaps - aluminum and alkaline-earth soaps - base-oils.

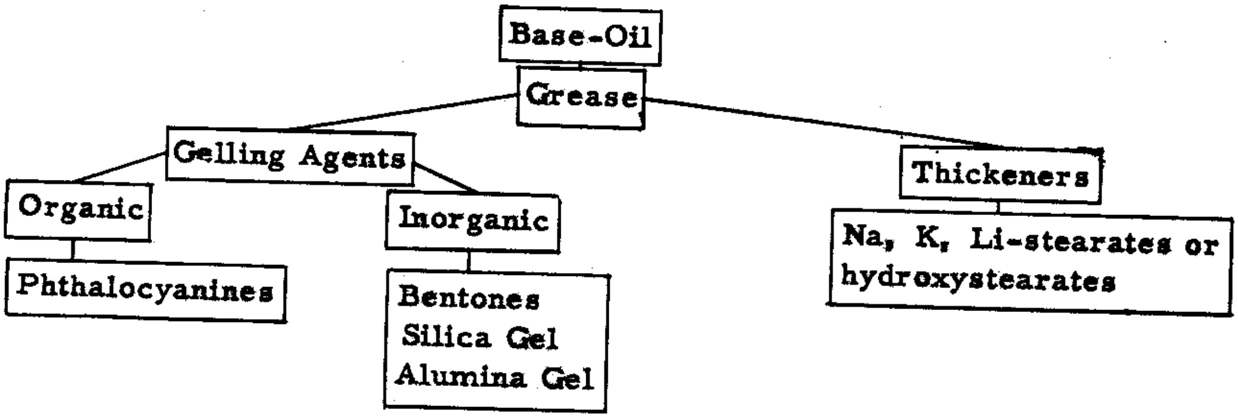
V. Urea type thickeners - base-oils.

The schematic methods for separation of these five combinations will be denoted as Schematic Methods I, II, III, IV, and V respectively.

The schematic analytical procedure for the identification of a grease which will be presented on p. 108, Table XX gives an indication as to which of the five methods should be chosen for a closer determination of the grease in question. It must be kept in mind, however, that such methods and approaches are not rigid rules. A successful analysis will depend very much on the experience of the analyst to estimate from general indications the probable combination of components in the grease and to choose the most effective method for their determination.

2.0 COMBINATION I (GELLING AGENTS - ALKALINE SOAPS - BASE-OILS)

This type of combination can be schematized as follows:



It is not likely that the thickeners would be admixed simultaneously with inorganic or organic gelling agents, but any schematic approach should include such theoretical possibilities.

2.1 QUALITATIVE IDENTIFICATION OF COMBINATION I

A two g. sample of the grease is dispersed in hexane, hot IPA-water mixture is added, and the vessel is shaken and centrifuged. The presence of a cuff at the interface indicates the possible presence of gelling agents. After separation of hexane phase, cuff, and IPA phase, the cuff and the IPA phase are investigated separately:

(1) Cuff:

(A) Cuff a blue or green color indicates phthalocyanines. Treat with con. H_2S0_4.

(a) If cuff is completely soluble in the acid, leaving no residue, only phthalocyanines are present.

(b) If cuff is partially soluble and leaves a residue, the possible presence of inorganic gelling agents is indicated.

(B) Cuff white or cream color indicates the presence of inorganic gelling agents and absence of phthalocyanine.

(2) IPA extract is acidified with HCl (1:1) and heated for several minutes. After cooling, it is extracted with ether and separated.

(A) Aqueous phase will contain chlorides of Na, K, Li. Identification of one or more of these ions indicates presence of alkali soaps.

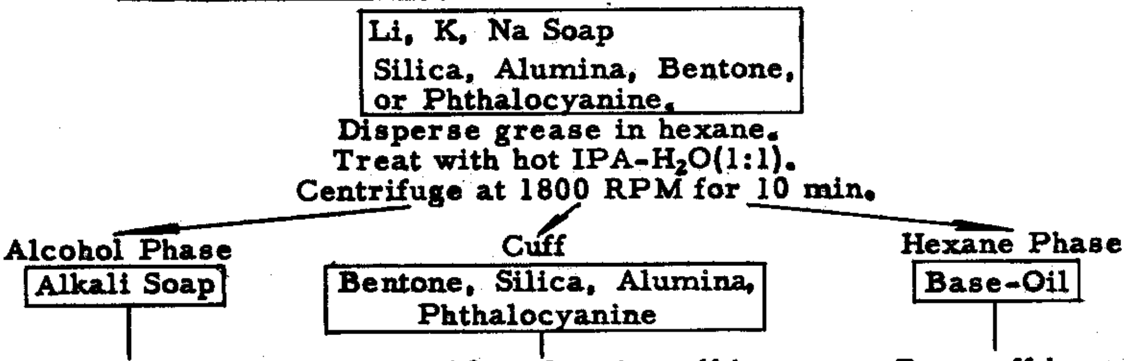
(B) Ether extract: evaporate ether. White platelet-shaped crystals indicate fatty acid. Recrystallize from boiling alcohol and determine melting point.

2.2 QUANTITATIVE SEPARATION OF COMBINATION I

The quantitative separation follows the same pattern as the qualitative identification set forth in Par. 2.1 above and described in more detail in Section B, Par. 4.3, p. 64, for the separation of alkaline soaps from base-oils. The presence of gelling agents does not interfere with separation of the alkaline soap thickeners, if adequate precaution is taken in washing the cuff several times with hexane and IPA-water mixture to extract completely residual base-oil and soap. Thus, the following schematic separation method can be followed:

SCHEMATIC METHOD I

Grease With Gelling Agents - Alkaline Soap - Base-Oil



Evaporate aliquot part of alcohol-water mixture to dryness. Dry in vacuum at 50°C. Weigh. Retain remainder of mixture for

After drawing off hexane phase, wash three times with 20, 15, and 10 ml. hexane to remove residual oil. Add washing to hexane phase. Wash cuff

Draw off hexane in separatory funnel. Wash three times with hot IPA-water. Return washings to alcohol phase. Distill off further analysis for metal ions Li, Na, K, and for fatty acids (Section B, Par. 4.3, p. 64).

with hot alcohol-water mixture three times to remove soap from cuff. Centrifuge and remove alcohol phase by suction each time. Slowly dry cuff on water bath, after removing alcohol phase, then in vacuum at 50°C. Weigh. If needed, take aliquot part to analyze for bentone nitrogen, alumina, silica, and phthalocyanines (Section A, Par. 4.3, p. 46).

hexane. Dry oil in vacuum at 50°C. Weigh.

2.3 FEASIBILITY OF THE METHOD

The feasibility of Schematic Method I is demonstrated in a series of separation tests presented in Table XVIII. The results of these analyses are in good agreement with the actual values;

TABLE XVIII

Separation of Gelling Agents - Alkaline Soaps - Base-Oils

Grease Type	Number of Runs	Base-Oil %		Gelling Agents%		Alkaline Soap%	
		Present	Found	Present	Found	Present	Found
IVB100	3	80	79.1	8	8.2	12	11.8
IB7c3	3	83	82.0	3	2.6	14	14.5

3.0 COMBINATION II (GELLING AGENTS - ALUMINUM AND ALKALINE-EARTH SOAPS - BASE-OILS)

3.1 QUALITATIVE IDENTIFICATION OF COMBINATION II

The qualitative identification of Combination II follows essentially the same procedure as that presented in Par. 2.1, p.98, with the following modification: at point 1-B in the procedure, the cuff must be treated with hot HCl (1:1) to hydrolyze Al or alkaline-earth soaps present. After extraction with ether, the metals from the soap can be detected in the aqueous phase, and fatty acid can be identified in the ether extract by routine tests.

3.2 QUANTITATIVE SEPARATION OF COMBINATION II

Application of the Schematic Method I developed for greases with alkali (Na, K, Li) soap-thickeners and gelling agents to the separation of Al and alkaline-earth soap-thickeners from base-oils and gelling agents resulted in inconsistencies in the quatitative values and other difficulties, which can be summarized as follows:

(a) Small amounts of Al-soap are soluble in the hexane phase when mineral oils are present in the base-oil; therefore, the soap must be removed from the hexane phase before the base-oils are further investigated.

(b) Metathesis of alkaline-earth soaps by hydrolysis with cold acetic or hydrochloric acid in the presence of an inorganic gelling agent results in the formation of a heavy gel. This gel is very stable and the stearic acids cannot be extracted quantitatively from it.

(c) If acetic acid is used for the hydrolysis of the Al-stearate, a part of the acetic acid is carried along in the separation process as acetate and complicates the final separation of stearic acid.

Because of these factors, the separation method developed for separation of alkali soaps from base-oils had to be modified. Attempts to extract first the base-oils from the gelling agent and Al-soap before metathesis, followed by hydrolization of the soap with hydrochloric or acetic acid, were not satisfactory. A stiff gel was again formed between the inorganic gelling agent and stearic acid with considerable swelling.

It, therefore, appeared more advantageous to separate the soap itself from the inorganic gelling agents so that gel formation could be avoided. Consequently the solubility of Al-stearate and the alkaline-earth stearates in different organic solvents was checked. This study indicated that esters, particularly amyl acetate, are good solvents for both the alkaline-earth soaps and base-oils. A series of extraction runs with different types of greases was carried out with amyl acetate, the results of which are shown in Table XIX.

These results indicated that base-oil and alkaline-earth soaps can be extracted with amyl acetate and hence separated from the inorganic gelling agents quantitatively, within the limits of error. It was found that an extraction from six to eight hours was sufficient to achieve the recoveries shown in the Table, and that longer runs did not increase the percent of recovery. After the extraction the amyl acetate was removed by distillation, resulting in reformation of the alkaline-earth soap grease which no longer contained the inorganic gelling agents. The soap and base-oil could then be determined by the modified method (see Section B, Par. 6.0, p. 70) with no difficulty from gel formation.

The amyl acetate extraction of base-oil and alkaline-earth soap greatly facilitates the analysis of greases, since it immediately isolates the entire group of inorganic gelling agents in the first step of the analytical procedure. In addition, it removed most of the antioxidants which frequently are strongly adsorbed in the bentones.

TABLE XIX

Extraction of Base-Oil and Al-Stearate Soap From Inorganic Gelling Agents With Amyl Acetate

Mixture or Grease	No. of Runs	Gelling Agent%		Soap and Base-Oil%		Antioxidant%		Total
		Present	Found	Present	Found	Present	Found	Recovery%
Mixture: Al-Stearate Bentone-34	2	50.1	49.46	49.9	49.34	----	----	98.80
ID300*	2	4.5	4.45	95.5	94.47	----	----	98.92
ID1a0	2	7.5	7.48	91.5	91.38	1.00	0.83	99.69
I, II, D1b0	2	10.0	9.85	88.0	87.64	2.00	1.86	99.35
II, IV, D300	1	4.7	4.55	95.3	94.17	----	----	98.72

* DRI Classification

3.2.1 Runs With Mineral Oil-Dibasic Acid Ester Mixtures

In order to investigate the feasibility of the amyl acetate extraction, runs with mixtures of mineral oil and dibasic acid esters were carried out. The results of these runs showed that in the presence of these mixtures quantitative separation of alkaline-earth soap and base-oil from gelling agents is possible. Separation of the soap from the base-oil combination followed the routine method developed for the metathesis and separation of such soaps. In case antioxidants are present, the extraction time must be extended about six hours because antioxidants, particularly the phenothiazine types, are usually more strongly adsorbed in the bentone than are the base-oil components.

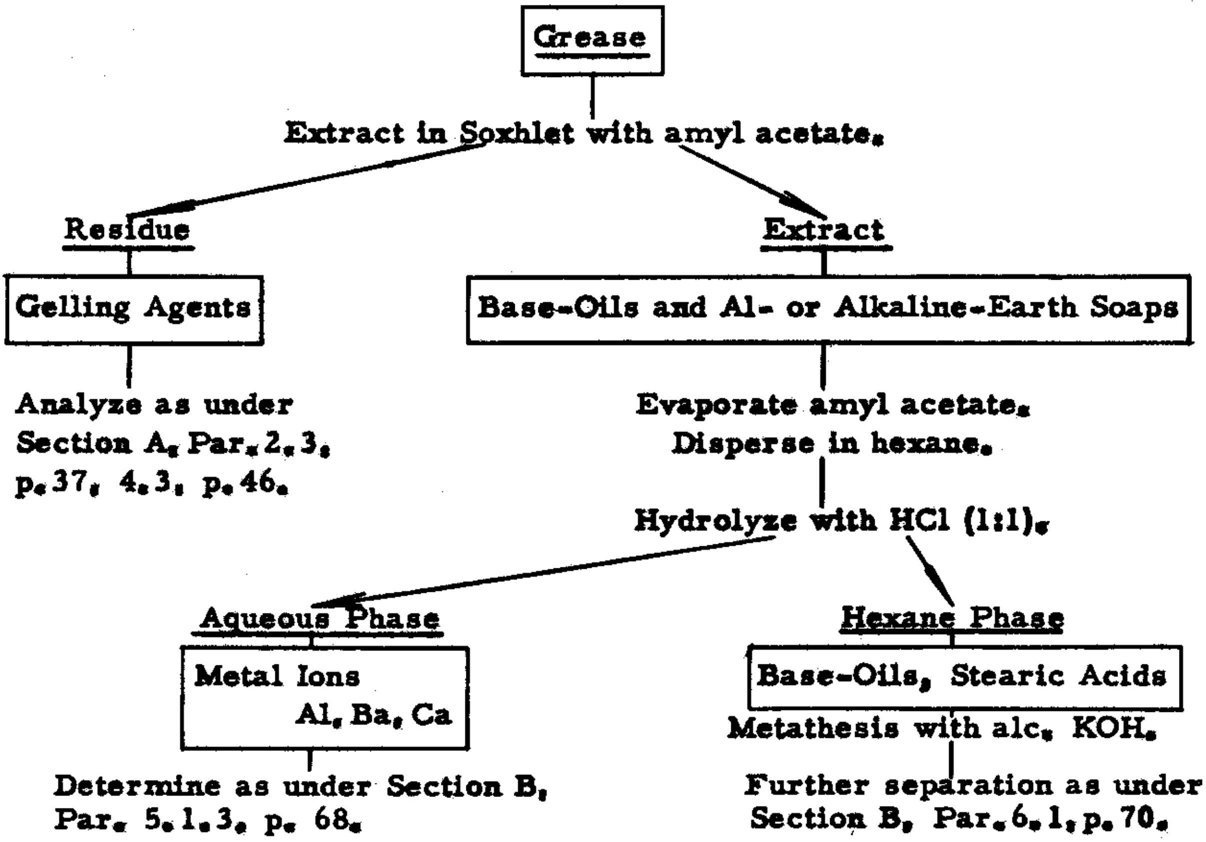
3.2.2 Runs With Mixtures of Dibasic Acid Esters and Silicone Fluids

Several runs were made by submitting a mixture of silicone (Silicone Fluid 550), dibasic acid ester, and Al-stearate soap to the same procedure of extraction in the presence of Bentone-34 as gelling agent. Separation of the soap and base-oils was quantitative. The alkaline-earth soap could be separated afterwards by hydrolysis with cold HCl followed by metathesis to an alkali soap, extraction with IPA-water mixture, and separation from the base-oils.

In all these cases the formation of heavy gels is avoided, regardless of the nature of the gelling agents, e.g., bentone, silica gel, alumina gel, or mixtures. Further separation of the base-oils themselves was not pursued, as this phase of the problem had been planned for Part II of the research program. Thus, in this case the following schematic method of separation can be followed:

SCHEMATIC METHOD II

Grease With Gelling Agents-Al- and Alkaline-Earth Soaps - Base-Oils



4.0 COMBINATION III (ALKALINE SOAPS - ALUMINUM OR ALKALINE-EARTH SOAPS - BASE-OILS)

The simultaneous presence of these two types of thickeners in the base-oils is conceivable. As a matter of fact any Al- or Ba- stearate soap also contains some residual Na-stearate from the manufacturing process.

4.1 QUALITATIVE IDENTIFICATION OF COMBINATION III

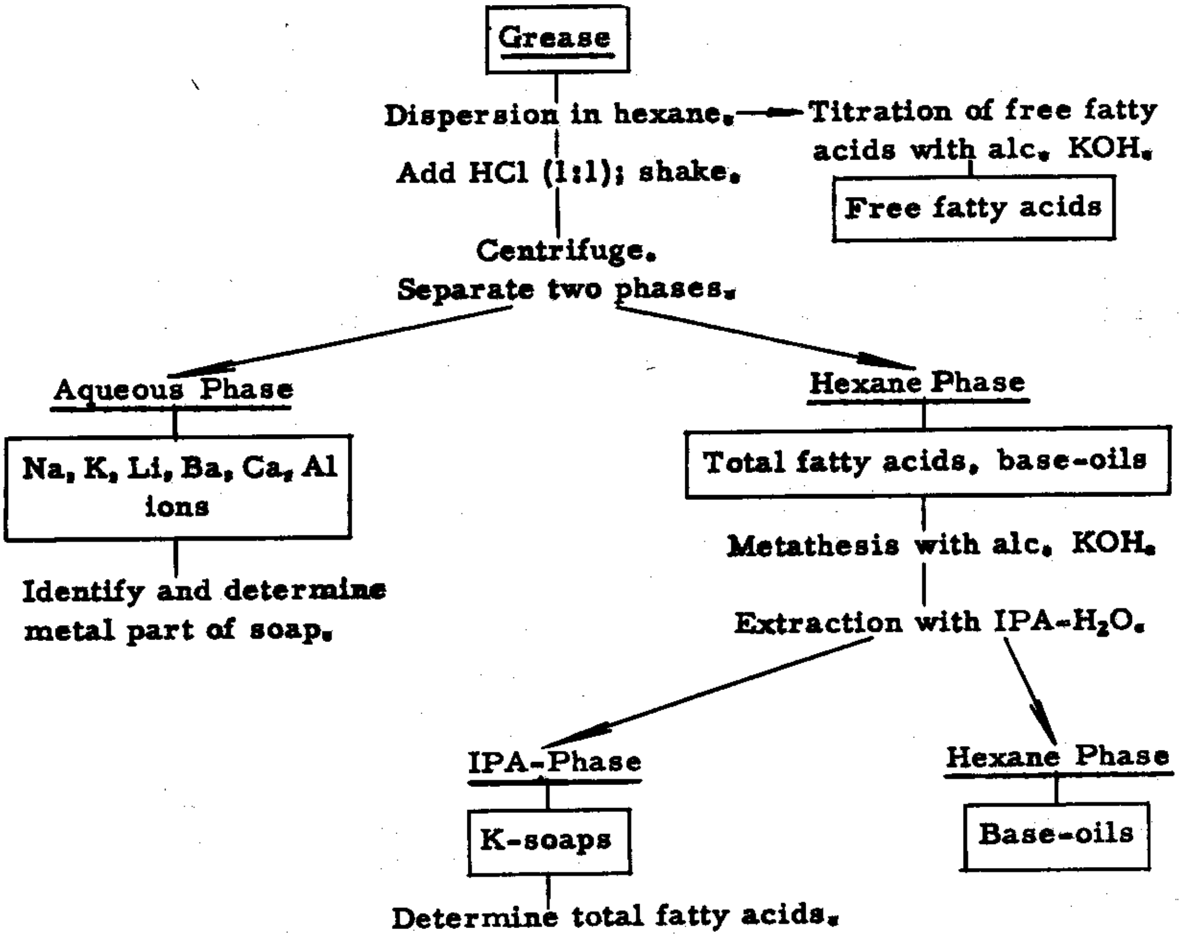
The identification of such a combination is done by dispersing the grease in hexane and treating with IPA-water mixture. The alkaline soap dissolves in the IPA phase, whereas the aluminum or alkaline-earth soaps are practically insoluble in the IPA phase and only slightly soluble in the hexane phase. Therefore, the aluminum and alkaline-earth soaps will concentrate at the interface of the two solvents. After centrifugation and separation of the two phases, the cuff is checked for the presence of Al-stearate. Complete solubility in HCl (1:1) indicates the presence of these soaps. After extraction of the fatty acids with ether, the metal ions can be identified in the aqueous solution. The check for Al- and Ba-stearate soaps can also be done at once in the centrifuge tube. After centrifugation and separation of the cuff, the HCl (1:1) is added to the centrifuge tube, shaken, and again centrifuged. Disappearance of the cuff at the interface indicates that only Al- or alkaline-earth soaps are present. In the IPA phase the alkaline soaps can be identified in the routine manner.

4.2 QUANTITATIVE SEPARATION OF COMBINATION III

The quantitative separation of such a combination would proceed similarly to separation of Al soaps from base-oils (see Section B, Par. 6.0, p. 70). After dispersion of the grease in hexane, hydrolysis of the Al or alkaline-earth soaps is carried out as demonstrated with cold HCl (1:1). In the aqueous phase the metal ions from both thickeners can be determined. In the hexane phase all stearic acids from both soap types are present. The total free fatty acids can be determined in the hexane dispersion by titration with alc. KOH. From the amount of total fatty acids, free fatty acid, Na, K, or Li, the distribution of the fatty acids between the alkaline soaps, Al-soaps, or alkaline-earth soaps can be estimated. Thus in this case the following schematic separation method can be followed:

SCHEMATIC METHOD III

Grease With Alkaline and Aluminum or Alkaline-Earth Soap



5.0 COMBINATION IV (GELLING AGENTS - ALKALI SOAPS - ALUMINUM OR ALKALINE-EARTH SOAPS - BASE-OILS)

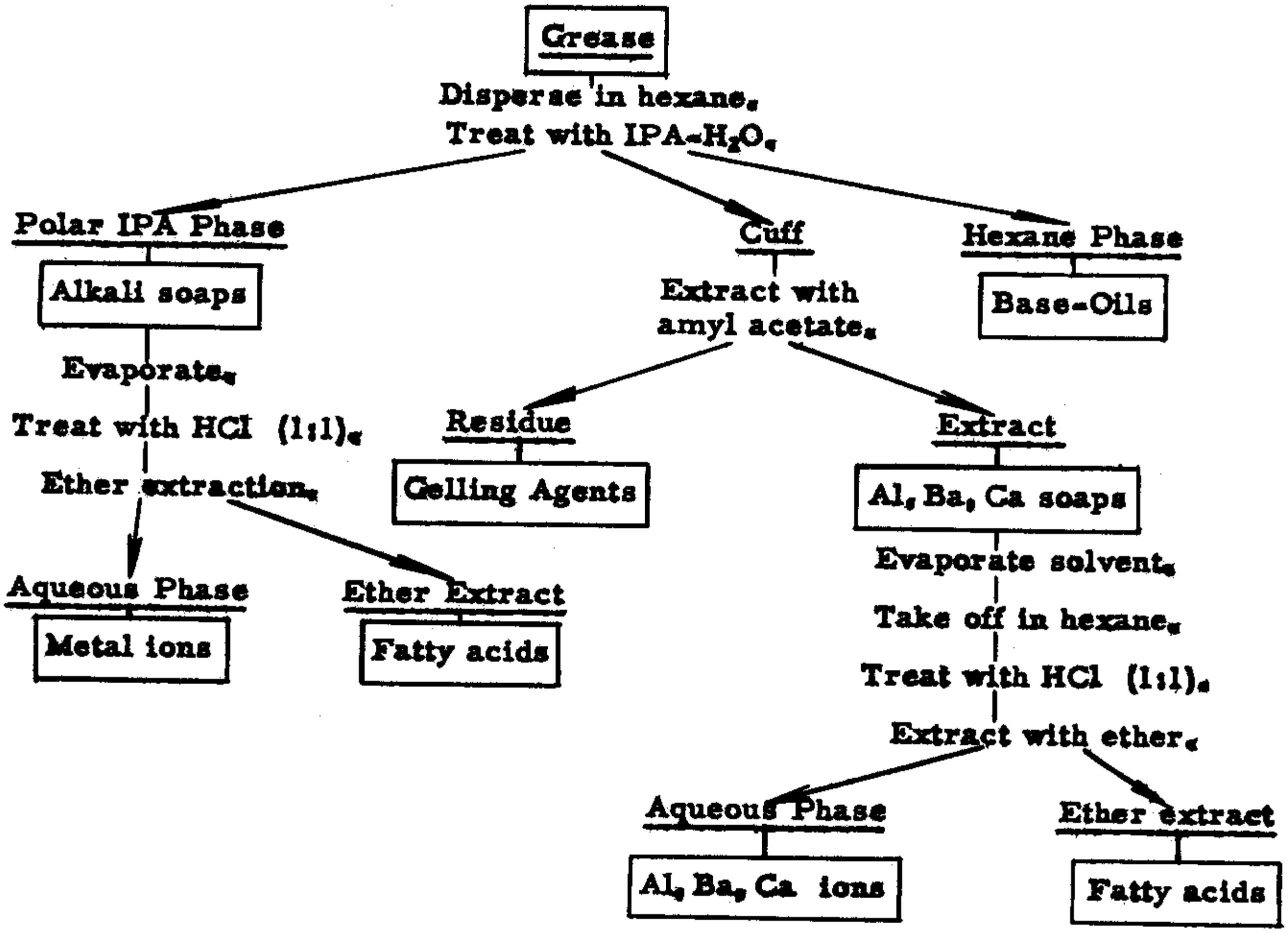
This type of combination is a theoretical one, because it is very improbable that such a combination would ever occur in the practical formulation of a grease, since the simultaneous presence of different gelling agents and thickeners may cause interference with each other rather than improve the performance properties of a grease. However, because a schematic separation method should consider every major combination possibility, regardless of its practicability, and because such a scheme would be part of a general method for the identification and classification of unknown greases, a short outline of such a method shall be given.

In order to identify the different gelling agents and thickeners in such a combination, the grease would be treated in a manner generally similar to Schematic Method III.

The cuff after centrifugation could contain gelling agents, and also Al- or alkaline-earth soaps. Therefore, the three phases, IPA, hexane, and the cuff, are separated. In the IPA phase the alkaline soaps can be detected; in the hexane phase the base-oils. The cuff is now extracted with amyl acetate which dissolves the Al- or alkaline-earth soaps present. In the residue of the cuff are the gelling agents and in the amyl acetate are the soaps which, after distillation of the amyl acetate, can be identified by their metal ions. The following scheme can, therefore, be followed:

SCHEMATIC METHOD IV

Separation of Gelling Agents - Thickeners - Base-Oils

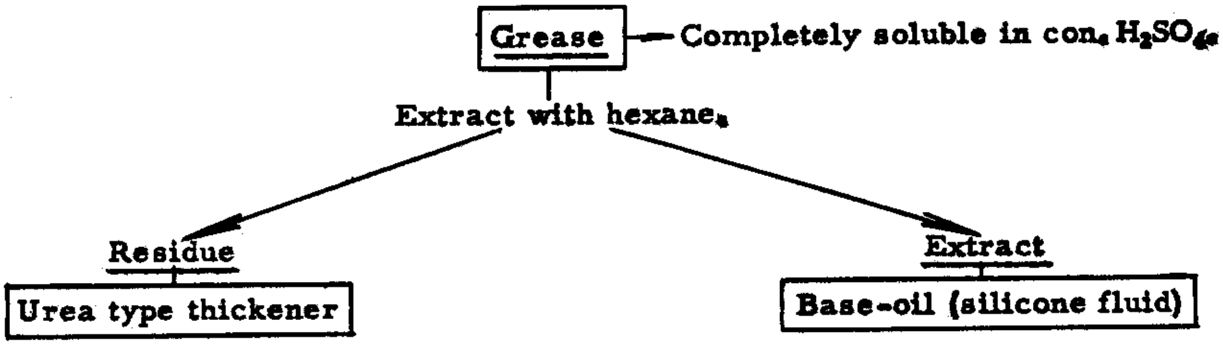


6.0 COMBINATION V (UREA THICKENERS - BASE-OILS)

Because of the special characteristics of urea thickened greases, it is very unlikely that these greases would contain any other gelling agents or soap thickener. Therefore, such greases are identified and separated as discussed in Section B, Par. 8.0, p. 79. This method is, therefore, identical with Schematic Method V:

SCHEMATIC METHOD V

Urea Type Thickener - Base-Oil



7.0 GENERAL METHOD OF APPROACH FOR THE IDENTIFICATION, SEPARATION, AND DETERMINATION OF SYNTHETIC GREASE TYPES

With the application of the different schematic methods described above a general schematic approach for the identification and separation of the different types of greases can be visualized. Once the general type of grease is identified, the proper method for further quantitative separation can be chosen. The schematic procedure for such a separation should consist of the following steps:

(A) Determination of physical constants of the unknown grease as, for example, dropping point, penetration, etc.

(B) General appearance of the grease can give some indication with respect to the grease type:

  (a) Clear, jelly-like, and light honey-colored greases indicate aluminum or alkaline-earth soap thickeners.

  (b) Pinkish, opaque color may indicate urea type grease.

(c) Intense blue or green greases, especially when smeared on a white procelain plate, indicate phthalocyanine gelling agents.

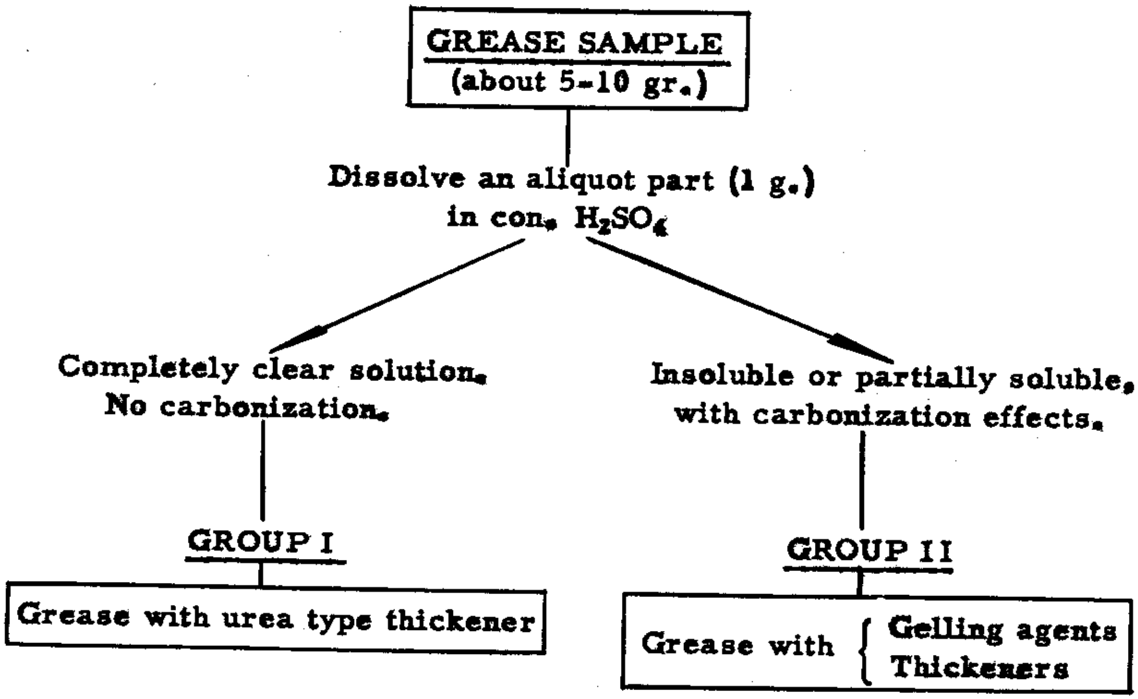
(d) Creamy or white opaque greases may indicate bentone or other inorganic gelling agents.

(C) Chemical group identification of the grease.

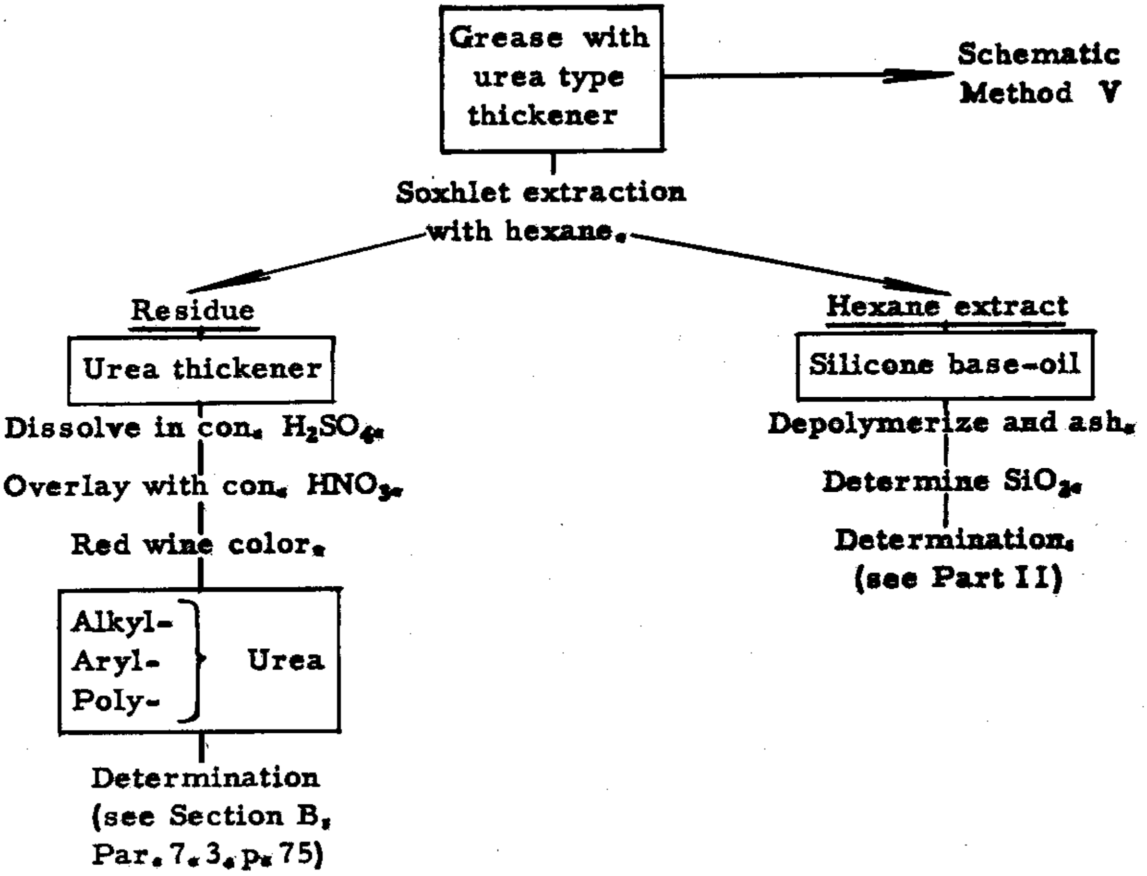
The more precise identification of the type of grease present in an unknown sample is based on the different solubilities of its components in different solvents and upon the specific reactions of those components. For the determination, a sample of 5-10 grams is sufficient. This sample is divided into several aliquot parts of about 2-3 grams each. The schematic procedure for the analysis of such synthetic greases is presented in Table XX.

TABLE XX

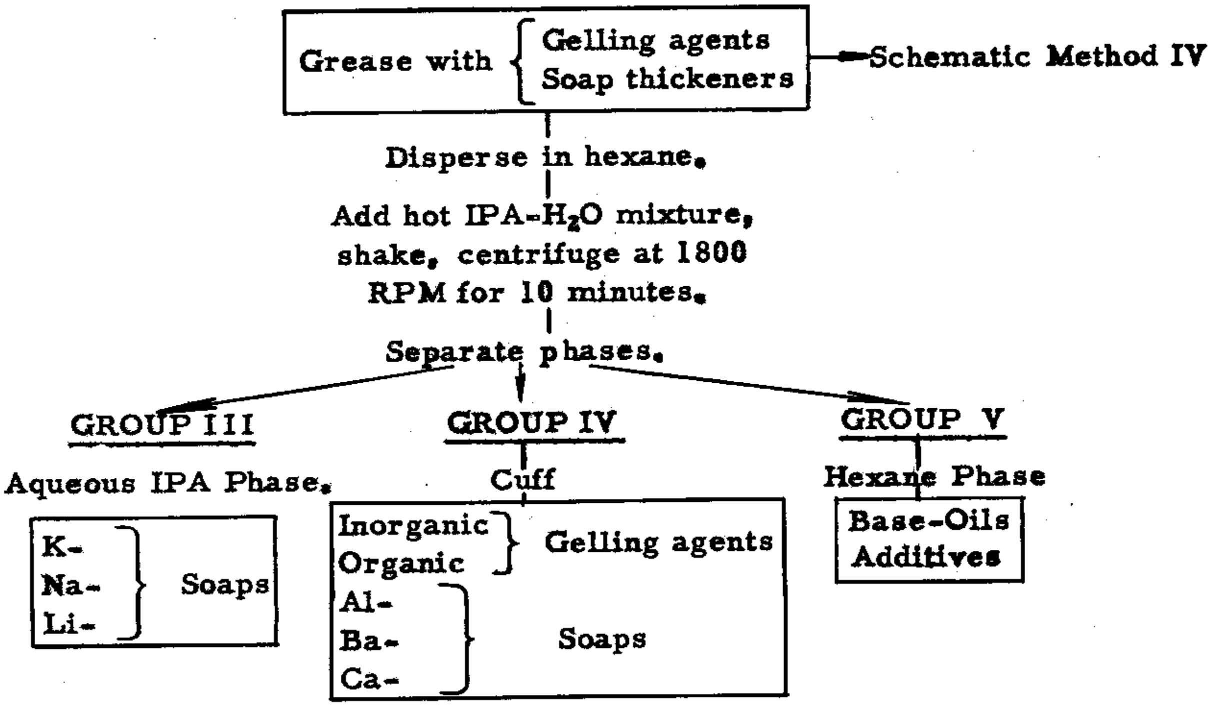
Schematic Analytical Procedure for the Identification and Separation of Synthetic Greases



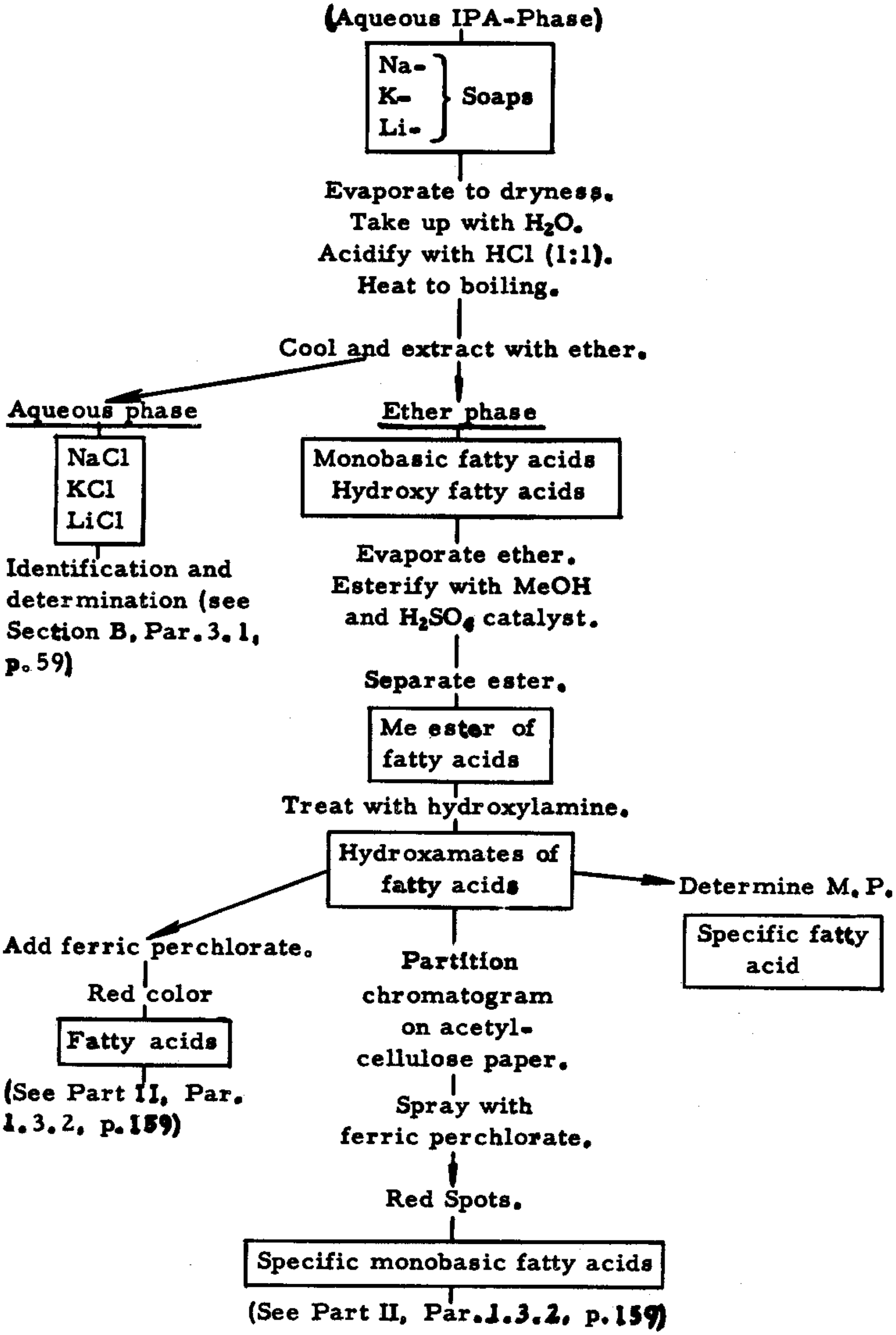
GROUP I



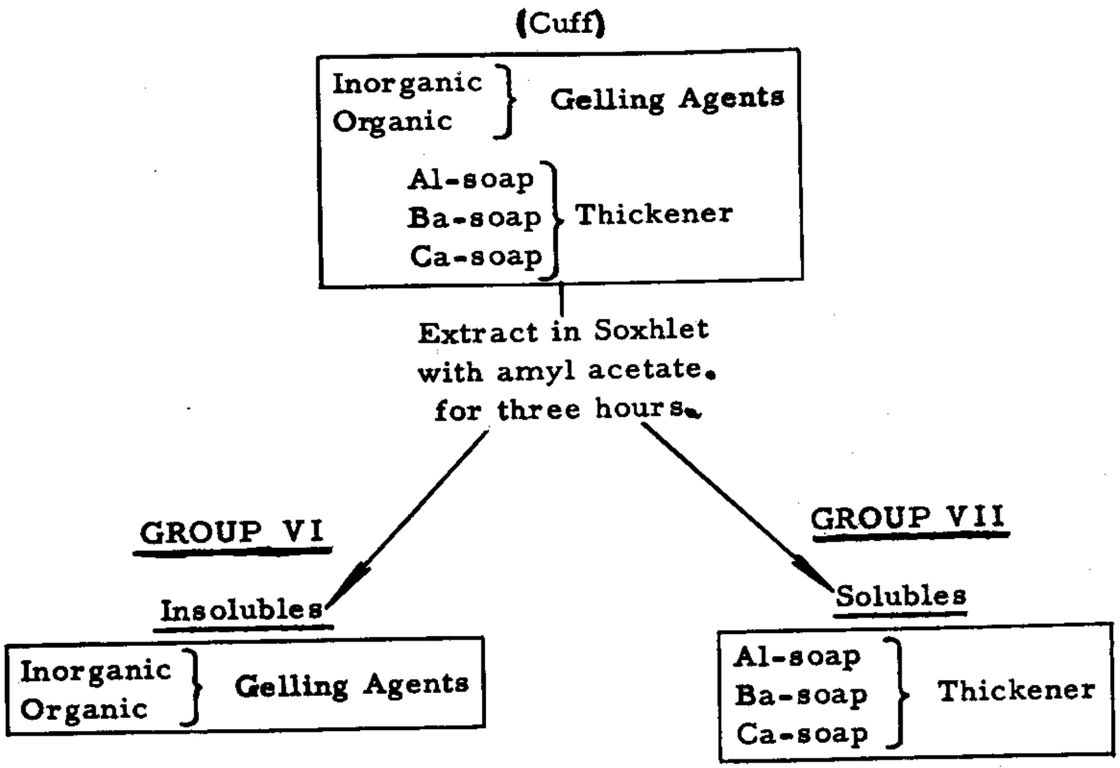
GROUP II



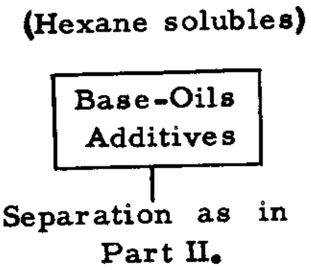
GROUP III


(Aqueous IPA-Phase)
Na-
K-
Li-
Soaps
Evaporate to dryness.
Take up with H_2O.
Acidify with HCl (1:1).
Heat to boiling.
Cool and extract with ether.
Aqueous phase
NaCl
KCl
LiCl
Identification and determination (see Section B, Par. 3.1, p. 59)
Ether phase
Monobasic fatty acids
Hydroxy fatty acids
Evaporate ether.
Esterify with MeOH and H_2SO_4 catalyst.
Separate ester.
Me ester of fatty acids
Treat with hydroxylamine.
Hydroxamates of fatty acids
Determine M.P.
Specific fatty acid
Add ferric perchlorate.
Red color
Fatty acids
(See Part II, Par. 1.3.2, p. 159)
Partition chromatogram on acetyl-cellulose paper.
Spray with ferric perchlorate.
Red Spots.
Specific monobasic fatty acids
(See Part II, Par. 1.3.2, p. 159)

GROUP IV

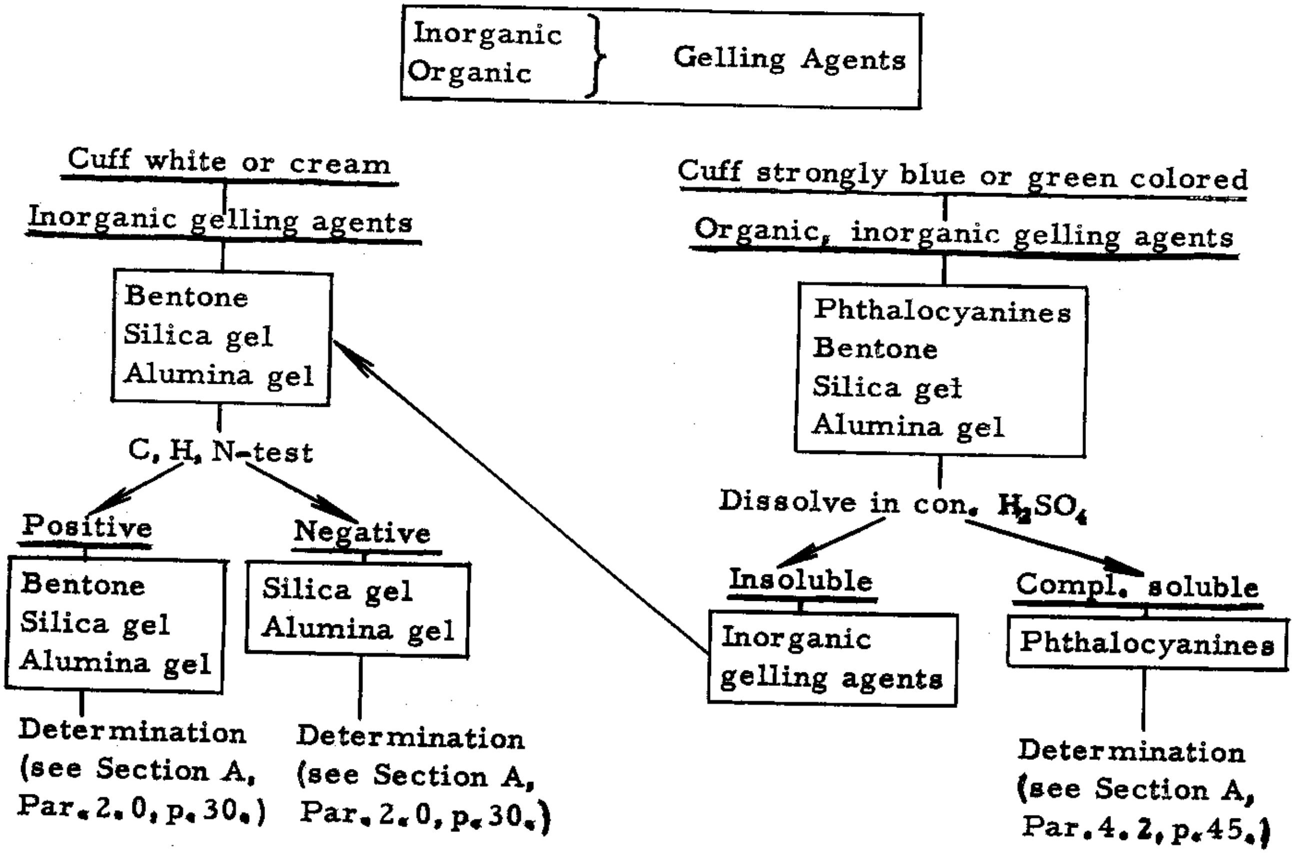


GROUP V



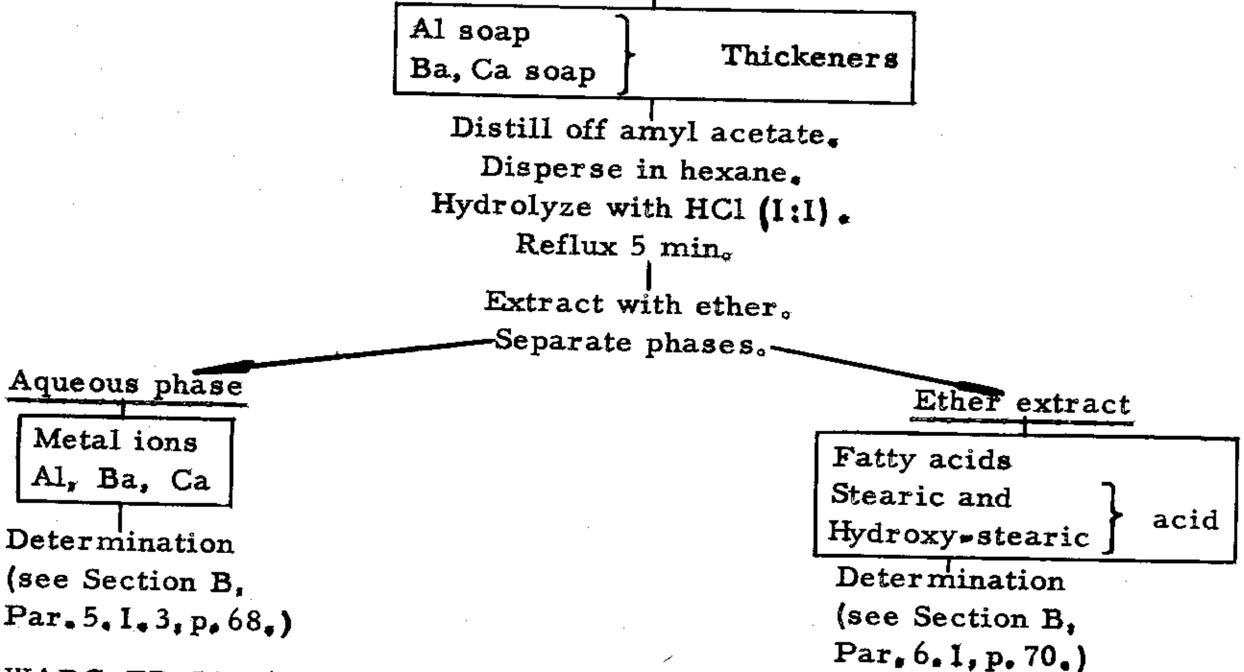
GROUP VI

(Insolubles in cuff)



GROUP VII

(Solubles from cuff extraction)



7.1 FEASIBILITY OF THE ANALYTICAL SCHEME FOR THE SEPARATION OF SYNTHETIC GREASES

Although most of the separation steps presented in groups I-VII of the analytical scheme have been confirmed by experimental investigations, the schematic procedure is not complete and does not claim to be complete. This scheme was developed from experiences gained with the analysis of different test greases. These greases, in order to avoid unnecessary complications had none or only a restricted number of other additives such as antioxidants, corrosion inhibitors, etc. The presence of such additional compounds in the grease may very well influence the method of separation. It is intended to investigate these influences in the course of an extended research program.

As an example, the presence of Ba-sulfonate inhibitor may lead to a misinterpretation of the Ba ions present and interfere with the detection of Ba-stearates. The presence of sorbitan-mono-oleate can cause interferences with fatty acids, etc. In a later more elaborate scheme these influences will be considered. In most cases it will probably be necessary to determine these compounds before the actual schematic procedure is used in order to take into account all possible sources of interferences. The methods for the analysis of such additives is the incentive for the following chapter and a part of an extended research program. The general methods of approach presented above, however, will not change drastically and may, therefore, be used as a general guide for the analysis of synthetic greases.

SECTION D

ANTIOXIDANTS

I.0 INTRODUCTION

The formulation of synthetic greases includes, besides specific gelling agents and thickeners, the admixture of small amounts of other chemical compounds, so-called additives, which improve the stability and performance of a grease. The most important and commonly used additives are antioxidants and corrosion preventive agents. Both types of additives are used to improve the characteristics of synthetic lubricating oils, and since these oils are used for the preparation of greases, they will consequently be found in such greases. Thus, the discussions and methods of determination developed for the analysis of antioxidants in greases will consequently also apply to the analysis of these compounds in the base-oils or lube-oils themselves.

The basic function of antioxidants is to prevent the formation and accumulation of oxidation products formed from lubricating greases and fuels during the performance of the component in which they are used. Considerable efforts have been made to elucidate the mechanism of breakdown through oxidation of the organic materials during operational performance. Based on these investigations the most commonly accepted idea today is that all lubricants and combustion fuels are subject to oxidative degradation during storage or performance and that the intermediate compounds so-formed are supposedly certain types of peroxides.

I.1 MECHANISM OF THE OXIDATION PROCESS

It is the function of antioxidants to break up peroxide compounds formed during operation and to take up the oxygen generated from the peroxides. Elimination of the peroxide by the antioxidants breaks the chain reaction of auto-oxidation of the lubricant, which is the determining factor in the oxidation of the lube-oils. This function of susceptibility for peroxides determines the physical and chemical properties of a compound which possibly could be used as an antioxidant; in other words, the type of organic molecules which have potential feasibilities to serve as antioxidants. Depending upon the ability of the antioxidant to accept the oxygen from the peroxides to form a stable compound, or the ability to restore the original configuration, an antioxidant can be either of the sacrificial or the regenerating type.

The number of compounds investigated in the past few years as potential antioxidants is very large. A short account (247) revealed about 3000 specific compounds. The actual number of feasible compounds used in practice as antioxidants is, however, restricted to a few larger groups.

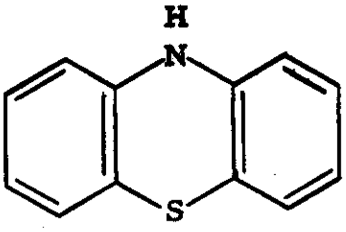
1.2 TYPES OF ANTIOXIDANTS

From the viewpoint of their chemical structures and chemical properties and thus also from the viewpoint of the analyst, three larger groups of antioxidants can be distinguished:

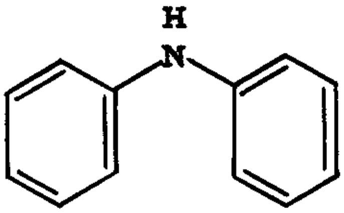
(1) Amine-type antioxidants.

(a) Phenothiazine-type antioxidants with the typical example of phenothiazine itself (I).

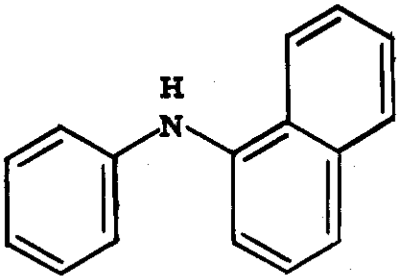
(b) Aromatic amine type antioxidants, related to phenothiazine, with diphenylamine and N-phenyl-1-naphthylamine as examples (II, III).



(I)



(II)

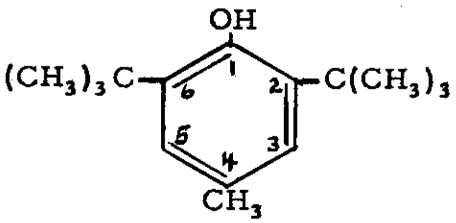


(III)

These shall be referred to as N-type antioxidants in further discussions. The mechanism of their action seems to be due to their ability to form resonance-stabilized free radicals capable of reducing peroxides.

(2) Phenolic-type antioxidants.

A typical example of this group are the hindered phenols, such as 2,6-ditertiarybutyl-4-methylphenol (IV). In this compound the OH group is hindered, i.e. inactivated so far as to supress the normal phenolic reactions (for instance, to oxidize with air oxygen), but still have enough activation energy to act as an antioxidant.



(I V)

(3) Organic selenide compounds, especially seleno-ethers.

These compounds are very effective antioxidants, superior to the respective sulfur compounds. Acting as antioxidants, the seleno-compounds reduce organic peroxides from lube-oils, the seleno-ethers being transformed into selenoxides but not in the hexavalent state. Since such selenoxides decompose thermally, a part of the antioxidant is regenerated. A typical example of such a compound is dilauryl selenide (V).

$$Se(C_{12}H_{25}O)_2 \qquad (V)$$

Although there are a great number of other types of compounds which may be used as inhibitors, these three groups of compounds are actually used at the present time as antioxidants in synthetic lubricants and greases; therefore, emphasis has been placed first on the analysis of these groups of compounds only.

1.3 METHODS OF ANALYSIS FOR ANTIOXIDANTS

Although there are a number of possible color reactions for determination of both amine-type and phenolic-type antioxidants as well as for the selenide type antioxidants, the use of such color reactions for qualitative identification and quantitative determination is limited. The reason is, of course, the small quantity of antioxidant (0.05-2%) present along with such a great number of quite complex organic molecules which on the one hand make separation very difficult, and on the other hand affect the qualitative and quantitative determination. This is particularly the case with certain phenolic type antioxidants, such as the hindered phenols. Therefore, many methods developed to date employ infrared spectroscopic methods for the identification of antioxidants.

However, in certain cases the application of colorimetric methods is possible, and a few of these methods for qualitative and quantitative determination of AO*were developed in this Institute. Nevertheless, because the contractual requirements were of such nature as to avoid all types of more elaborate colorimetric methods, this approach had to be abandoned and another technique developed for solution of the problem.

From experiences in connection with similar problems, it appeared that application of paper partition chromatography for the identification and quantitative determination of AO would possibly be a feasible and uncomplicated method of choice. In the course of the investigation this proved to be the case, and it was shown that this relatively new analytical method will probably be a generally applicable tool for the analysis of AO in synthetic lubricants and greases. In addition, this method could also be extended to the separation and determination of base-oil constituents like monobasic and dibasic esters, corrosion preventive agents, some types of organic phosphoric esters, and also, in connection with column chromatography, to a certain extent for separation of polymer compounds.

2.0 GENERAL PRINCIPLE OF PAPER PARTITION CHROMATOGRAPHY

Although the technique of partition paper chromatography is used in more and more different fields of chemical analysis and several good books dealing with this topic are available (316, 317, 320, etc.), it should not be out of order to outline briefly its general principle before specific methods are discussed. However, since the aim of this report is the practical analysis of lubricant constituents, details of the technique and practices will be kept to a minimum, and the operator should consult the respective manuals to gain a complete picture of the technique. A series of good laboratory manuals on this topic are listed in the bibliography.

Paper partition chromatography was developed to its present stage by Consden, Gordon, Martin, and Synge. Its principle is based on the fact that a solute may be separated from another solute

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* AO = antioxidant

in solution by shaking the solution with an immiscible solvent in which one of the solutes is more soluble than the other. Any desired degree of separation may be obtained by a repetition of the process. Partition chromatography makes use of this principle, but instead of working by discontinuous steps the mixed substances are applied to an inert solid support which holds one of the liquid phases statically (stable phase), while a second phase is allowed to flow continuously down or upwards. Such an inert support can be for example a column of silica gel. If, instead of silica gel, cellulose filter paper is used as the solid inert support for the stable phase, then such a technique is called paper partition chromatography.

In the case of normal paper partition chromatography, the stable or static solvent is H_2O, which is held firmly by capillary forces in the filter paper. The movable phase is usually an organic solvent such as butyl alcohol. If a substance A is slightly soluble in water and fairly soluble in butyl alcohol, then such substance A applied to the paper will be carried along by the organic phase if the butyl alcohol is allowed to run on the pre-wetted filter paper; if a substance B is more soluble in water than A, it will be carried along by the butyl alcohol less distance than A in the same period of time, and thus the two substances can be separated. For practical purposes the movable and stable phases are applied simultaneously, i.e., a mixture of the phases runs simultaneously on the paper. This can be achieved by applying a mixture of the stable phase (usually water) and the movable phase. Such mixtures are called solvent combinations.

The method of partition chromatography consists of applying a small drop of the solution containing the substances to be separated with a micro-pipet to a strip of filter paper a short distance from the end immersed in the solvent (start line). The drop is usually a constant volume of the solution of the compounds, e.g. 2.5-5.0 λ*. The drop is allowed to dry and the end of the paper nearest the spot is placed into the developing solvent combination, so that the solvent passes the "spot" by capillary action either upwards or downwards the length of the paper. Although it was originally believed that the paper functioned solely as an inert support for the stationary phase of the solvent combination (in this case water), it was found that in most cases the filter paper acts by a combination of adsorption,

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* One λ (lambda) = 0.001 ml.

partition, and even ion-exchange. Adequate separation and identification of the different substances requires certain technical working conditions which influence the choice of apparatus used for partition chromatography:

(a) Solvents. The solvents used should have a small but definite solubility for the substances to be separated. If the substances are too soluble, they will travel with the "front" of the chromatogram, which means they will be at the top where the solvent wets the dry filter paper; if the substances are too insoluble in the solvent they will not be carried along and remain "sitting" on the start line where the spot first was applied. In general water soluble substances will be separated best with water-containing organic compounds, whereas water insoluble substances but soluble in organic solvents will be separated best by aqueous solutions of organic solvents.

(b) The developing solvent should not move too fast on the paper. (2-3 cm. per hour). This rate of flow will depend on the type of paper used, the type of solvent used, and the temperature at which the chromatogram is run.

(c) The concentration of the solvent should be constant during the run. This can be achieved by running the chromatogram in an enclosed chamber (chromatographic chamber), in an atmosphere saturated with the vapors of the developing solvents, and with a constant temperature.

2.I GENERAL METHODS OF PAPER PARTITION CHROMATOGRAPHY

Many different methods and techniques have been devised for paper chromatography. Some of these methods can be generally adopted for the separation of many classes of compounds; others have a limited application, for instance, the "reversed phase chromatography" for water insoluble compounds.

The main techniques of paper partition chromatography are:

(a) Ascending chromatography.

(b) Circular chromatography.

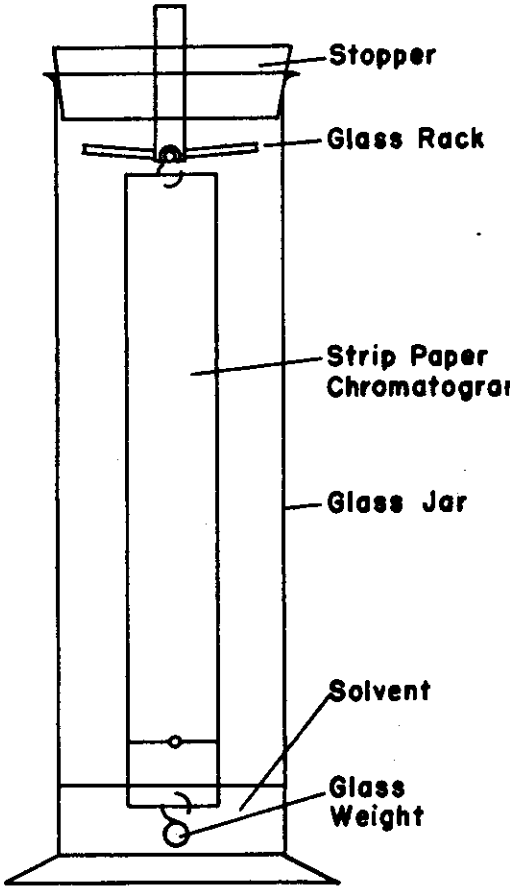
(c) Descending chromatography.

2.2 ASCENDING METHOD

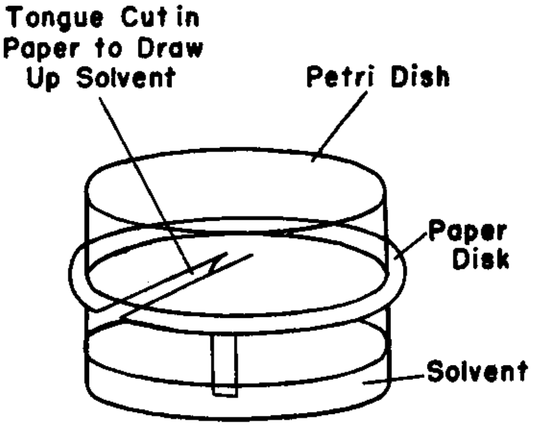
The ascending method has many advantages over other techniques, e.g., consistency of results, simplicity of apparatus, and the ease with which a large number of analyses may be made. The apparatus illustrated in Figure 14 consists simply of an air tight chamber (a glass cylinder can be used). The paper strips are attached to a glass rack which is inserted into the rubber stopper used for closing the cylinder. The solvent is placed at the bottom of the chamber, and after application of the spot the paper strips are immersed about half an inch into the solvent. In order to hold the paper strips straight a glass weight is hooked to the end of the paper. The glass rack can be lowered or raised in the rubber stopper so that the strips, after being exposed for one hour to the vapors of the solvent, may be lowered and immersed in the liquid. The ascending technique is faster than the descending technique and is usually employed for qualitative separations. The spot can be developed after drying the paper by spraying with a suitable color reagent.

2.3 CIRCULAR CHROMATOGRAPHY

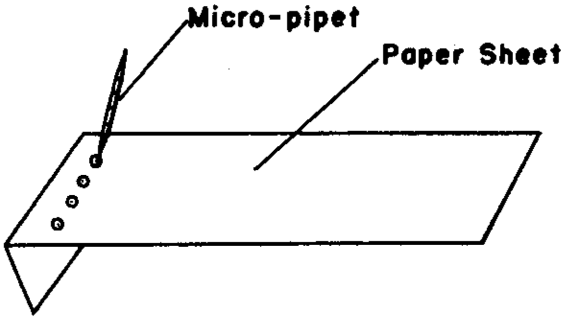
The principle of this technique is that the substances to be analyzed are resolved into circular zones instead of bands and spots. A "tongue" is cut from a circular filter paper disc and immersed into the developing solvents after a drop of the substances to be analyzed has been applied to the paper near the joint. The apparatus, Figure 14, consists of two sections of a Petri dish and a filter paper disc slightly larger than the glass section. The tail or tongue is bent at the joint perpendicular to the plane of the paper and cut down to about 1.5 cm. in length. It is important to note that the cuts are of equal length because otherwise the development may not result in circular zones but rather in ellipses. After the drop to be analyzed has been applied to the paper, the disc is placed between the Petri dishes, the lower of which contains the solvent. Through the "tongue" the solvent rises, and the rate of development may be controlled by the width of the "tongue" and the distance between the surface of the liquid and the paper. For most qualitative separations, development to a circle of six cm. diameter or less is sufficient. This takes about ten minutes. The color development can be made, after the paper disc is dried between blotting papers, by cutting out sectors and impregnating the sectors with a suitable color reagent.



Apparatus for Ascending Chromatography



Apparatus for Circular Paper Chromatography



Placing Spots on the Paper With Micro-pipet

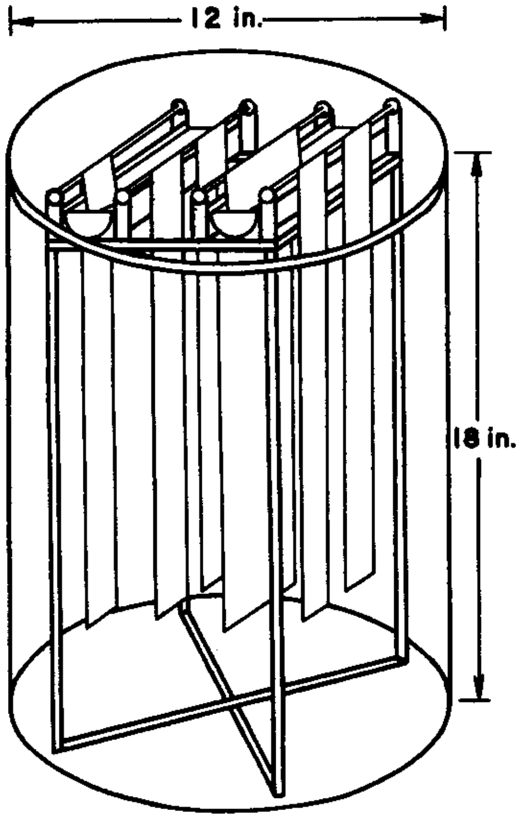
Figure 14. Basic Technique and Apparatus For Partition Paper Chromatography.

2.4 DESCENDING METHOD

The descending method uses paper strips or sheets hung on a rack with the solvents siphoning downwards on the paper. The whole rack is placed in a closed chamber which prior to the actual run is saturated with the vapors of the solvent. The essential parts of the apparatus (Figures 15 and 25) consist of filter paper strips whose upper ends are immersed in a trough containing the solvents. Trough and paper strips are placed in an air tight chamber (e.g., glass jar with glass cover can be used). The atmosphere of the chamber is saturated with water and solvent. This can be achieved by placing one or two Petri dishes with solvent mixtures at the bottom of the chamber. The trough is equipped with a bar over which the paper passes to prevent capillary siphoning. To run off a one-dimensional chromatogram, a strip of filter paper 1.5 cm. in width and 20 to 56 cm. in length is used. A pencil line about 5 cm. from one end is drawn across the strip. The solution (2-5 λ), containing for example approximately 10-50 γ (gamma) of antioxidant, is applied on a pre-marked pencilled circle on the starting line with a micro-pipet. For quantitative runs larger paper strips are used and several drops placed on the start line in 2.5 cm. intervals. The end of the paper is now placed in the trough and held in place by a glass rod weight. Trough and paper are transferred to the chamber which has been previously saturated with the vapors of the two phase mixture. The trough is filled with the developing solvent and the lid put on the chamber. The descending chromatograms run much slower and take an average of 12-15 hours (distance depending on the paper, solvent, and temperature). The paper is removed and the position of the "front" marked. The strip is dried and then sprayed with a color reagent. The spots developed are encircled in case the color should fade later. A simplified apparatus (Figure 15) can be built from a glass jar in which a glass cylinder replaces the rack. The trough can be improvised with a Petri dish. Such an apparatus is adequate when preliminary qualitative runs must be made.

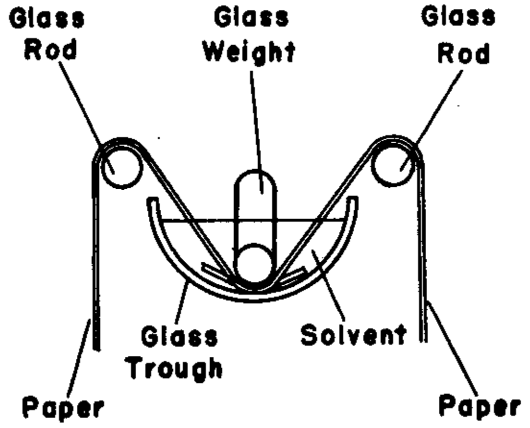
2.5 FILTER PAPER

The type of filter paper used, of course, influences the running of any chromatogram. If consistent and reproducible results shall be achieved, it is necessary always to use the same type of filter paper. For qualitative separations the following types of filter paper are most suitable:

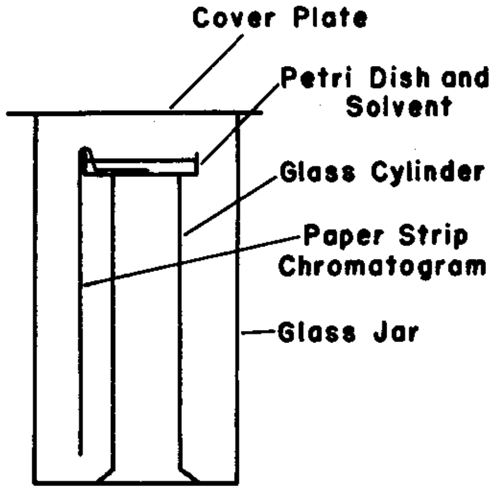


Detail of Large Apparatus
for
Descending Chromatography

(Trough Supports and
Rack Are Stainless Steel.)



Cross-section of Small Trough
for
Descending Chromatography



Simplified Apparatus
for
Descending Chromatography

Figure 15. Apparatus For Descending Paper Chromatography.

Whatman No. 1
Whatman No. 4
Schleicher & Schüll No. 598

For quantitative separation:

Whatman No. 1
Schleicher & Schüll No. 589

2.6 REVERSED PHASE PAPER CHROMATOGRAPHY

In such cases in which the substances to be separated are water insoluble, e.g. certain "hindered phenols," dibasic acid esters, and higher fatty acids, normal filter paper cannot be used because these substances will run constantly with the organic solvent front. In this case the stable and movable phases may be reversed, i.e. the non-polar phase (e.g., benzene) becomes the static phase and the polar solvent (e.g., alcohol) becomes the movable phase. In order to retain the stable non-polar phase on the inert support (filter paper), the latter must be made lipophilic and hydrophobic. This can be achieved in several ways, e.g., by impregnating the paper with vaseline, latex, or with silicone fluids.

It has been found in the course of these investigations that the best results for qualitative and quantitative identification and separation of water insoluble AO and mono- and dibasic acid esters and acids can be achieved by using an acetylated cellulose filter paper with about 23% acetyl-cellulose content. This type of paper has several advantages over normal paper and other impregnated papers. Its preparation along with the laboratory technique is described in detail in the experimental part, Par. 8.0, p.145. Reversed phase paper chromatography will probably have an even wider range of application in the field of synthetic lubricants than normal paper chromatography.

2.7 IDENTIFICATION OF COMPOUNDS - THE R_f-VALUE

Identification of the separated compounds on the paper chromatogram is relatively simple in the case of colored compounds such as dyestuffs. One or more colored spots appear on the chromatogram and can be identified from their color. With colorless substances, however, the "spot" must first be made visible or changed into a colored material, a process called "developing the spot." This can be done either with a suitable color reagent or by investigation of the paper strip under UV light, since many compounds fluoresce and can therefore be detected in this way. Development of the spots is done by spraying the dried strip with reagent from a spray apparatus or by dipping the paper strip in the developing reagent and blotting the excess reagent off. The substance will appear as a colored spot, strip, or circle, depending on the type of chromatography used.

If the chromatogram is run under standard conditions (that is, at a definite temperature and with a specific paper), then for a specific type of solvent combination the relative distance of the spot from the starting line is constant and characteristic for a specific substance. This relative distance is the so-called "R_f-Value" of the substance with respect to the solvent combination used for its separation. The R_f value is determined as the ratio of the movement of the spot to the movement of the advancing front of the liquid and is illustrated in Figure 16.

Thus, in Figure 16 and R_f value of the substance "A" (spot A on the chromatogram) is determined as

$$R_{f(A)} = \frac{X}{Z}$$

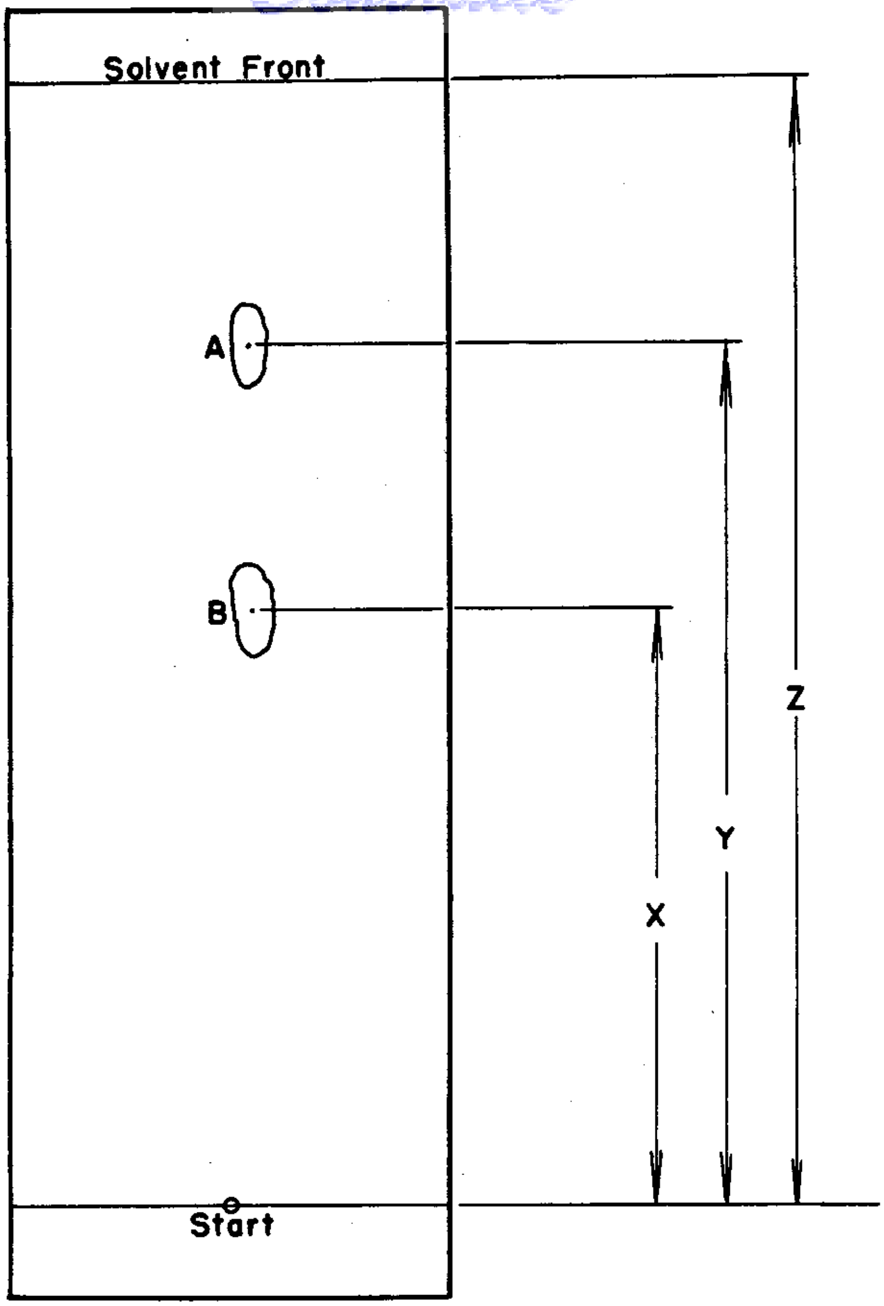
and for the substance "B"

$$R_{f(B)} = \frac{Y}{Z}$$

The distances X and Y are measured from the start line to the geometrical center of the spots A and B respectively, which is also the center of density; and Z is the distance from the starting line to the solvent front. The R_f value of a substance is thus another characteristic value in addition to its other properties, such as melting point, boiling point, density, spectrum, etc.

3.0 FEASIBILITY OF PAPER PARTITION CHROMATOGRAPHY FOR IDENTIFICATION AND DETERMINATION OF ANTIOXIDANTS

The fact that paper partition chromatography is in its principle a micro-method, i.e., it can detect and separate small amounts of substances, would make this technique very suitable for the detection and determination of AOs and other additives (e.g. corrosion inhibitors) present in small amounts in lubricating oils and greases. The question



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

Figure 16. Schematic Determination of R_f-Value on a Paper Chromatogram.

whether these organic compounds can be identified and separated from the rest of the organic components present in the oil is a matter of finding the right solvent combination and color test. Once the general feasibility of the method for a few specific compounds of a certain group of AOs is established, the method is usually applicable to the whole group.

It was therefore the main aim of this part of our investigation to determine the general feasibility of paper partition chromatography for the separation and determination of typical representatives of the different groups of AOs. The three groups investigated included:

(a) Phenothiazine and aryl amine type AOs.
(b) Phenolic type AOs.
(c) Organic selenide type AOs.

All three groups of AOs proved to be separable and detectable by paper partition chromatography either with normal filter paper (the amines and selenides) or with the reversed phase partition chromatography, which is applicable to all three type of AOs.

4.0 PAPER CHROMATOGRAPHY OF N-TYPE ANTIOXIDANTS OF THE PHENOTHIAZINE AND ARYLAMINE TYPES

4.1 CHROMATOGRAPHY ON NORMAL PAPER

As typical representatives of the thiazine and the aromatic amine type AOs, phenothiazine (PT) and N-phenyl-1-naphthylamine (NPNA) have been chosen for the investigation along with other types of aromatic amines such as alpha-naphthylamine (ANA), beta-naphthylamine (BNA), benzidine, etc. All these amines have a slight but definite solubility in water. Therefore it was very probable that they could be separated and identified on normal filter paper with water as the stable phase.

Their identification is based on their ability to couple with diazotized amines (e.g. diazotized sulfanilic acid) to form colored diazo dyes, which are characteristic in color for the specific compound. Paper chromatography has in this respect some advantage over routine colorimetric methods, because it is feasible even though the developed color might precipitate out, since the precipitated color is supported by the paper. It has been found that diazotized sulfanilic acid is a very satisfactory color developer for most AOs of this group. A spot of a benzene solution of the AO or of a benzene extract of the grease is placed on a strip of Whatman No. 4 filter paper at the starting point, and the solvent is evaporated by a drying fan. After running a descending chromatogram with an ethanol-water (4:1, v/v) solvent combination at 20°C. for four hours, the strips are removed from the chamber and dried. An alcoholic solution of diazotized sulfanilic acid is sprayed over the paper (the diazotization is carried out shortly before the reaction), and after the color has developed the paper is dried again with the fan. The diazo color develops quickly and distinctively. However, some of the colors are pH-dependent and hence change color if the development takes place in the vicinity of, for example, an NH_3 atmosphere. The colors developed are characteristic for the different amines or thiazines. PT itself develops a bluish-green color, whereas strongly oxidized PT gives a greenish-violet color. NPNA gives a definite violet color which under the influence of ammonia vapor changes to light orange. Benzidine gives a yellow spot and ANA a crimson color.

Development of the spot can be achieved in a simpler way by first spraying the dried spot with a 0.2% solution of $NaNO_2$ which has been acidified shortly before with a few drops of dil. HCl, drying with a fan, and developing with a 0.5% aqueous solution of sulfanilic acid. This method avoids the time-consuming preparation of fresh diazotized sulfanilic acid.

The results of three parallel runs with PT and NPNA of different concentrations are shown in Figure 17 and 27. The R_f-values for these compounds and for a series of other amines run in the same way are summarized in Table XXI. About 20 different solvent combinations have been tried, and the two most effective proved to be: EtOH-water (4:1, v/v) (Solvent No. 1), and also MeOH-amyl alcohol-benzene-water (2:1:1:1, v/v) (Solvent No. 2).

The R_f values for PT and NPNA are relatively close, but still different enough to be able to differentiate the two in a mixture. Runs with several other compounds of similar chemical consitution corroborated these findings so that it can be expected that this method will be applicable to the whole group of compounds. Lack of time, however, prevented a more complete determination of R_f -values for such compounds as potential antioxidants. These gaps will be eventually filled in an extended program.

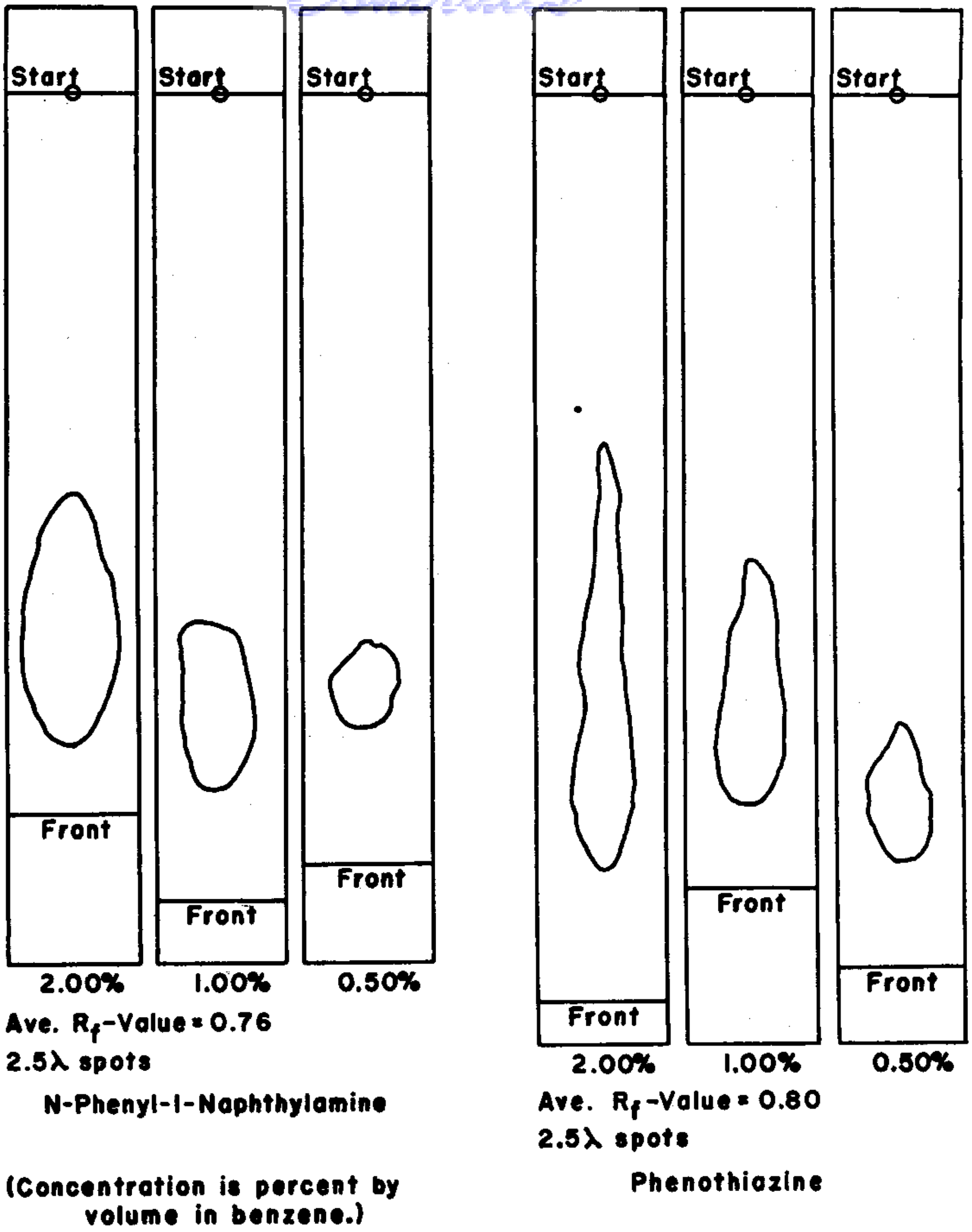


Figure 17. Quantitative Paper Chromatograms of Two Amine-Type AOs on Individual Paper Strips. Normal Paper With EtOH-Water (4:1, v/v) Solvent Combination, At 25°C.

TABLE XXI

R_f-Values For Different N-Type AOs and Other Amines on Normal Paper

Substance	R_f-Value (Solvent No. 1)	R_f-Value (Solvent No. 2)
Phenothiazine (PT)	0.80	0.95
N-Phenyl-1-Naphthylamine(NPNA)	0.76	0.90
Dimethyl-diphenyl-sulfate	----	0.89
Sulfanilic acid	----	0.74
Alpha-Naphthylamine(ANA)	0.84	0.92
Beta-Naphthylamine(BNA)	0.84	0.92
Aniline	----	0.88
p-Aminophenol	----	0.88
p-Phenylenediamine	----	0.25
m-Phenylenediamine	----	0.62

4.2 REVERSED PHASE CHROMATOGRAPHY OF N-TYPE ANTIOXIDANTS

Because of the insolubility of the hindered phenols in water, reversed phase chromatography was used for successful separation of these substances (the technique will be discussed in more detail in Par. 5.0, below). Consequently it was of interest to investigate the feasibility of this method for the separation of N-type AOs. If both types of AOs could be separated and determined with this method on acetylated cellulose paper, then all three groups of AOs could be chromatographed at the same time, possibly even with the same solvent. Therefore several test solutions of the N-type AOs with different concentrations were chromatographed on acetyl-cellulose paper, using the same solvent combination as was used for the hindered phenols, namely, butyl acetate-pyridine-water (1:5:10, v/v).

The results of these runs are shown in Figures 20 and 27. These and runs with various other similar compounds corroborated the feasibility of the separation on acetyl-cellulose paper. This type of separation is in some respects preferable to runs on normal paper because of sharper separations and shorter time requirements. The R_f-values of the different substances run on the acetyl paper are shown in Table XXII.

TABLE XXII

R_f-Values For Different N-Type AOs and Other Amines On Acetyl-Cellulose Paper

(Solvent: BuAc-Pyridine-Water(1:5:10, v/v))

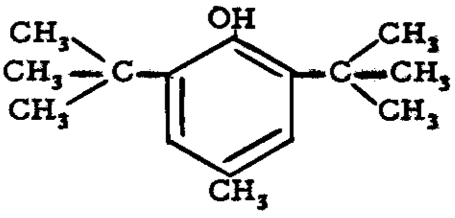
Substance	R_f-Value	Substance	R_f-Value
Phenothiazine(PT)	0.20	Aniline	0.15
N-Phenyl-1-Naphthylamine (NPNA)	0.15	o-Toluidine	0.11
		p-Toluidine	0.22
Alpha-Naphthylamine(ANA)	0.19	p-Anisidine	0.42
Beta-Naphthylamine(BNA)	0.26		
Benzidine	0.38		

5.0 PAPER CHROMATOGRAPHY OF PHENOL-TYPE ANTIOXIDANTS

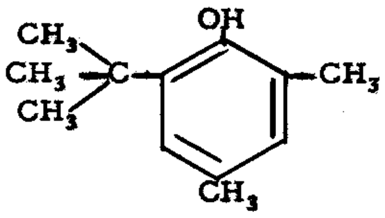
The paper chromatographic identification and separation of phenolic-type AOs encountered considerable difficulties. These were caused by the peculiar chemical properties of the hindered phenols (the most commonly used phenolic antioxidants in synthetic lubricants and greases). The hindered phenols show a lack of adequate color reactions, and a very low solubility in water.

5.1 IDENTIFICATION OF THE HINDERED PHENOLS

Although there is no lack of simple yet sensitive color reactions for phenols, they fail altogether with hindered phenols such as 2,6-ditertiary-butyl-4-methylphenol (2,6Ph) of the formula (I) and 2,4-dimethyl-6-tertiary-butylphenol (2,4Ph) of the formula (II).



(I)



(II)

In these compounds the phenolic OH-group, which is responsible for most phenolic color reactions, is hindered or blocked due to the presence of substituents in the 2, 4, and 6 positions of the benzene ring. A great number of different identification reactions have been tried; most of them failed and those which gave reasonable results were usually too complicated, particularly for application on a paper chromatogram. The only reagent which gave a simple color reaction with this type of phenols was phosphomolybdic acid (228). All attempts to develop another color reaction have failed to date. If the reaction and development of the color complex are done properly, the spots are distinctive and characteristic.

With phenolic AOs, the color of the spot is developed by immersing the filter paper strip for about one minute in a 10% aqueous or dilute alcoholic solution of phosphomolybdic acid; the excess reagent is blotted off quickly by pressing gently between two sheets of filter paper. The yellow strip, still wet, is placed in an NH_3 atmosphere (a few ml. of con. NH_4OH on the bottom of a glass jar or cylinder); within a few seconds the yellow color of the reagent disappears, and the phenol develops a bluish-violet spot. Care must be taken that development in the NH_3 atmosphere is not extended too long because it may cause fading of the spot. After the spots have been developed, the area is encircled immediately on the still wet paper (or photostatted), since the color fades quickly.

5.2 SEPARATION OF PHENOLIC-TYPE ANTIOXIDANTS

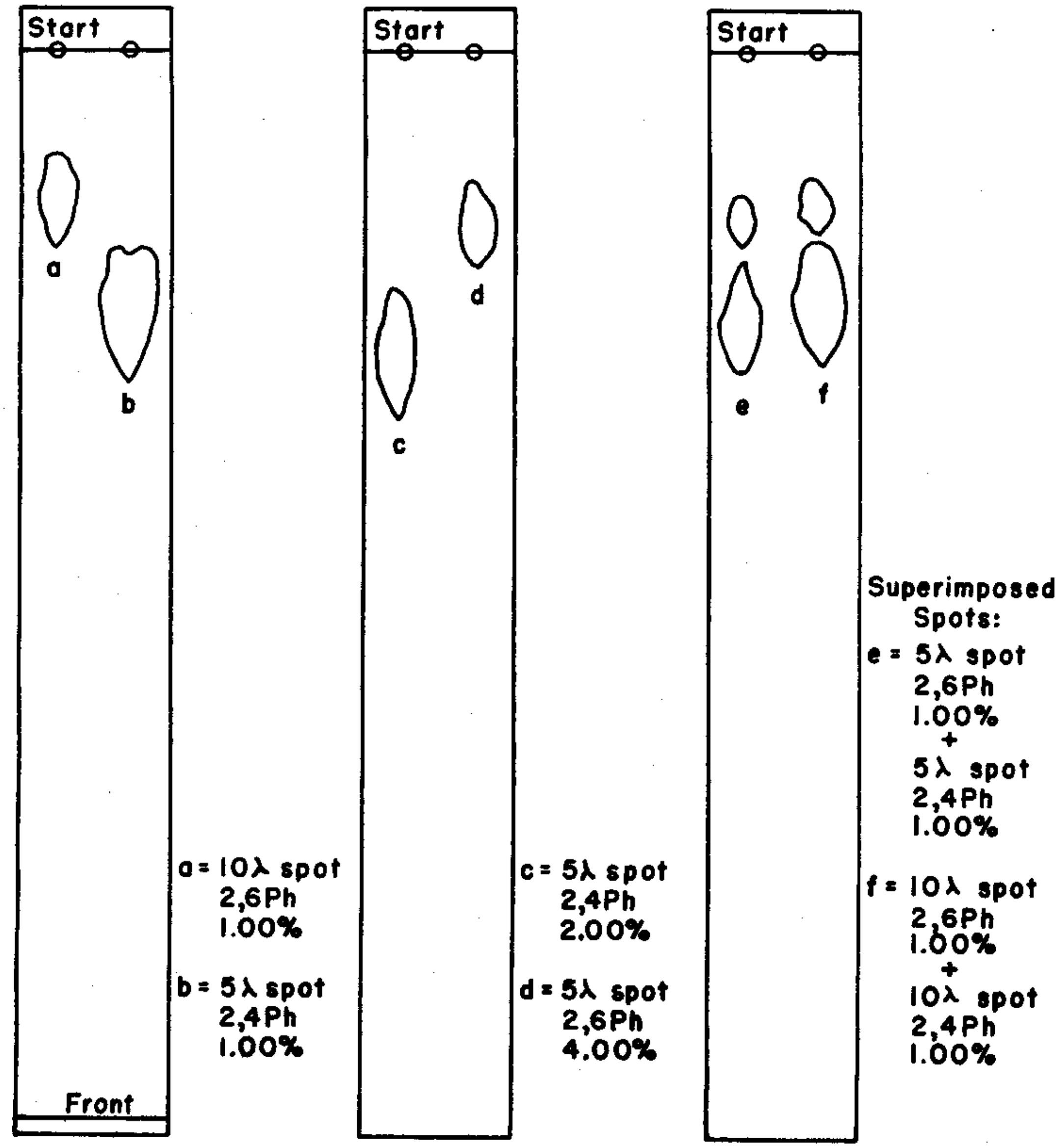
The second reason for the difficulties encountered in the separation of hindered phenols from base-oils and other AOs is due to their lack of solubility in H_2O. On normal paper only such compounds can be separated which are at least slightly soluble in H_2O. Otherwise the substance cannot be retained by the stable phase and travels constantly with the front. Thus, although about 25 different solvent combinations were tried, it was very difficult to develop spots of either the 2,4 or the 2,6 compound, because they were soluble in most organic solvents but practically insoluble in water.

Therefore the only possible way for separation of these AOs could be seen in the application of a reversed phase chromatogram. After having tried a series of different filter papers, as for example paper impregnated with vaseline or silicone liquid, etc., the most feasible was acetyl-cellulose paper. (The preparation of this paper is described in Par. 8.1, p.148). Descending runs with this paper were consequently carried out for both types of hindered phenols in greases and in lubricating oils, as well as with other phenols, using a solvent combination of butyl acetate-pyridine-water (1:5:10, v/v) and developing the spots with an alcoholic solution of phosphomolybdic acid and NH_3 as described in Par. 5.1 above. The blue color of the spots developed rapidly and was much more stable than on normal paper. The results were positive in all cases and not only could the hindered phenols be separated from the base-oils and other AOs, but even from each other as shown in Figure 18 and 27.

The R_f-values of the 2,4PH and the 2,6Ph compounds are far enough apart to allow their distinctive separation. In order to achieve a sharp separation of the spots, however, the chromatogram must be "overrun," which means the solvent front passes over the lower edge of the paper and runs out of the paper strips. To facilitate this, the ends of the paper strips are slit into small tips to permit easy drop formation and to increase the dripping rate. After 12 hours the spots are well enough separated to be able to make quantitative determinations.

Another experience was gained during the running of these hindered phenols. The temperature at which the chromatograms with hindered phenols are run is especially important because of the high volatility of the compounds. When the chromatograms on normal paper were run at about 70°F., a great part of the substance from the spot volatilized, consequently making it impossible to detect the spot after the run. Runs under refrigerated conditions corroborated these findings. Therefore the chromatograms should be carried out in a fairly cool room. The acetylated paper behaved in these cases much better than normal paper.

The intensity of the color, using the same concentration is much greater with the 2,4 compound than with the 2,6 compound. This again points to the fact that the tertiary butyl groups in the 2,6 positions cause stronger steric hindrance than the one in the 2 position in the 2,4 compound. The R_f-values for different phenols obtained by this method are given in Table XXIII.



R_f-Values: 2,6Ph = 0.16 (spot a)
2,4Ph = 0.27 (spot b)

Key: 2,4Ph = 2,4-dimethyl-6-tertiarybutylphenol
2,6Ph = 2,6-ditertiarybutyl-4-methylphenol

Figure 18. Paper Chromatograms, Illustrating Single Runs and Separation of a Mixture of Two Phenolic AOs. Acetyl-Cellulose Paper With BuAc-Pyridine-Water (1:5:10, v/v) Solvent Combination, At 25°C.

TABLE XXIII

R_f-Values of Phenolic Compounds On Acetyl-Cellulose Paper

(Solvent: BuAc-Pyridine-Water (1:5:10, v/v))

Substance	R_f-Value	Substance	R_f-Value
2, 6-Ditertiarybutyl-4-methylphenol(2, 6Ph)	0.16	1-Naphthol	0.13
		Hydroquinone	0.39
2, 4-Dimethyl-6-tertiarybutylphenol(2, 4Ph)	0.27	Pyrogallol	0.34
		Resorcinol	0.32
Guaiacol	0.25		

6.0 QUANTITATIVE CHROMATOGRAPHIC DETERMINATION OF ANTIOXIDANTS

6.1 GENERAL PRINCIPLES

The use of paper chromatography as a quick, convenient, and accurate means of qualitative analysis immediately aroused the question whether this technique could be used also for the quantitative determination of AOs and other additives in synthetic lubricants and greases. The following possible methods could be visualized:

6.1.1 Method I - Elution

The most widely used and probably the most accurate quantitative procedure in paper partition chromatography is based on the simple expedient of cutting out the section of the developed chromatogram (spot, band, or circle) which contains the substance, removing the substance from the paper by elution with a convenient solvent, and determining the amount in the eluate by, for example, a colorimetric method. The accuracy of such a method is better than 4%. However, because colorimetric methods were to be avoided, another method had to be chosen. Among the other quantitative procedures, visual comparison and measurement of the area of the spots have been taken into consideration because neither of these required optical instruments for their determination.

6.1.2 Method II - Visual Comparison

Casual inspection of a finished paper chromatogram reveals that the intensity of color and the size of the spot varies with the quantity of the substance chromatographed. Thus, a reasonably accurate estimation of the quantity of unknown substance may be obtained by developing on the same chromatogram a series of dilutions of known concentrations of the same substance and a series of dilutions of the unknown concentration. Where a spot of unknown concentration matches a spot of known concentration with respect to color and size, it may be assumed that the quantitites in both spots are of the same order of magnitude. It must be noted that in all these cases the same volume of starting spot must be applied (about 2.5-10 λ).

This method, however, is often subject to gross errors because of the subjectivity of judgment, and is also laborious, demanding a large number of replica analyses at various dilutions. The accuracy is at the best only 10%. Therefore such a method could not be considered as adequate for the required purposes.

6.1.3 Method III - Area of Spot

A more accurate quantitative method consists in the estimation or actual measurement of the spot area, which is a function of the concentration of the substance. This method was adapted after several experimental runs proved its feasibility. It may be used with success if its accuracy is of an acceptable value. The following paragraphs discuss in detail the application of this method to the quantitative determination of antioxidants.

6.2 DETERMINATION OF ANTIOXIDANTS BY THE SPOT AREA METHOD

The principle of quantitative paper chromatography of AOs is based on measurement of the spot area, after the spot has been identified either by developing a diazocolor with amine-type AOs or in case of the phenols by reacting with phosphomolybdic acid. Quantitative estimation of the substance is suitable for a one-dimensional paper chromatogram. When the volumes of the solution applied to the paper strip are of constant size, the areas of the resultant spots are proportional to the logarithm of the concentration of materials in each spot. In practice 2.5 to 5 λ of solutions containing 25-50 γ */ml. of the AOs are carefully placed on the paper

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* 1 γ (gamma) = 10^{-6} grams.

2 cm. apart. At the completion of the chromatogram, the circumferences of the spots are carefully marked in pencil and then the areas are determined with a planimeter. If a planimeter is not available the spots are cut out of the paper and weighed. It has been found that six to ten replicate analyses should be carried out for each concentration of the standard and the unknown solutions.

When the numerical values of the areas derived from the standards are plotted on semi-logarithmic paper against the concentrations, a straight line relationship is obtained. This type of experiment can also be calculated. The procedure of assay is to develop at least four spots in parallel, containing amounts S_1, S_2, U_1 and U_2 of the components to be assayed, where the S's are known and the U's are unknown, and where $S_1/S_2 - U_1/U_2 = K$. If the corresponding areas of spots on the developed chromatogram are S_1, S_2, U_1, and U_2, then the logarithmic relation gives

$$\log \frac{U_1}{S_1} = \frac{(U_1 + U_2) - (S_1 + S_2)}{(U_1 - U_2) + (S_1 - S_2)} \cdot \log K$$

With this method accuracies of ± 4% are readily obtained when the spots have distinct edges. If there is an overlapping or if the spot is distorted for any reason whatsoever, this method is not applicable and another solvent combination should be tried until distinct spots can be developed. In the case of most AOs it was found that this method is applicable. In case the circumferences of the spots are fuzzy, a more successful outline can be obtained by reproducing the chromatogram on photographic paper by means of reproduction equipment.

In many cases the circumference can be drawn also in an ultraviolet light chamber, since many AOs fluoresce in ultra-violet light. In this way PT and NPNA can be detected. NPNA shows a brilliant violet fluorescence, whereas PT shows a slight yellowish-green fluorescence. It was observed that in UV light PT sometimes exhibited two zones of fluorescence, in some cases even two distinct spots, whereas the visible color reaction showed only one spot. A closer investigation revealed that the difference in the fluorescence in the UV light was due to the presence of some oxidized PT which fluoresced dark violet, whereas the non-oxidized PT fluoresced yellowish-green. The color reaction with sulfanilic acid did not distinguish between the two types of phenothiazine. Thus, in the case of PT at least a qualitative estimation of the unoxidized and oxidized parts can be made, if the chromatogram is investigated under the UV lamp before the color development is carried out and the spots marked. After this investigation, the color development can be made to determine the total area of the PT. Technically it is a very simple and easy to handle method, which can be employed readily in small laboratories.

6.3 DETERMINATION OF ANTIOXIDANTS IN GREASES

6.3.1 Runs With Test Substances

Test runs with different AOs were made to check the feasibility of the method for these compounds. For quantitative paper chromatography the descendent method is the most adequate. In the first runs individual paper strips for each separate AO were chosen, using Whatman No. 4 paper or Schleicher &Schüll No. 275. A series of solvent combination were employed in order to achieve adequate spot formation and to avoid fuzziness: n-butanol–HAc-water (4:1:5, v/v), amyl alcohol-HAc-water (4:1:5, v/v), n-butanol-ammonia (9:4, v/v), lutidine-collidine-water (1:1:1, v/v) MeOH-water (4:1, v/v), buffered EtOH-water (7:3, v/v), and EtOH-water (4:1, v/v). For quantitative development of the N-type AOs, the combination EtOH-water (4:1, v/v) proved to be adequate and was preferred to the lutidine-type solvent combinations which have obnoxious odors. For development of the phenol-type AOs a buffered lutidine or butanol-pyridine-saturated aqueous NaCl (1:1:2, v/v) solvent is the most suitable combination on normal paper.

As test substances for the N-type AOs, PT, NPNA, ANA, and benzidine were chosen, and for the phenolic-type AOs 2,4Ph, 2,6Ph, and alpha-naphthol. For the N-type AOs 2.5 lambda spots of 0.25, 0.50, 1.0 and 2% benzene solutions of the AO were applied to the starting point of the paper strip. Since the color intensity of the hindered phenols with phosphomolybdic acid was not so intense as the diazo dye colors, 5.0 lambda spots of the phenols were applied to have sufficient concentration of the substance. After drying the spots, the strips were placed in the chromatographic chamber and kept 12 hours in the solvent-saturated atmosphere. This has been done overnight. The next day the solvent was placed in the trough and the chromatogram developed for about 10 hours. After removing the strips from the chamber and marking the solvent front, the spots were developed according to the type of AO. The area of the spots was marked with a soft pencil and measured with a planimeter.

Standardization curves were obtained by plotting on semi-logarithmic paper the areas of the spots against the concentration in gammas. The standardization diagrams show a straight line for all AOs. The individual chromatograms for different concentrations of PT and NPNA are shown in Figures 17 and 27. The corresponding curves are included in Figure 19. These curves show a good agreement with theory. Such standardization test spots can be run simultaneously with the spot of unknown concentration, and after plotting the standard curve the quantitative estimation of the AO in the grease or lubricant can be read. The errors which enter into this type of quantitative estimation are in drawing the circumference of the spot, in planimetric measurements, and in reading the unknown concentration. All these errors result in about 4% accuracy for the method. If greater accuracy is required, the developed spots can be eluted from the paper and determined colorimetrically. In the case of the N-type AOs the spots can be cut out and nitrogen determined quantitatively by the micro-Kjehldal method. In the case of phenol-type AOs it is feasible to cut out the spots and determine the molybdenum or phosphorus which is bound to the complex with the hindered phenol. However, for the purposes of a quick quantitative estimation of AOs as specified by the contractual requirements, the proposed method is feasible. It has the advantage of being simple in its technical requirements and yet provides sufficient accuracy.

6.3.2 Runs With Test Greases

In order to test the feasibility of the method, several runs have been made with test greases and lubricants supplied by WADC and with greases prepared at this Institute. The first sample was a DRI grease, type IO4aO, with 94% mineral oil, 3% Bentone-34, 2% silica gel, and 1% phenothiazine. The hexane extract of the grease was concentrated, transferred to a 50 ml. volumetric flask, and made up to volume. Whatman No. 4 paper strips were spotted at the starting line with 2.5 lambda spots. Six spots were run simultaneously on six different strips. After evaporation of the solvent from the spots, the strips were placed in the chromatographic chamber and allowed to saturate for 12 hours with the vapor of the solvent, which was placed on the bottom of the chamber in a Petri dish. When the solvent front was about 2 in. from the edge of the paper, the run was stopped. This required about 10 hours. The temperature during the run was held at 25°C. After drying, the spot was developed with diazotized sulfanilic acid, dried, and the spot area marked and planimetered.

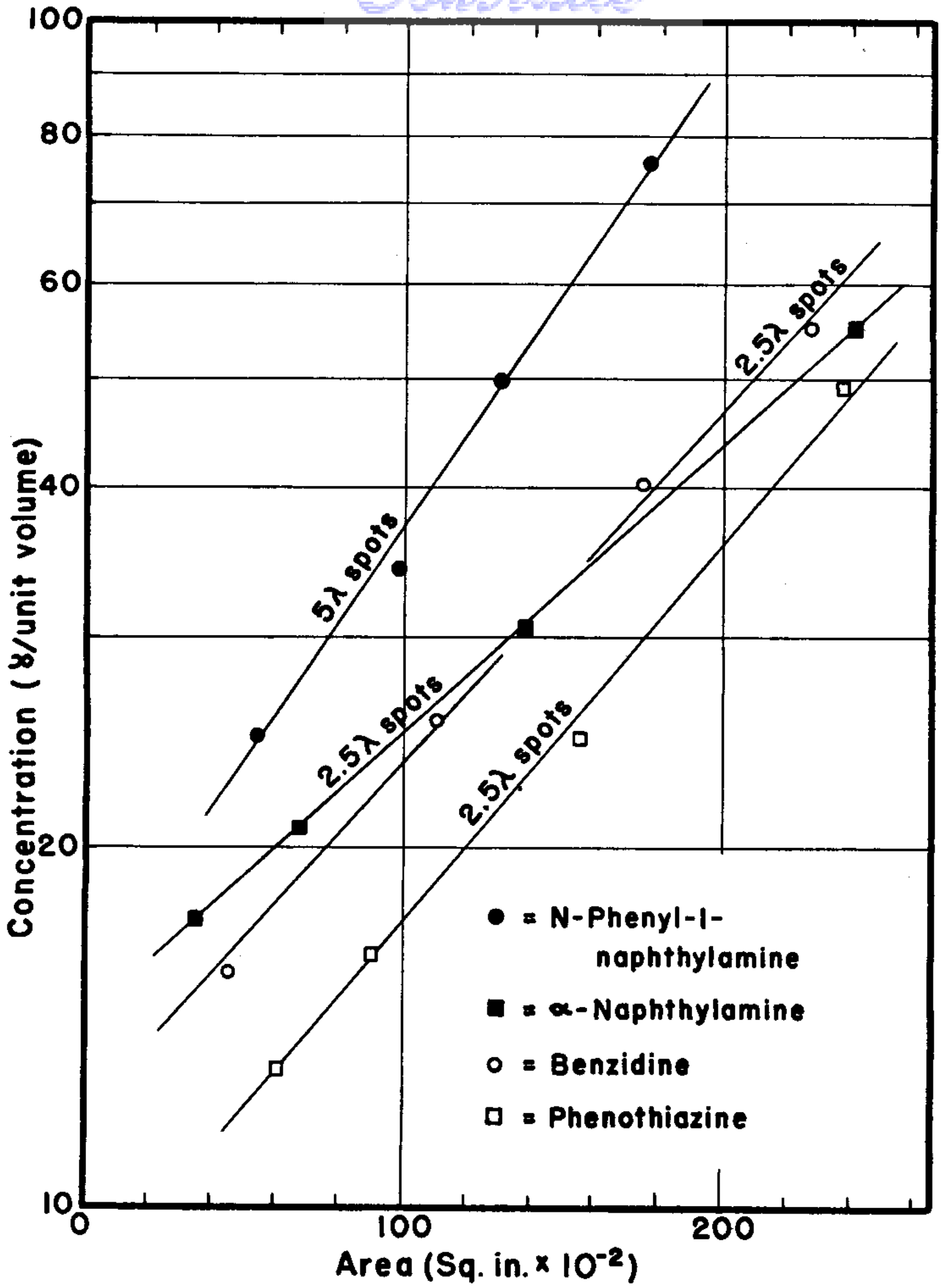


Figure 19. Quantitative Paper Chromatographic Standard Curves For Amine-Type AOs. Normal Paper With EtOH-Water (4:1, v/v) Solvent Combination, At 25°C.

The concentration was determined from the standard curves (Figure 19), and the results are summarized in Table XXIV. The spots were then cut out and weighed on a micro analytical balance and the nitrogen determined in a micro-Kjeldahl apparatus. A blank of the same filter paper sample and of the same size was run. Calculation of the amount of AOs from the nitrogen values are also shown in Table XXIV. The presence of mineral oil or of dibasic acid esters does not interfere with the determination.

6.3.3 Runs With Synthetic Lubricant (WADC Specification MLO-5277)

A 20% benzene solution of the lubricating oil was placed in a 50 ml. volumetric flask, made up to volume, and 2.5 lambda spots were applied to the paper strips. After drying, the spots were developed with the same solvent combination in the manner indicated in Par. 6.3.2. above. The strips were immersed in sulfanilic acid solution and then in aqueous $NaNO_2$. Excess liquid was blotted and dried by a gentle air stream. Intense brownish-orange colored spots indicated the presence of NPNA. The spot areas were measured in the usual manner and the concentration determined from the standard curves (Figure 19). Results of these runs are given in Table XXIV.

TABLE XXIV

Quantitative Determination of Antioxidants In Grease And Lubricants By Paper Chromatography

Grease or Lubricant	Run	PT %		NPNA %		2,4Ph %		Determination From Kjeldahl N.
		Present	Found	Present	Found	Present	Found	
IO4aO*	1	1	0.96					0.987
	2		0.95					
	3		0.94					
	4		0.96					
	5		----					
WADC Spec. MLO-5277	1			1	0.97			1.12
	2				0.95			
	3				0.92			
	4				0.95			
	5				0.96			
	6				0.96			
WADC Spec. MIL-L-6085A	1					0.5	0.46	
	2						0.48	
	3						0.42	
	4						0.45	
	5						0.48	
	6						spoiled	

*DRI Classification

7.0 QUANTITATIVE PAPER CHROMATOGRAPHY OF PHENOL-TYPE ANTIOXIDANTS BY SPOT AREA METHOD

7.1 FEASIBILITY OF THE METHOD

Because of the difficulty of the separation and determination of phenolic-type AOs on normal paper, the possibility for the quantitative determination of these AOs on acetylated paper was considered. However, since acetylated paper had different physical and chemical properties, such as adsorption power and ion exchange properties, it was not known whether the quantitative relationship between spot area and concentration would also apply for this type of paper.

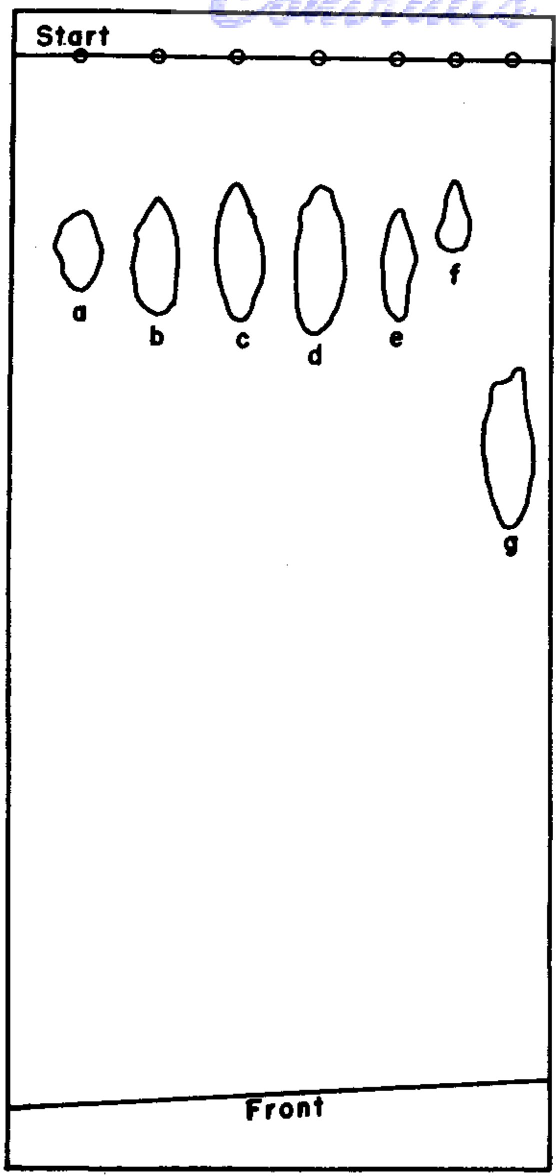
In order to establish this fact it was necessary to run a comparison test with N-type AOs on normal paper as well as on acetylated paper. The results of the runs with alpha-naphthylamine in four concentrations on acetylated paper are included in Figure 20, and the plotted quantitative values for both types of paper are shown in Figure 21. From these curves it can be seen that for the test substance the measured values for both types of paper lie in a straight line, demonstrating that the formula for the logarithmic relationship between concentration and spot area is valid also for acetylated paper. The difference is in the slope of the curve, which probably expresses the influence of the nature of the paper.

7.2 QUANTITATIVE CHROMATOGRAPHY OF PHENOL-TYPE ANTIOXIDANTS ON ACETYLATED PAPER

Once the feasibility of the method was established, test runs with hindered phenols were made to obtain standard curves for these substances. A series of spots with different concentrations of 2,4Ph were run on a descending chromatogram on a single sheet of paper. After development of the spots, the areas were measured and plotted against the concentrations as usual. These runs are shown in Figures 22 and 27, and are plotted in Figure 23. The spots lie close to the straight line of the curve. Once the curve was established, runs with unknown greases and lubricants were carried out.

7.3 RUNS WITH SYNTHETIC LUBRICANT (WADC SPECIFICATION MIL-L-6085A)

A run was made with WADC lubricant oil, Specification MIL-L-6085A. A previous qualitative run showed the presence of a hindered



a = α-Naphthylamine, 0.25%
b = α-Naphthylamine, 0.50%
c = α-Naphthylamine, 1.00%
d = α-Naphthylamine, 2.00%

e = Phenothiazine, 1.00%
f = N-Phenyl-1-Naphthylamine, 1.00%
g = Benzidine, 1.00%

Volume of Spots = 2.5λ

R_f-values:
Ave. α-Naphthylamine = 0.19 Phenothiazine = 0.20
N-Phenyl-1-Naphthylamine = 0.15 Benzidine = 0.38

Concentration is percent by volume in benzene.

Figure 20. Combined Quantitative and Qualitative Paper Chromatogram of Amine-Type AOs. Acetyl-Cellulose Paper With BuAc-Pyridine-Water (1:5:10, v/v) Solvent Combination, At 26°C.

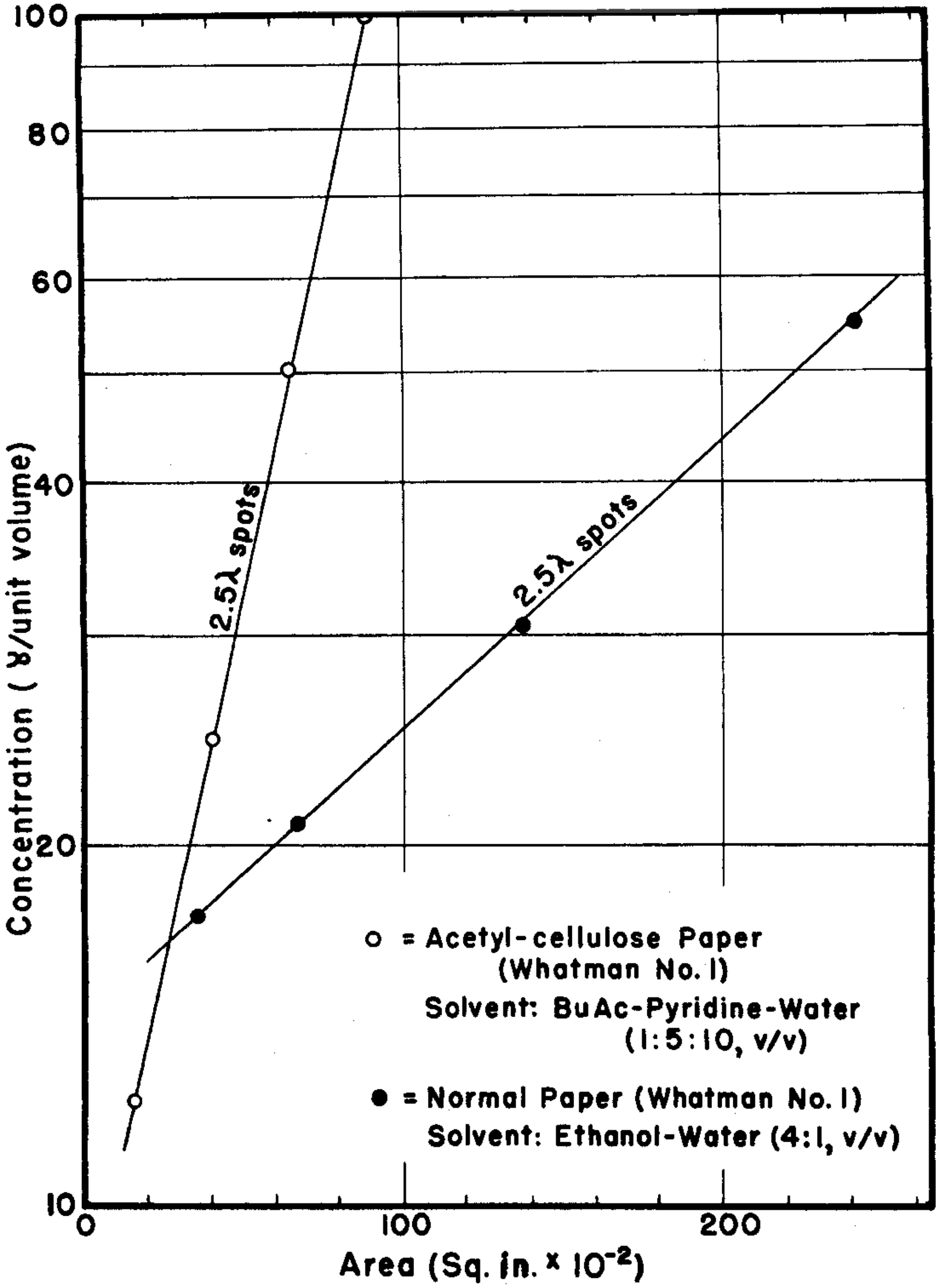


Figure 21. Quantitative Paper Chromatographic Standard Curves For Alpha-Naphthylamine on Two Types of Paper, At 25°C.

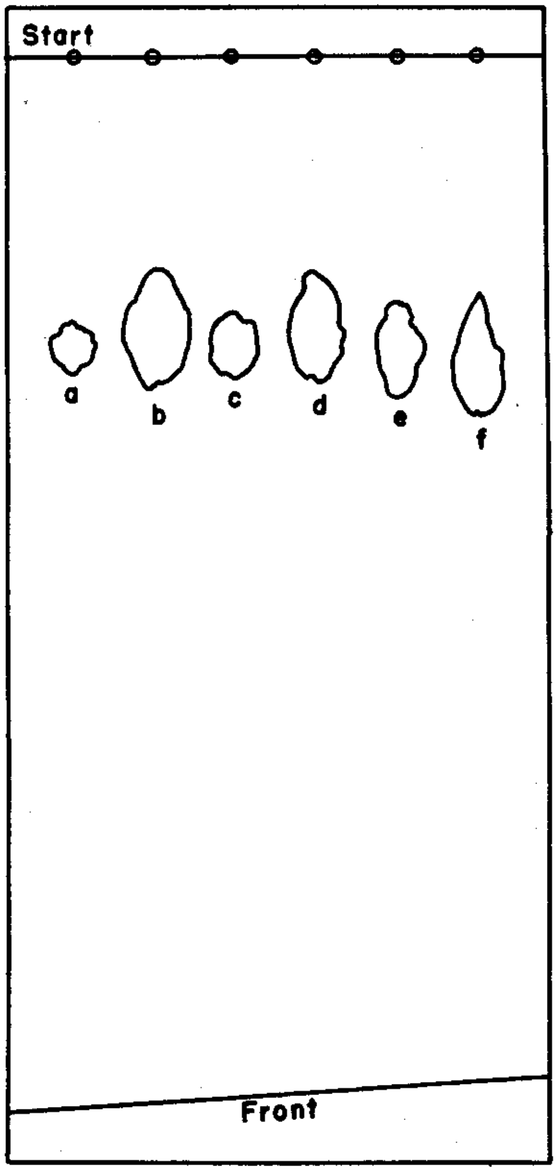
phenol, hence the quantitative run was made with a BuAc-pyridine-water (1:5:10, v/v) solvent combination using 5 lambda spots. Acetylated paper was used for the strips and the chromatogram was developed in the usual manner. The strips were immersed in a 20% alcoholic solution of phosphomolybdic acid for about 1/2 minute. Excess reagent was blotted quickly between filter papers and after a few minutes exposed to a saturated atmosphere of ammonia. The yellow color of the phosphomolybdic acid disappeared quickly and the blue spots of the phenol appeared. At this moment the strips were withdrawn from the container, immersed for 1-2 seconds in 5% HAc, blotted, and dried. The spots were circled as soon as the paper was sufficiently dry, and the area was measured. From Figure 23 the concentration was determined. Results of these tests are shown in Table XXIV.

From these experiments it is evident that the method of determination of AOs is not influenced by the presence of dibasic acid esters, sulfonates, mineral oils, or silicone fluids, and is thus feasible for the quantitative detection of phenolic AOs.

Summarizing the experiences with the application of partition chromatographic techniques to identification and separation of AOs in synthetic lubricants and greases, it can be concluded that the experimental data showed the feasibility of these methods for all three groups of AOs (the selenides can be separated in the same way as the phenolic-type compounds or the phenothiazines). There is a strong indication that these methods will also be useful for the separation of other additives and basic components in these lube-oils as, for instance, corrosion preventive agents, fatty acids, etc. Considering the large number of potential compounds investigated for their feasibility as AOs and inhibitors it was not possible in the year's program to carry out more than the most crucial experiments to establish the feasibility of such methods. It will be a matter of further experimentation to complete such specific tests and to establish tables of R_f-values for the majority of such compounds.

8.0 EXPERIMENTAL PART ON ANTIOXIDANTS

Since the techniques applied in the paper chromatographic analysis are described in much detail in the laboratory manuals indicated in the bibliography, and since the specific determination of the compounds investigated is described in detail in preceding paragraphs in this



a = 0.50%
b = 2.50%
c = 0.75%
d = 2.00%
e = 1.00%
f = 1.50%

Volume of Spots = 5λ
Average R_f-value = 0.28
Concentration is percent by volume in benzene.

Figure 22. Quantitative Paper Chromatogram of 2,4Ph. Acetyl-Cellulose Paper With BuAc-Pyridine-Water (1:5:10, v/v) Solvent Combination, At 26°C.

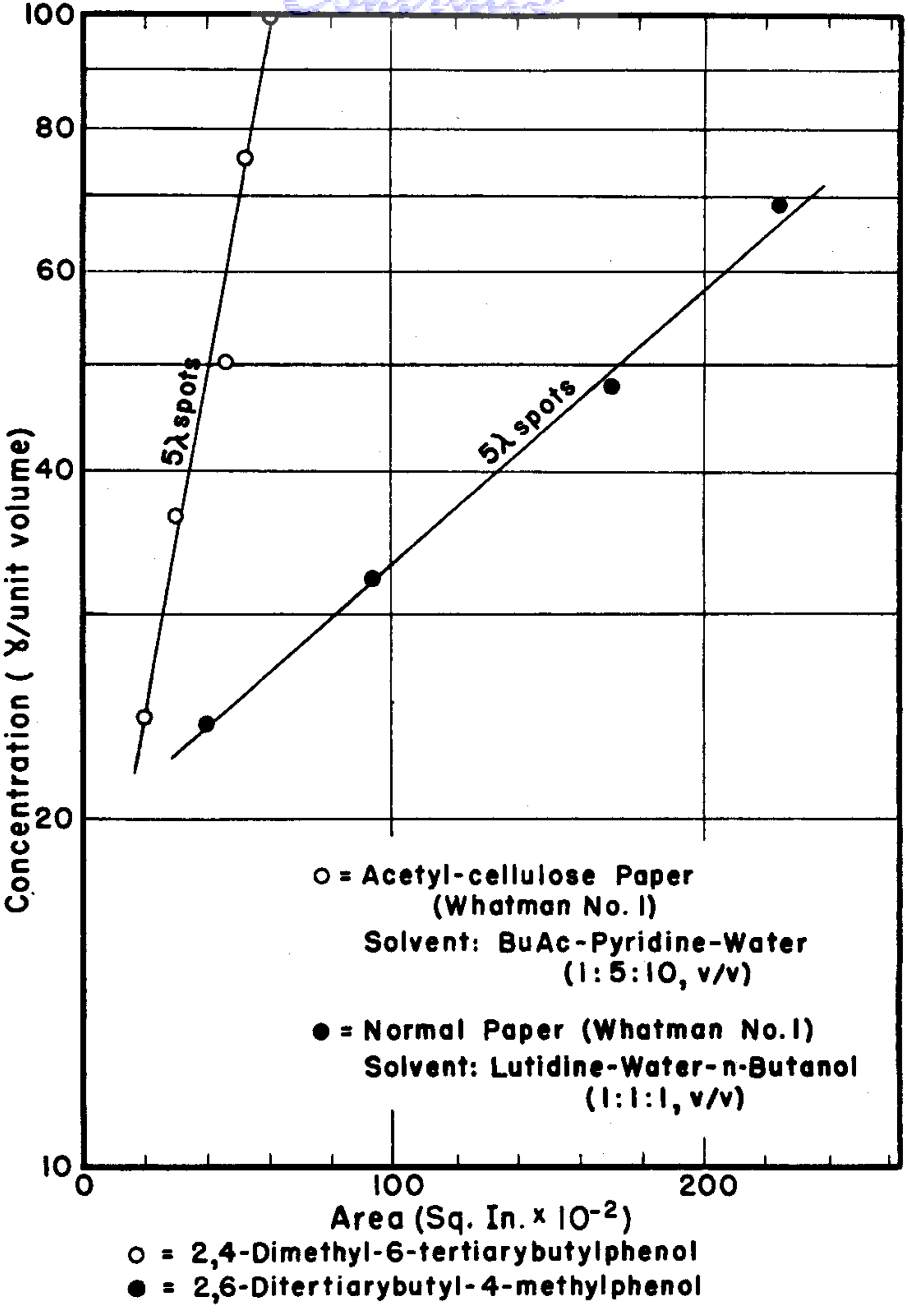


Figure 23. Quantitative Paper Chromatographic Standard Curves For Two Phenol-Type AOs on Two Types of Paper, At 26°C.

section, only the special technique for preparation of acetylated paper shall be described because this technique cannot be found in handbooks.

8.1 PREPARATION OF ACETYL-CELLULOSE PAPER FOR REVERSED PHASE CHROMATOGRAPHY

The acetylation of filter paper (strips or sheets) is carried out in a cylindrical vessel of Pyrex glass. In this laboratory a Pyrex glass resin pot of 5" diameter and 12" height with a 4-neck top with standard-taper joints was used, as illustrated in Figures 24 and 26. The top of the container is connected with a reflux condenser, a thermometer, and a dropping funnel. For the acetylation, the whole apparatus is immersed in a thermostat and kept at 70°C. for six hours. Inside the acetylation vessel is a removable glass rack which provides even spacing for the filter paper.

The filter paper (Whatman No. 1) is cut into strips of adequate sheets and wrapped around and through the glass rack in such a way as to provide spacing between the sheets in order to obtain equal acetylation. The rack is then placed in the vessel, and the cover pressed on tightly, and the whole resin pot placed in the thermostat as shown in Figure 26. The acetylation is carried out with a solution of acetic anhydride in benzene (1:3, v/v), which contains 0.1% con. H_2SO_4 (by volume) as catalyst. After placing the acetylation vessel in the thermostat, the acetylation mixture including the catalyst is added through the dropping funnel in one portion. After 6 hours' reaction time the paper contains 23% acetyl-cellulose. This degree of acetylation is sufficient to make the paper water-repellant and lipophilic. After the acetylation is completed, the thermostat is drained and quickly filled with cold water to cool the acetylation mixture. After cooling to room temperature, the acetylation mixture is replaced with cold MeOH, and the rack with the filter paper is left overnight in the pot with the MeOH. In the morning the paper is removed from the glass rack, unrolled, washed in running tap water for three hours, and finally for a short time (about 10 minutes) in distilled water. The filter paper is then air dried while mounted between clips on a wire stretcher, which prevents wrinkling, and finally oven dried 10 minutes at 110°C.

The paper is water-repellant, does not show capillary action with water, but is wettable with most organic solvents. The acetyl content of this paper is fairly uniform for all parts of the surface of the sheet

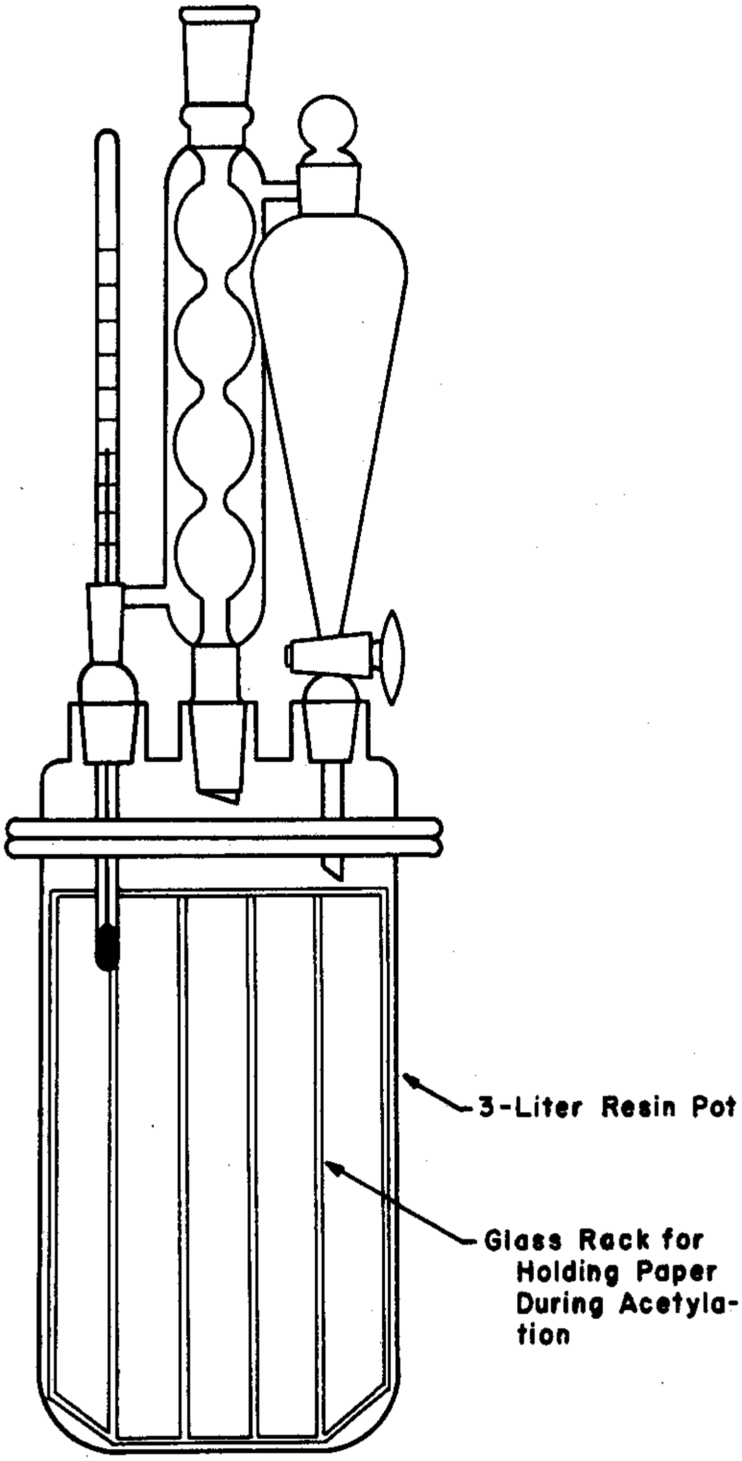


Figure 24. Acetylation Apparatus Used in Preparation of Lipophilic Chromatographic Paper.

within the range of experimental error. Acetone and any solvent combination which contains acetone cannot, of course, be applied because of the solubility of the acetyl-cellulose in this solvent. This must be kept in mind also for the application of the substance, since substances which are dissolved in acetone are very difficult to run from the starting line, if at all.

The acetyl number of this paper can be determined according to the method of Koevennagel and König (226).

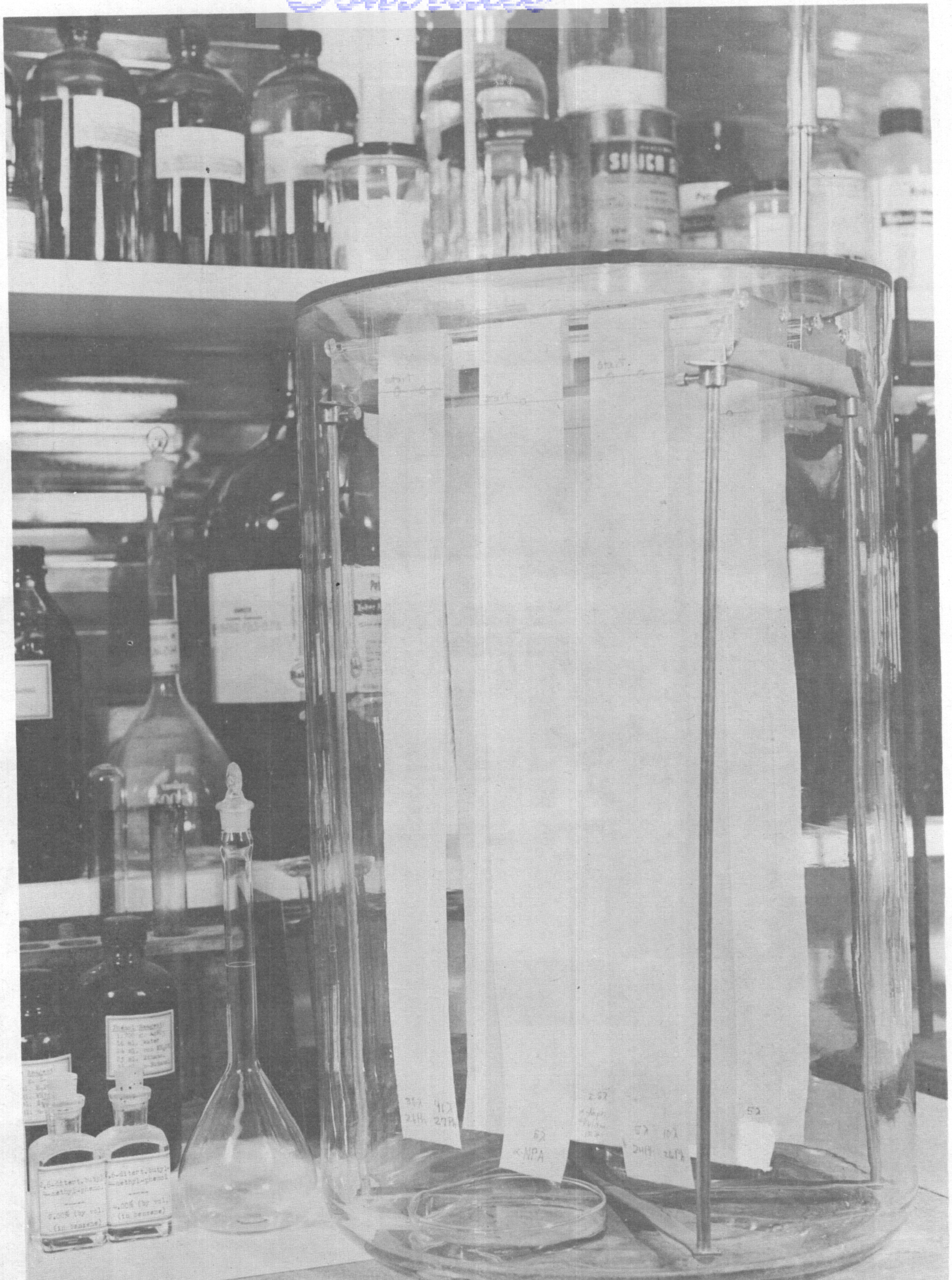


Figure 25. Apparatus For One-Dimensional Descending Partition Paper Chromatography.

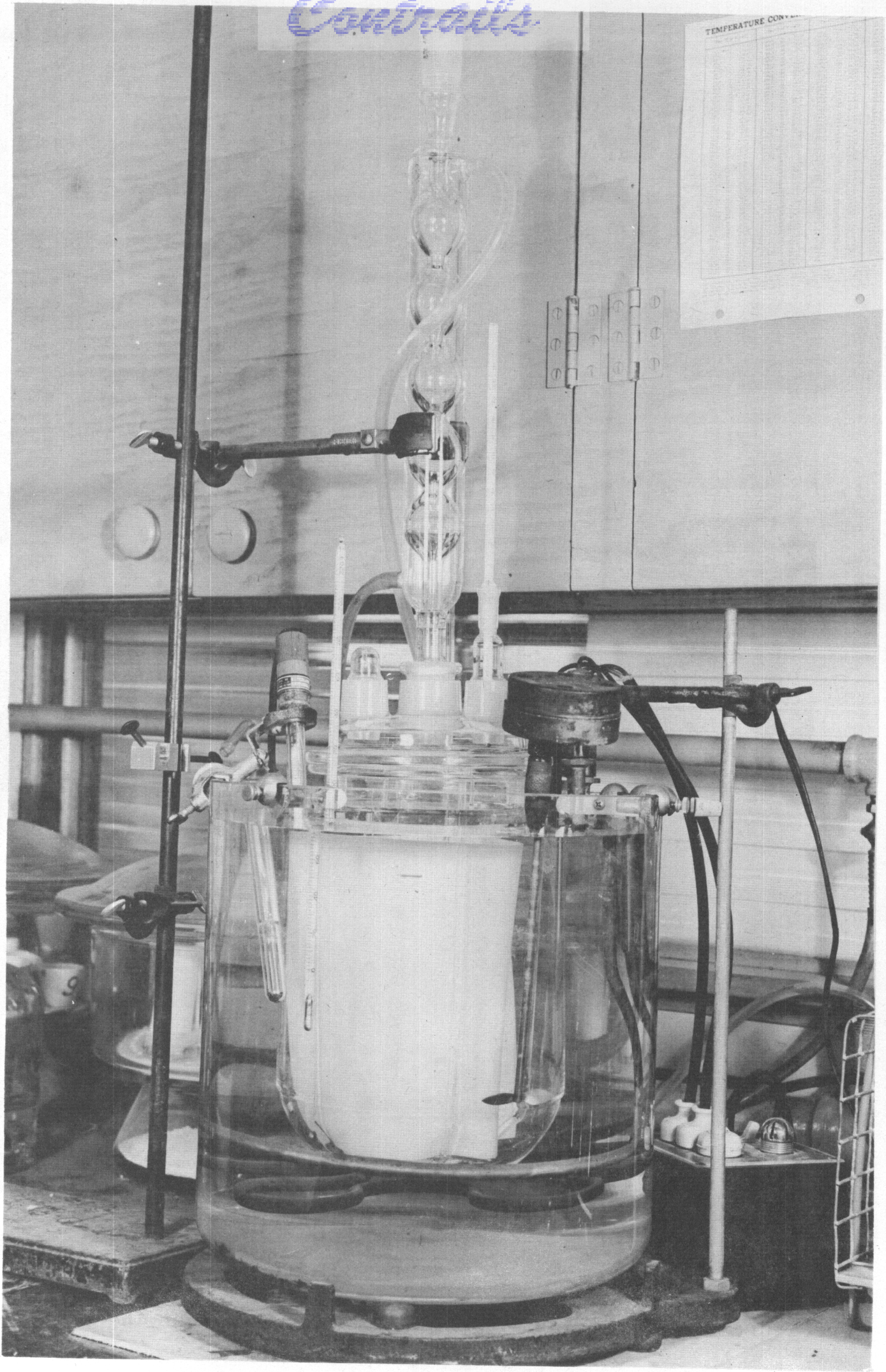


Figure 26. Paper Acetylation Apparatus in Thermostat.

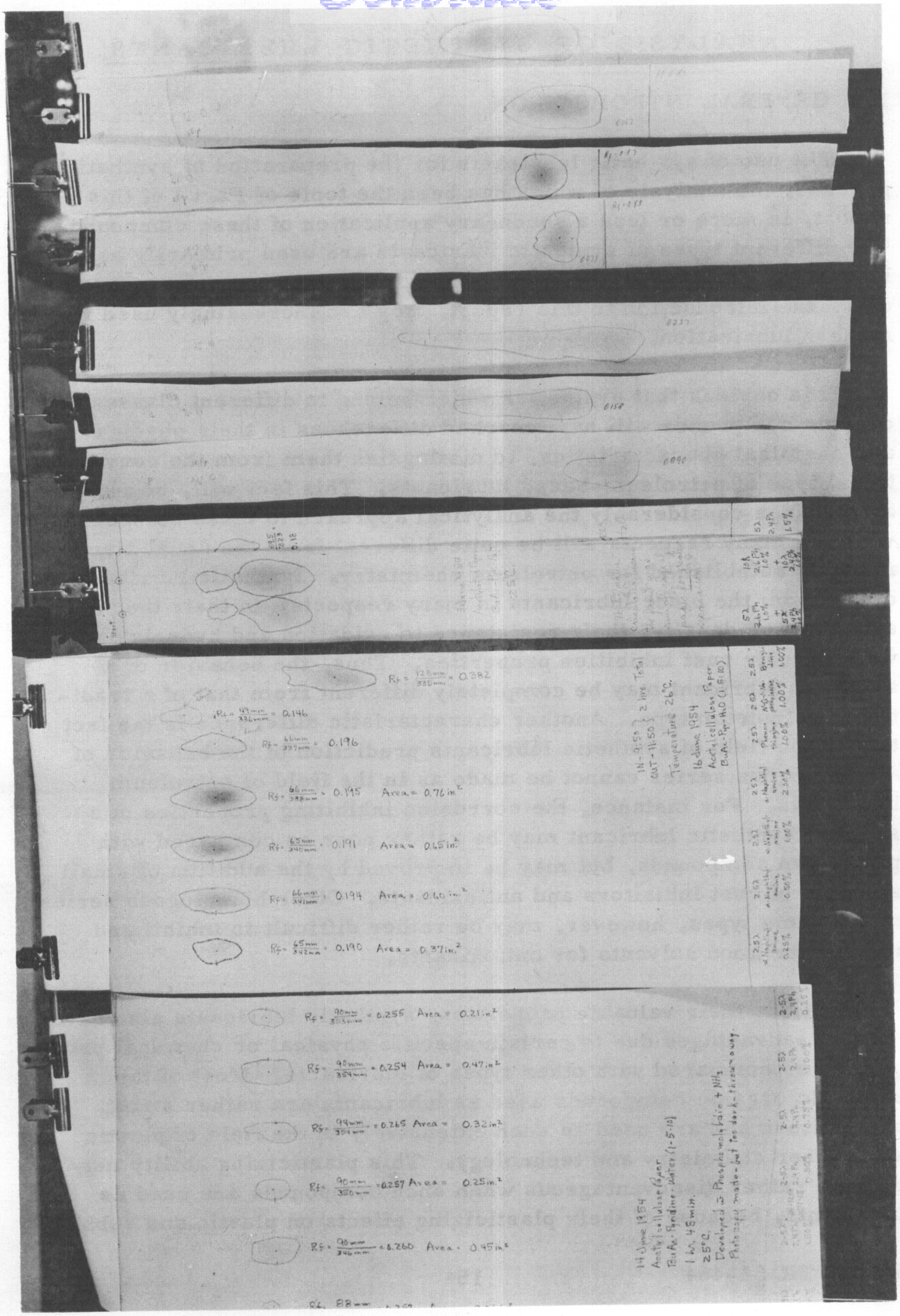


Figure 27. Photographs of One-Dimensional Paper Chromatograms of AOs.

PART II

ANALYSIS OF SYNTHETIC LUBRICANTS

1.0 GENERAL INTRODUCTION

The use of synthetic lubricants for the preparation of synthetic greases, the analysis of which has been the topic of Part I of this report, is more or less a secondary application of these compounds. The different types of synthetic lubricants are used primarily as lube-oils. Because of their outstanding properties, as was pointed out in the introduction to this report, they are increasingly used in modern lubrication.

It is obvious that synthetics which belong to different classes of organic compounds will have marked differences in their physical and chemical characteristics, to distinguish them from the conventional type of petroleum-based lubricants. This fact will, of course, also change considerably the analytical approach to these compounds, which in many respects will be quite different from the usual standard methods established for petroleum chemistry. Synthetic lubricants differ from the older lubricants in many respects; in their thermal stability and density, their resistance to oxidation and hydrolysis, as well as their rust inhibition properties. Thus, the behavior of a synthetic lubricant may be completely different from that of a traditional petroleum type. Another characteristic difference is the fact that in the field of synthetic lubricants prediction of the behavior of a homologous series cannot be made as in the field of petroleum lubricants. For instance, the corrosion inhibiting properties of a specific synthetic lubricant may be rather poor as compared with petroleum compounds, but may be improved by the addition of small amounts of rust inhibitors and antioxidants. Other homologous series of the same types, however, may be rather difficult to inhibit and may not be good solvents for antioxidants.

Besides their valuable properties, synthetic lubricants also have some disadvantages due to certain specific physical or chemical properties as compared with other types of lubricants. Most of the synthetic organic compounds used as lubricants are rather strong plasticizers and are used as such extensively in the field of plastic and rubber chemistry and technology. This plasticizing ability may become rather disadvantageous when such compounds are used as lubricants, because of their plasticizing effects on plastic and rubber derivatives which are used increasingly in the manufacture of engine components and accessories. Their solubility for paints is strong and can become at least a nuisance. Some synthetics on the contrary are poor solvents for rubber and rubber-like material but good solvents for the plasticizer used in these compounds. This can lead to a possible breakdown in machines, due to the hardening effect on gaskets and seals, etc. Therefore the increasing use of these new synthetics may consequently induce the development and application of newer types of plastics and also influence the design of new machines.

Analogously, the introduction of these substances influences the method of analysis, since the analyst is no longer faced with a wide variety of organic compounds belonging to a common group of hydrocarbons, but a mixture of complex different organic substances.

The synthetic lubricants used at the present time belong to a few larger groups of organic or metallo-organic compounds. Generally the following major groups may be distinguished:

I. Dibasic acid esters.
II. Silicate esters.
III. Silicones.
IV. Polyether and polyester compounds.
V. Phosphate esters.
VI. Fluorinated and chlorinated organic compounds.

Each of these groups has numerous specific derivatives which are used as actual (or may be considered as potential) synthetic lubricants. From the analytical standpoint each group consists of compounds with generally similar behavior which can be used for their identification and separation from the other groups.

I.1 METHOD OF APPROACH FOR THE ANALYSIS OF SYNTHETIC LUBRICANTS

The general properties of the different groups of synthetics are summarized further below. Based on differences of their chemical behavior, Part II of this report has been divided into six major sections corresponding to the general groups mentioned above. Time limitations have precluded work on any but dibasic acid esters, which in part is presented in SECTION A, on the following pages.

SECTION A

DIBASIC ACID ESTERS

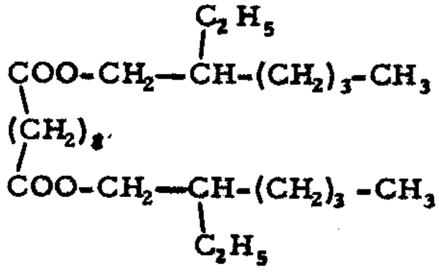
1.0 GENERAL PROPERTIES OF DIBASIC ACID ESTERS

This class of synthetic lubricants is the most commonly used and also the most thoroughly investigated because many of these compounds have long been used as plasiticizers in the field of plastics and rubber-like compounds. They are used in different base-oils for synthetic greases, as instrument lubricants of low volatility, and as turbine oils. Dibasic acid esters have excellent viscosity-temperature properties, low volatility, and low freezing points. Their lubricating properties vary with their structure, but in general are better than petroleum lubricants. Dibasic acid esters are good chemical solvents which easily dissolve additives as well as viscosity improvers. They are more stable to oxidation than petroleum oils and also blend readily with other types of synthetics like silicones, phosphate esters, mineral oils, etc. Dibasic acid esters have good resistance to hydrolysis, particularly the higher members of a homologous series. There are about thirty different types of dibasic acid esters used at the present time as plasiticizers and in synthetic lubricants.

The dibasic acid esters used as synthetic lubricants can be divided according to the dibasic acid present in the molecule. Thus, the following groups can be distinguished:

(1) Adipic acid esters.
(2) Azelaic acid esters.
(3) Sebacic acid esters.
(4) Phthalic acid esters.

Among the derivatives of these groups, the most extensively used ester at the present time for synthetic base-oils is di-2-ethylhexyl sebacate (I):



$$\begin{array}{l} \qquad\qquad\quad C_2H_5 \\ COO-CH_2-CH-(CH_2)_3-CH_3 \\ (CH_2)_8 \\ COO-CH_2-CH-(CH_2)_3-CH_3 \\ \qquad\qquad\quad C_2H_5 \end{array}$$

(I)

The stability of this compound to hydrolysis is quite high, which makes it possible to isolate the dibasic acid ester from monobasic acid esters, particularly from the alkali and alkaline-earth stearates or palmitates, etc., by hydrolysis with cold HCl(1:1), cold acetic acid, or even formic acid. The dibasic acid ester is not affected by this type of hydrolysis.

I.1 GENERAL METHODS OF ANALYSIS

The possible methods of analysis of dibasic acid esters have been investigated in connection with the analysis of plasticizers, and thus there are several possibilities for their determination available in the literature. However, since many of these methods are concerned with the analysis of such esters in connection with plastics, they cannot be applied unchanged for the separation and determination of such compounds in synthetic lubricants.

The basic problem of analysis in the field of synthetic lubricants is the primary separation of the group of dibasic acid esters from the other lube-oil components. These additional components are not insoluble solid polymers, as in the case of plastics, but are liquids of different viscosity grades which are soluble in many organic solvents. Therefore for the analysis of synthetic lubricants or greases as compared to plastics, the problem is more complicated.

I.2 SEPARATION OF LUBRICATING OILS (BASE-OILS)

Having removed all added materials such as gelling agents and antioxidants by precipitation or extraction, the final, and by far the most difficult, phase of the separation process still remains--identification and determination of the one or more base-oils which might be present in the grease or lubricant. The two most likely methods of separation under contractual limitations seem to be (1) selective extraction with various combinations of solvents and (2) column chromatography, probably with silica gel and a combination of eluents. Preliminary work has indicated that a method combining both of these working techniques will probably be the most useful for base-oil separation.

I.3 SEPARATION BY SELECTIVE EXTRACTION

Solubility properties of the major classes of base-oils are such that it is possible to separate a few, but not all, of the groups from each other by solvent extraction. It is quite conceivable, for instance, that silicone oils could be completely isolated from the other classes of oils quite easily, or that glycols could be separated from mineral oil. However, separation of mineral oils from diesters, for example, would be difficult if one were trying to recover the ester unchanged during the separation. Column chromatography offers the most likely prospect for success in separating compounds of similar solubility characteristics and the many compounds within any one class. Selective extraction, on the other hand, should prove most useful when used in conjunction with column chromatography, due to the rapidity with which it can be used, in contrast to the slow adsorption-elution process.

I.3.1 Runs With Mineral Oil-Dibasic Acid Ester Mixtures

The solubility properties of dibasic acid esters and mineral oil are very similar, and selective extraction would be most difficult when trying to recover the original ester unchanged. However, since the diesters are subject to saponification, it is quite simple to identify their presence in mineral oil mixtures by saponification with alcoholic KOH, followed by back titration with HCl. Communication received from the Naval Air Material Center in Philadelphia (265 (and see APPENDIX B)), indicated that the ester itself can be identified by collecting the alcoholic and acidic portions of the molecule in the following manner: the saponified solution is made alkaline, evaporated to drive off organic solvents, and extracted with ether. The ether will contain the alcoholic portion of the ester which can be identified by standard methods. The solution from the ether extraction is then acidified, and the precipitated dibasic acid filtered out, washed, and dried. Melting point is sufficient to identify the acid.

Having the alcohol and acid components of the ester and consequently the molecular weight, the weight of ester in the original oil can be calculated from the saponification and back titration data. In the event that there is more than one ester present in the oil, it will be necessary to resort to paper chromatography, as described on the following page.

Check runs on the above method were made using a mixture of mineral oil and di-n-butyl sebacate (Table XXV). The results show, within the limits of experimental error, that the separation and identification is complete.

TABLE XXV

Separation and Identification of Mineral Oil-Dibasic Acid Ester Mixture*

By Saponification of the Diester

Run No.	Dibasic Acid M.P. (°C.)	Alcohol	Mineral Oil%		Diester %	
			Present	Found	Present	Found
1	134° (Sebacic Acid-134.5°)	n-Butyl	50.25	50.1	49.75	50.9
2	134°	n-Butyl	25.72	25.6	74.28	74.4
3	134°	n-Butyl	10.07	9.95	89.93	90.5

* Mineral Oil:Di-n-Butyl Sebacate.

The above described method can be further adapted to show the presence of silicone oils and glycol oils by determining the solubility of any unsaponified oils in 95% ethanol (glycols are soluble; petroleum and silicone oils are not). Silicone oils are differentiated from petroleum oils by their performance during ashing. While this method has not been completely worked out to date, it should prove very useful for certain aspects of base-oil separation, quantitatively for diesters and mineral oil separation, qualitatively for silicone and glycol identification.

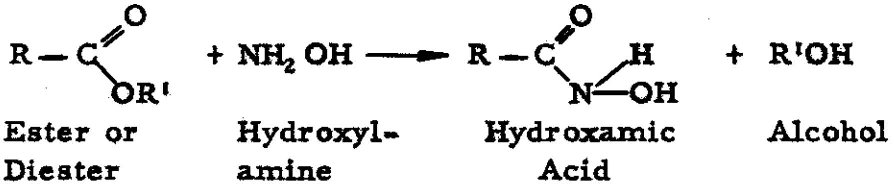
1.3.2 Complex Mixtures of Esters

In the case of base-oil mixtures containing more than one diester, the above method is very limited, except as a means for proving the presence of esters in the base-oil. In this situation two possibilities must be investigated:

(a) Column chromatography, in which the esters might be recovered intact as different portions of the eluate (see next page), and then identified individually, or

(b) Paper partition chromatography, in which the acid and alcohol portions, and possibly the whole ester, can be identified by their color reactions and positions on a two-dimensional paper chromatogram.

Experimental work has shown that esters (e.g. butyl stearate, tristearin, dioctyl phthalate, di-n-butyl adipate, etc.) can be hydrolyzed by freshly-prepared hydroxylamine (NH_2OH) according to the reaction:



The hydroxamic acid formed in the reaction can be identified as a purple spot on filter paper by spraying with dilute Fe^{+++} solution. To date monobasic esters and glycerides give a much better color reaction than dibasic esters. However, it is felt that by use of proper reaction conditions the dibasic esters will also give a definite reaction. The procedure consists of hydrolysis of the ester and formation of the corresponding hydroxamate, separation of the hydroxamates by development on a paper strip with the correct solvent combination, formation of the hydroxamate color, and determination of the R_f-values of the unknown acids. The R_f-value can then be compared to R_f-values for known acids. It must be pointed out that this operation detects only the number and type of acids in the esters.

It is felt that the alcohols can also be identified by paper chromatography. If the ether solutions of alcohols from the previously described separation method are run on a paper chromatogram with the proper solvent combination and color reaction, they can also be identified, and a close picture of the ester content of the original base-oil determined.

The ultimate aim of this phase of the separation will, of course, be to run the esters unchanged on a two-dimensional paper chromatogram with such solvents that the whole ester may be identified by its location on the paper square. With reference to this method, the fat-staining dyes, Sudan III and Sudan IV, will be most helpful, because fats and esters concentrate the dye, making spots quite easily visible.

1.3.3 Runs With Mineral Oil-Dibasic Acid Ester-Polyglycol Mixtures

Using the method described in the preceding section, one run was made with a mineral oil-dibasic acid ester-polyglycol mixture. The results of this single run are not conclusive and are not presented here for this reason. Separation and measurement of the amount of dibasic acid ester was quantitative; however, separation of the mineral oil from the polyglycol (Ucon LB-525) was not quantitative. After further runs, results of this method with glycols will be reported.

1.4 SEPARATION BY COLUMN CHROMATOGRAPHY

As indicated in the introduction to this section, column chromatography shows promise for the separation of not only base-oil mixtures, but also the various compounds within a major group, such as diesters. The use of selective adsorption has been used for many years, but only in the last two decades has its use become widespread. A notable amount of work has been done by the U. S. Bureau of Mines and the National Bureau of Standards in separating out the individual compounds from such complex mixtures as shale oil and petroleum. Since the present contract is concerned with somewhat the same type of compounds, it seems logical that many of the difficult problems in base-oil separation can be solved by this method.

The method consists simply of passing a solution of the base-oil in a solvent like hexane through a long column of silica gel, followed by elution of the adsorbed oils with solvents which are more strongly adsorbed than the oils themselves. Frequently, the oils can be washed out by a succession of increasingly adsorbed eluents, each eluent washing out one compound or group of compounds. The eluted compounds or groups of compounds can then be investigated and identified by their chemical and physical properties, i.e., refractive index, etc.

Preliminary studies of this separation method have been initiated in these laboratories. Mixtures of mineral oil and dibasic acid esters have been added to the column in a dilute hexane solution, after pre-wetting the column with hexane. Elution was carried out with benzene, followed by ethanol, and finally water. The eluate was received in about two ml. increments, and examined individually for their refractive index.

On the basis of these preliminary experiments, the program will be expanded to include (1) all combinations of base-oils, including several compounds in each group, (2) the most successful solvent combination to effect separation of the base-oils, and (3) the most successful adsorption media. While it is felt at the present time that silica gel holds the greatest promise, there are a number of other adsorbents which might be preferable to silica gel. If the method affords a means for separating base-oil groups, it will then be applied to separation of compounds within a group, and thus may prove a very useful tool in the overall scheme of analysis.

These further investigations of base-oils, however, will constitute the general scope of a second year's research program.

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APPENDIX A

METHOD OF ANALYSIS FOR SILICON, ALUMINUM, AND IRON

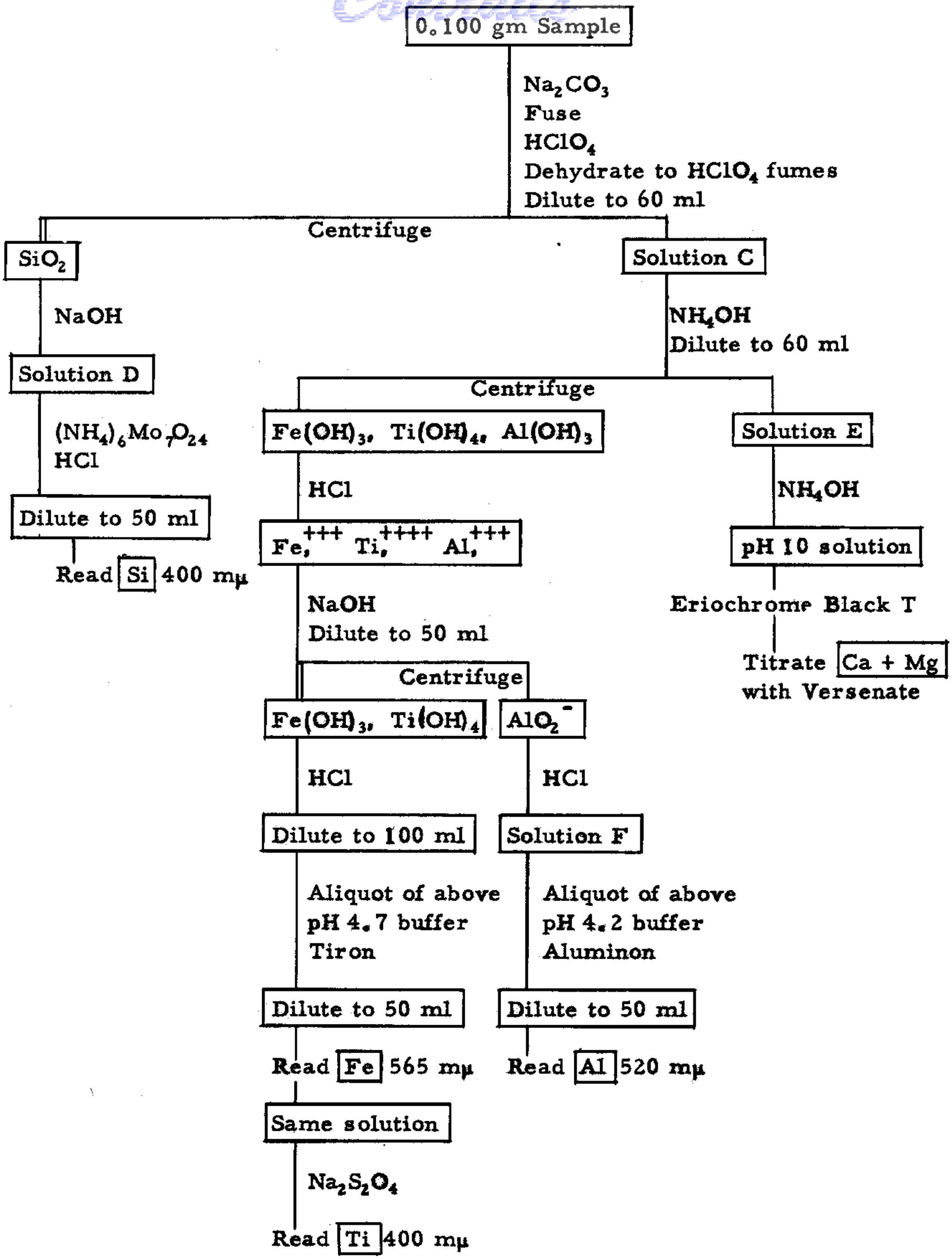
The following method of analysis is quoted from "Silicate Analysis By a Rapid Semimicrochemical System" (*Anal. Chem. 25,* 624-8 (1953)) by R. B. Corey and M. L. Jackson. Since the system presented in this publication is for the analysis of eight elements, only those parts of the article which apply to analysis for Si, Al, and Fe are reproduced here:

"....The sodium carbonate fused sample...is used for the determination of silicon, aluminum, and calcium plus magnesium. The sodium carbonate melt is dissolved with perchloric acid, and the silica is dehydrated by evaporation of the perchloric acid... The silica is separated by centrifugation and dissolved with sodium hydroxide. Silicon is determined in an aliquot of the resulting solution ... The classical ammonium hydroxide separation is next used to separate the calcium and magnesium from the hydroxy oxides of iron, aluminum, and titanium. The precipitated hydroxy oxides are separated by centrifugation, and an aliquot of the clear supernatant liquid is removed. The precipitates are then redissolved. Treatment with a concentrated sodium hydroxide sodium (*sic*) is used to separate the aluminum as the aluminate ion from the aluminon method...Iron and titanium could be determined by solution of the precipitate and use of the Tiron method...

SODIUM CARBONATE FUSION

Reagents. Sodium carbonate, anhydrous.

Procedure. A 0.1000-gram, finely ground sample which has been dried at 105°C. for 2 hours is weighed in a 30- to 45-ml. platinum crucible and approximately 0.75 gram of sodium carbonate is added. The sample and carbonate are thoroughly mixed by rotating the crucible with the fingers. Approximately 0.25 gram of sodium carbonate is then added on top of the mixture. The partially covered crucible is placed in a slanting position on a silica-covered triangle. The low flame of a Meker burner is placed so as to heat



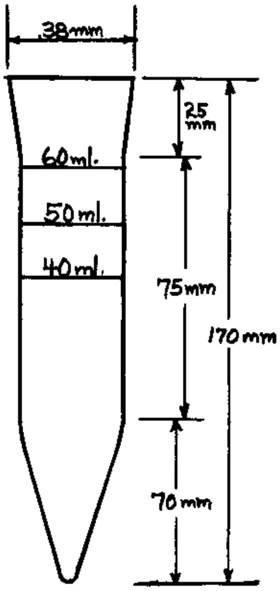
Flow Sheet for Sample Decomposed in Sodium Carbonate one side of the crucible, and the heat is gradually increased until melt is liquefied. If the material is finely ground the fusion is usually complete in 1 to 2 minutes, at which time the flux appears quiet with small curds of precipitate floating in the otherwise clear liquid, and the evolution of gas has ceased. The crucible is then grasped with nickel tongs and swirled so as to spread the flux in a thin layer over the sides of the lower half of the crucible, so that any silica adhering to the sides is fused. Heating is continued under full Meker flame for 2 or 3 minutes, after which the burner is removed and the crucible swirled again to spread the melt in a thin layer to facilitate its solution.

SILICON DETERMINATION

Reagents. Sodium hydroxide, pellets; perchloric acid, 60%; hydrochloric acid, 1/1 and 1/9. To prepare the ammonium molybdate solution, a 150-gram portion of ammonium molybdate tetrahydrate is dissolved in distilled water, diluted to 1 liter, and filtered if cloudy. Standard silicon solution, containing 50 micrograms of silicon per ml., is prepared by fusion of pure quartz crystals with sodium carbonate and subsequent solution of the melt in water. Aliquots (1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 ml.) of this solution are taken for the standard curve, and the color is developed as described below, the aliquots of standard solution being substituted for the Solution D aliquot.

Procedure. When the crucible from the sodium carbonate fusion has cooled, the cover is placed on the crucible, and 8 ml. of concentrated perchloric acid are added dropwise under the slightly raised lid. When effervescence has ceased, the lid and sides of the crucible are washed down with a minimum of water, the partially covered crucible is placed in a sand bath on an electric hot plate, and the suspension is evaporated to fumes of perchloric acid. Vigorous boiling must be prevented or loss of sample may result. When dense fumes of perchloric acid appear, the crucible is covered, and the suspension is boiled gently for 10 minutes at a temperature a little above 200°C.

When the crucible has cooled, approximately 5 ml. of distilled water are added, and the suspension is carefully mixed and heated almost to boiling to dissolve the salts which have solidified on cooling. The suspension is then transferred to a 60-ml. pointed centrifuge tube, and the crucible is rinsed with a wash bottle, the washings being added to the tube. All of the silica does not have to be removed from the crucible at this time. Approximately 2 ml. of 1 to 1 hydrochloric acid are added, and the suspension is diluted to exactly 60 ml. with water, thoroughly mixed with the air-jet stirrer, and centrifuged at 1800 r.p.m. for 5 minutes. The suspension adhering to the air-jet stirrer is washed back into the crucible. A 50-ml. aliquot is pipetted with a Lowy pipet from the supernatant liquid in the centrifuge tube and transferred to another 60-ml. pointed centrifuge tube. This is Solution C which is used for the determination of aluminum and calcium plus magnesium (and also iron and titanium if so desired). The pipetting operation is carried out by means of a Lowy pipet, although an ordinary pipet may be used if care is exercised. (ed. see figure.)



Special 60-ml. Pointed Centrifuge Tube and Special Rubber Pad for Support During Centrifugation.

The silica in the tube is washed by adding about 50 ml. of 1 to 9 hydrochloric acid, stirring, and centrifuging again at 1800 r.p.m. for 5 minutes. The supernatant liquid is then decanted by suction and subsequently discarded, since an aliquot has already been taken of the solutes.

The silica is then washed from the tube into a 250- to 500-ml. nickel or platinum beaker with a stream from the wash bottle, and the silica adhering to the sides of the crucible in which the dehydration was carried out is also transferred. The silica adheres rather tightly to the crucible, so that it must be loosened with a policeman and washed out with a stream from the wash bottle. The final washing of both the crucible and centrifuge tube is made with warm 5% sodium hydroxide to make sure all of the silica is removed. Approximately 2.5 grams of sodium hydroxide pellets are added to the suspension in the nickel or platinum beaker, and the volume is adjusted to approximately 100 ml. The solution is then boiled for 5 minutes to dissolve the silica. When cool, this solution is transferred to a 500-ml. volumetric flask and diluted to the mark with distilled water. This is Solution D, used for the determination of silicon.

A 10-ml. portion of ammonium molybdate solution is placed in a 50-ml. volumetric flask, and the volume is adjusted to about 30 ml. with distilled water. Then 5 ml. of 1 to 1 hydrochloric acid are added, and the flask is swirled to dissolve the white precipitate that forms. Finally, a Solution D aliquot containing 50 to 500 micrograms of silicon is added, and the solution is diluted to the mark with distilled water. A 5-ml. aliquot of Solution D is desirable for samples containing from 5 to 50% silicon. The solution is mixed well, transferred to a colorimeter tube, and allowed to stand for 30 minutes before the percentage light transmittance is read with a 400-mμ light filter. Reference to the standard curve gives the micrograms of silicon per 50 ml. The percentage of silicon in the sample is (micrograms of silicon per 50 ml.) × (0.05/ml. in aliquot × weight of sample).

ALUMINUM DETERMINATION

Reagents. Hydrochloric acid, 1 to 1; ammonium hydroxide; ammonium hydroxide, 1 to 4; ammonium chloride, 1% solution. Sodium hydroxide solution, approximately 25 grams of sodium hydroxide dissolved in 100 ml. of distilled water (this solution is made up fresh for each set of determinations and is used while hot). To prepare the buffer solution, pH 4.2, approximately 60 ml. of glacial acetic acid are diluted to about 900 ml. with distilled water, a 100-ml. portion of 10% sodium hydroxide solution is added, and the pH, as measured on the glass electrode is adjusted with small increments of 10% sodium hydroxide. For the aluminon reagent, exactly 0.200 gram of aluminon, synthesized by the method of Smith _et al._, is dissolved in 100 ml. of pH 4.2 buffer solution, and the volume is adjusted to 500 ml. with distilled water. Standard aluminum solution, stock solution containing 5 micrograms of aluminum per ml. of solution. Aliquots (1, 2, 3, 4, 5, 6, 7, and 8 ml.) of this solution are taken for the standard curve, and the color is developed as described below, the aliquots of standard solution being substituted for the Solution F aliquot.

Procedure. To the 50-ml. portion of Solution C (the supernatant solution from the silica centrifugation) in a 60-ml. pointed centrifuge tube are added 3 drops of bromocresol purple. The tube is brought to a boiling water bath temperature and concentrated ammonium hydroxide is then added until the first traces of precipitate start to form, the solution being agitated constantly with the air-jet stirrer. Dilute ammonium hydroxide (1 to 4) is then added dropwise until the indicator turns from yellow to purple. The tube is placed in a hot water bath for 5 minutes and cooled, and the volume is adjusted to exactly 60 ml. If the indicator has changed back to yellow, dilute ammonium hydroxide is added until the purple color reappears. The suspension is mixed thoroughly with the air-jet stirrer, then centrifuged for 5 minutes at 1800 r.p.m. The supernatant solution contains calcium, magnesium, and manganese, while the precipitate contains the hydroxy oxides of iron, titanium, and aluminum. A 50-ml. aliquot of the supernatant liquid is pipetted with a Lowy pipet into a 125-ml. conical flask, care being taken that the precipitate is not disturbed. This is Solution E, used for the determination of calcium plus magnesium.

Approximately 50 ml. of a 1% ammonium chloride solution are then added to the tube, and the precipitate is thoroughly mixed with the air-jet stirrer. The suspension is again centrifuged at 1800 r.p.m. for 5 minutes, after which the supernatant liquid is drawn off by gentle suction and discarded.

The precipitate is dissolved by the addition of 3 ml. of 1 to 1 hydrochloric acid, and the suspension is stirred until solution is complete. Next, 10 ml. of hot sodium hydroxide solution are added with stirring, and the suspension is placed in a hot water bath for 5 minutes and then allowed to cool. It is then diluted to exactly 50 ml. with distilled water and mixed with the air-jet stirrer. The stirrer is allowed to drain completely, but the adhering solution is not washed back into the tube. The suspension is centrifuged for 5 minutes at 1800 r.p.m. A 5-ml. aliquot of the supernatant solution is transferred to a 100-ml. volumetric flask, and 3 ml. of 1 to 1 hydrochloric acid are added. The solution is diluted to the mark with distilled water and mixed. This is Solution F, used for the determination of aluminum.

A 10-ml. portion of pH 4.2 buffer solution is placed in a 50-ml. volumetric flask, and the volume of the solution is adjusted to about 30 ml. Exactly 10 ml. of 0.04% aluminon reagent are added, and the flask is swirled to mix the solution. Finally, a Solution F aliquot containing 5 to 35 micrograms of an aluminum is added, and the solution is immediately diluted to the mark and the contents mixed well. (A 5-ml. aliquot is suitable for samples containing 1 to 8% aluminum.) The solution is transferred to a colorimeter tube, and the per cent light transmittance is read 25 minutes after the addition of the sample solution. A 520-mμ light filter is used. Reference to the standard curve gives the concentration of aluminum in solution. The percentage of aluminum in the sample is (micrograms of aluminum per 50 ml./ml. in aliquot) × (0.12/weight of sample).

IRON AND TITANIUM DETERMINATIONS

Reagents. Hydrochloric acid; sodium dithionite ($Na_2S_2O_4$, from Amend Drug and Chemical Co., New York). To prepare the Tiron reagent solution, a 4-gram portion of Tiron (LaMotte Chemical Products Co., Department H, Towson 4, Md.) is dissolved in water, and the solution is diluted to 100 ml. For the buffer solution, pH 4.7, equal volumes of 1 M acetic acid and 1 M sodium acetate are mixed, and the pH is checked on the glass electrode and adjusted as needed with sodium hydroxide or acid. Standard iron solution, stock solution containing 50 micrograms of iron per ml. Aliquots (2, 4, 6, and 8 ml.) of this solution are taken for the standard curve, and the color is developed as described below, the standard solutions being substituted for the Solution A aliquot. Standard titanium solution, stock solution containing 10 micrograms of titanium per ml. Aliquots (2, 4, 6, and 8 ml.) are taken for the standard curve, and the color is developed as described below, the standard solutions being substituted for the Solution A aliquot.

Procedure. A 10-ml. portion of pH 4.7 buffer solution is placed in a 50-ml. volumetric flask. The volume is adjusted to approximately 30 ml. with water, and 5 ml. of 4% Tiron solution are added. A drop of 3% hydrogen peroxide is added to the remaining portion of Solution A, and an aliquot containing from 50 to 250 micrograms of iron and 10 to 100 micrograms of titanium is transferred from Solution A, to the flask. (A 5-ml. aliquot is convenient for samples containing up to 6% iron and 1.2% titanium.) The solution is diluted to the mark with distilled water, and approximately 20 ml. of this solution are transferred to a colorimeter tube. The per cent light transmittance of the blue-violet color of the iron complex is read with a 565-mμ light filter. The color is stable for a long time. Approximately 3 mg. of sodium dithionite is then added to this same solution in the colorimeter tube to destroy the color due to the iron complex by reduction of the iron. The colorimeter tube is stoppered with a No. 3 rubber stopper, and the contents of the tube are mixed gently; the tube is inverted 4 or 5 times. The per cent light transmittance of the yellow titanium complex is obtained within 10 minutes after the addition of the sodium dithionite with the 400-mμ light filter. The concentrations of iron and titanium are then obtained from the standard curves. The percentage of iron in the sample is (micrograms of iron per 50 ml./ml. in aliquot) × (0.01/weight of sample). The percentage of titanium in the sample is (micrograms of titanium per 50 ml./ml. in aliquot) × (0.01/weight sample).

ACCURACY

An analysis of the errors involved in this analytical system shows that the over-all accuracy should be within approximately ±2%. There is an inherent error of approximately ±1% involved in colorimeter readings. The error involved in making volume measurements in the pointed centrifuge tubes is also approximately ±1%. The flame photometer can be assumed to be accurate within ±2% in favorable concentration ranges, and the Versenate titrations involve absoltue errors of approximately ±0.1 ml., which is equivalent to approximately 0.03% of calcium or magnesium. Thus, the maximum relative inherent error for the individual determinations (except in the very low concentration ranges) will be approximately as follows: silicon, ±1%; aluminum, ±3%; iron, ±1%; titanium, ±1%; calcium, ±1% plus titration error; magnesium, ±3% plus double the titration error; sodium, ±2%; and potassium, ±2%. Thus, it is apparent that the maximum inherent error for the complete analysis should be approximately ±2%.

RESULTS

Two samples obtained from the National Bureau of Standards were analyzed to check the accuracy of the new system against standard gravimetric procedures. The two samples, plastic clay and argillaceous limestone, were picked because they exhibited rather extreme variations in their compositions. The results of these analyses are presented in the accompanying Table.

Analyses of Bureau of Standards Samples

(Microchemical system compared to those obtained by National Bureau of Standards (standard)

Elements Determined	Plastic Clay, No. 98		Argillaceous Limestone No. 1A	
	Found	Standard	Found	Standard
SiO_2	59.6	59.1	14.2	14.1
Al_2O_3	25.7	25.5	4.07	4.16
Fe_2O_3	2.07	2.05	1.60	1.63
TiO_2	1.44	1.43	0.19	0.16
CaO	0.21	0.21	41.6	41.3
MgO	0.69	0.72	2.23	2.19
Na_2O	0.24	0.28	0.34	0.39
K_2O	3.26	3.17	0.76	0.71

The values presented for the new system are averages of three determinations. The precision of the individual determinations was within the limits discussed in the section of accuracy.

This system has been applied successfully in this laboratory to the analysis of a variety of materials including soil, clays, tropical soils containing up to 70% iron oxide and 35% titanium oxide, and various relatively pure minerals exhibiting a vast range in chemical composition. In the separation of aluminum from iron, there was noticeable coprecipitation of aluminum on large amounts of hydroxy oxide precipitates of iron and titanium, resulting in low aluminum results. This situation could probably be corrected by converting the precipitated iron oxide to ferrous sulfide by the method presented by Snell and Snell. However, this coprecipitation is not of great significance if the iron oxide content of the sample is less than 15%."

APPENDIX B

METHOD OF SEPARATION AND ANALYSIS OF DIBASIC ACID ESTERS

This analytical method was part of a private communication from Commander W. H. Hilands, USN, Supt., Aero. Materials Lab, Naval Air Material Center, Naval Air Experimental Station, Philadelphia 12, Pennsylvania, on 4 March 1954;

METHODS OF ANALYSIS

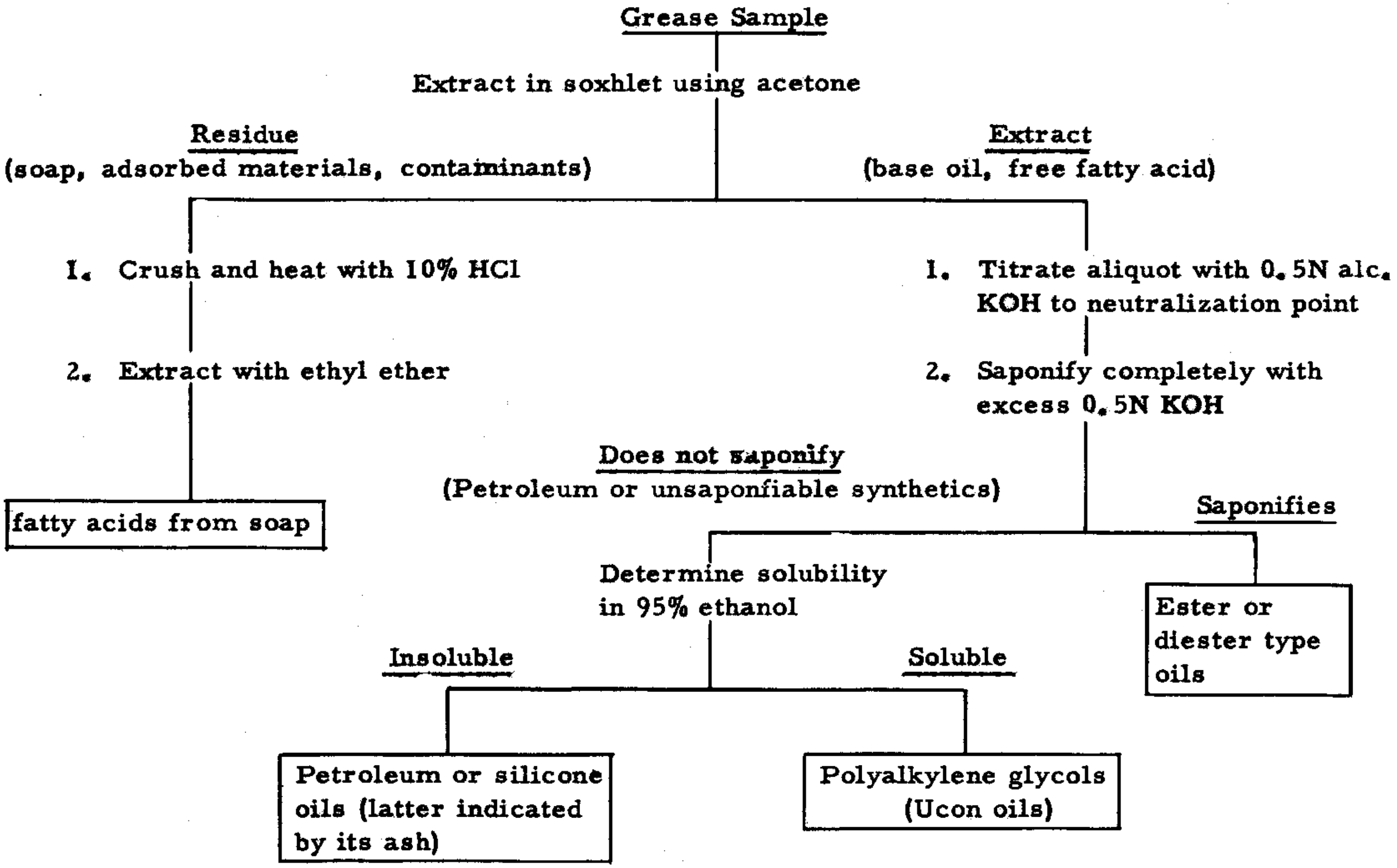
1. SCOPE: This method of analysis was developed because present grease analysis methods (such as Method 541.2.2 of Federal Specification VV-L-791-d) are not satisfactory for determining various synthetic components such as diester, polyalkylene glycol and silicone oils now in common use. The method has been developed in the course of the analysis of ten greases submitted for qualification under the various grease specifications and is limited generally to those items requested; namely:

Ash, Sulfated	Percent
Soap base	
Soap (calc. from ash)	Percent
Free fatty acids	Percent
Oil:	Percent
Viscosity SUV at 100°F.	
Viscosity SUV at 210°F.	
Viscosity Index	

2. REAGENTS: All reagents used were of the quality recommended in Method 541.2.2 of Federal Specification VV-L-791-d.

3. SULFATED ASH: All sulfated ash determinations were made according to the procedure outlined in Method 541.2.2 of Federal Specification VV-L-791-d. When silicone base greases are ashed, the results are meaningless because of the conversion of the oil to SiO_2. The appearance after burning off all combustibles is that of a voluminous fluffy grey mass which is characteristic. Considerable SiO_2 escapes as smoke.

SCHEME OF SEPARATION



4. **SOAP BASE:** Soap bases were determined by flame tests and checked by spectrographic analysis.

5. **FREE FATTY ACIDS:** These determinations were made by shaking up a 10 to 20 gram sample of the grease with 150 cc of acetone or other suitable solvent and titrating with .5N alcoholic KOH. Blanks were also run on the solvents used. The values were then determined as the percent of that fatty acid identified as having been used in the production of the soap. Check determinations of free fatty acid may usually be made on the soxhlet extracted oils since it may be assumed that all free fatty acids in the grease are extracted by the dissolving action of the acetone.

DETAILS OF THE SCHEME OF SEPARATION

a. The soxhlet extraction is conducted by placing as loosely as possible, 10-20 grams of the grease sample into a weighed paper soxhlet thimble which is placed into a soxhlet assembly containing 100cc of solvent in such a manner that the thimble is continuously flushed with condensed solvent. Sealing the top of the thimble with a bit of weighed cotton will prevent the loss of residue through overflow. Acetone is usually a satisfactory solvent; however in cases where heavy oils are present, petroleum ether will be a better choice. The extraction must be conducted for at least 16 continuous hours; some greases will require longer periods. The time required to complete the extraction of a particular grease can best be gauged by the dryness of the residue.

b. After extraction is complete, the residue in the thimble is placed in an oven and dried at a moderate temperature (160°F.). When all the solvent has evaporated, the thimble and residue are weighed. The weight of the residue can then be calculated as the precent of soap present. The value is usually a high one due to the presence of various insoluble materials such as certain additives and contaminants. In order to determine the fatty acid base, the soap residue can be crushed and heated with 10% HCl and thus converted to acid. Melting points and molecular weight determinations may be used to identify the acid.

c. The extracted oils from the grease are concentrated by driving off the solvent on a steam bath. An aliquot portion of 1-2 grams of the oils is then dissolved in 50 ml of methyl ethyl ketone and 15 ml of water and the solution titrated to the phenolphthalein end point with

.5N alcoholic KOH. From this titration can then be calculated the free fatty acid, if a sharp end point is obtained. If light weight esters are present, they sometimes saponify immediately and cause a fading end point. Next, the same solution is treated with 50 ml of .5N alcoholic KOH and heated under reflux. Saponification is complete in 1/2-1 hour and the solution may be back titrated with .5N HCl. A blank is prepared and run using the same solvents. From these data the weight of esters or diesters can be readily calculated after the particular ester has been identified.

d. The esters can be identified in the following manner: The solution that has been saponified and back titrated with HCl is made distinctly alkaline with KOH and evaporated on a steam bath. When all organic solvents are removed, the solution is added to a separatory funnel and extracted several times with small amounts of ethyl ether. The ether solution when evaporated will leave behind the long chain alcohol which was used in the ester. This can be identified by its characteristic odor in most cases. The remaining water solution is treated with 10% HCl until acid and the fatty acid or dibasic acid is filtered off. This acid is washed several times with water and dried in an oven. Molecular weight determinations and melting points will identify the acid.

e. Since diester oils are often blended with petroleum oils, the weight of diester oil should be calculated as the percent of the base oil. It can usually be assumed that the unsaponified portion is a petroleum oil.

f. In the event that there is no significant saponification of the extracted oil, the solubility of it in 95% ethanol is determined. Oils which dissolve completely may be considered to be polyalkylene glycols. These "Ucons" can also be identified by the infra-red spectrophotometer.

g. If the oil is not soluble in alcohol, it then is either a petroleum or silicone oil. An ash of the grease will differentiate between them. If a petroleum type oil is present, the results of this analysis are best checked by running another complete analysis according to Method 541.2.2 of Federal Specification VV-L-791-d.