WADC TECHNICAL REPORT 54-464
PART 2

DEVELOPMENT OF SCHEMATIC ANALYTICAL PROCEDURES FOR SYNTHETIC LUBRICANTS AND THEIR ADDITIVES

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FOREWORD

This report was prepared by the Denver Research Institute under USAF Contract No. AF 33(616)-2204. This contract was initiated under Project No. 3044, "Aviation Lubricants", Task No. 73314, "Lubricants", 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, Lt. H. D. Hill, and Mr. G. Baum acting as successive project engineers.

This report covers period of work from October 1954 to September 1955.

ABSTRACT

General properties and methods for the identification and determination of components of synthetic lubricants and base-oils and their additives are presented and discussed.

Included in these compounds are dibasic acid esters, silicate esters, and silicone oils, and such additives as antioxidants. Analytical procedures employing column and paper partition chromatographic techniques are presented for the identification and separation of different groups of components, such as dibasic acid esters from silicate esters and silicone oils as well as different dibasic esters from each other, along with methods for the paper chromatographic identification and separation of antioxidants in synthetic lubricants.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. WHITMORE
Technical Director
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Directorate of Research

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INTRODUCTION

The incentive of the investigations presented in this report was to develop analytical procedures applicable to synthetic base-oils used as lubricants by the U. S. Air Force.

According to contractual requirement these methods should:

(a) avoid the use of elaborate and expensive optical equipment,

(b) be applicable to the majority of synthetic lubricants and greases, and

(c) have an acceptable accuracy and reproducibility.

This report presents Part 2 of WADC Technical Report 54-464 (141). The latter was concerned primarily with analysis of greases and their additives such as gelling agents, antioxidants, etc. The investigations presented in this report, as Part II of the overall program, deal principally with methods for the analysis of synthetic lube-oils proper and base-oils from greases. Because of the contractual specifications mentioned above the investigations had to be restricted primarily to development of methods such as column chromatography and paper partition chromatography, including a few standard wet chemical methods which seemed sufficiently adequate for the analysis of several groups of base-oil components.

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

I. Dibasic acid esters.

II. Silicate esters.

III. Silicone oils.

IV. Polyethers and polyesters.

V. Fluorinated organic compounds.

Primary emphasis has been placed on investigation of Groups I through III, i.e., on identification and determination of dibasic acid esters, silicate esters, silicone oils, and separation of these compounds from each other. Methods of identification of different types of compounds within the same group were developed, particularly for dibasic acid esters, applying paper partition chromatographic techniques.

The second part of the investigations presented is concerned with identification and determination of antioxidants, and thus represents a continuation of work presented in WADC Technical Report 54-464 (141). It includes the investigation of new types of antioxidants, and thus is an extension and improvement of qualitative and quantitative determinations developed previously.

In accordance with the general scope of these investigations as discussed in more detail in the Foreword, WADC TR 54-464 Part 1 (141), there is presented at the beginning of each section a short discussion of the general constitution and physical properties of the groups of compounds, in order to provide an adequate background for the analyst who is not necessarily a specialist in the field of lubricants. To avoid too many duplications we have referred whenever feasible to methods, procedures, and data already presented in the previous volume.

Future research work on this program must complete the current investigations and must also include new types of components with potential usefulness as lubricants or blends, such as fluorinated compounds, silanes, and polyaromatic compounds.

PART I

ANALYSIS OF SYNTHETIC LUBRICANT BASE-OILS

1.0 INTRODUCTION

The first part of the investigations presented here is concerned primarily with identification and determination of base-oil components present in synthetic lube-oils per se, as well as analysis of base-oils used in the preparation of greases. In Part 1 of this report (141) analytical methods were discussed for the identification and determination of different types of gelling agents and other additives, such as antioxidants, and methods for separation of the different petroleum and synthetic base-oils from thickeners and gelling agents. The present report deals with further analysis of these separated base-oils. The first groups to be attacked were those synthetic base-oils which are most frequently used at the present time in practical compounding of USAF lube-oils and greases in accordance with the emphasis placed by the WADC Materials Laboratory, Lubricants Section. Thus the following groups were placed under primary consideration:

(a) Dibasic acid esters.

(b) Silicate esters.

(c) Silicone oils.

(d) Polyesters and polyethers.

Of these only (a), (b), and (c) could be taken into more detailed consideration, and (d) had to be postponed in favor of further research on antioxidants, presented on Page 83 of this report. The first part of the report has been sub-divided into several Sections, according to the major emphasis placed on the different phases in carrying out the program:

SECTION A: DIBASIC ACID ESTERS.

SECTION B: SILICATE ESTERS AND SILICONE OILS.

SECTION C: QUALITATIVE SEPARATION OF DIBASIC ACID ESTERS, SILICONE OILS, AND SILICATE ESTERS.

SECTION D: QUANTITATIVE SEPARATION OF DIBASIC ACID ESTERS, SILICONE OILS, AND SILICATE ESTERS.

SECTION A

DIBASIC ACID ESTERS

1.0 INTRODUCTION

Dibasic acid esters were the first synthetic base-oils to be investigated more closely during the research program. This class of synthetic lubricants is the most commonly used and also the most thoroughly studied, because many of these compounds have long been used as plasticizers in the field of plastic and rubber-like materials. Initial investigations had already been initiated in the previous year's program (141), and have been continued in this year's program with emphasis on two main aspects:

(a) Separation of dibasic acid esters as a group from other groups of compounds such as silicate esters and silicone oils.

(b) Identification and separation of individual dibasic acid esters from each other.

As was pointed out in the previous year's report, the difficulty in analyzing these compounds is due to the lack of characteristic chemical reactions of the DBAEs* as such, and to the similarity in chemical behavior and physical constants of the individual esters, particularly with the higher molecular weight compounds of the homologous series. Chromatographic methods have been found satisfactory both for separation of the groups as well as for separation of the individual esters. These methods have therefore been further developed in conjunction with subsequent application of other chemical methods such as titration and gravimetric determination for the quantitative estimation of the isolated dibasic acid esters.

* DBAE = dibasic acid ester

1.1 STRUCTURE AND CHEMICAL PROPERTIES OF DIBASIC ACID ESTERS

Dibasic acid esters are compounds of higher molecular weight alkyl dibasic acids (with 4 to 12 carbon atoms) or aromatic dibasic acids (such as phthalic acid) combined with higher molecular weight primary alcohols such as iso-amyl alcohol, 2-ethyl-hexyl alcohol (octyl alcohol), etc. The dibasic acid esters (abbreviated as DBAE) used as synthetic lubricants can be classified according to the dibasic acid present in the molecule. Thus, the following groups may be distinguished:

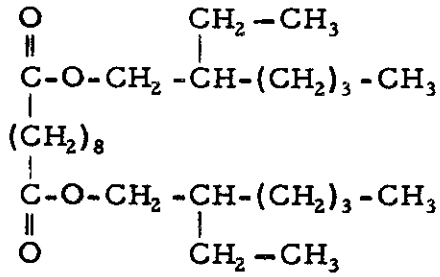
(1) Adipic acid esters.

(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 is di-2-ethylhexyl-sebacate:



DBAEs are mostly colorless liquids having molecular weights of 300-400, high boiling points, and low melting points. They are soluble in most organic solvents and practically insoluble in water. Their oxidative and hydrolytic stability is higher than that of monocarboxylic esters; this latter property can be used for their separation from monobasic esters, particularly from alkali and alkaline-earth stearates or palmitates, etc., by hydrolysis of the monobasic ester with cold HCl (1:1), cold acetic acid, or even formic acid.

The different homologous derivatives of the same dibasic acid are quite similar in their physical properties such as boiling point, refractive index, solubility, as well as with respect to certain

characterization constants such as saponification number. Thus these physical constants can be used only in a limited way for characterization of the diesters in mixtures. Direct trans-esterification of the diesters to acetyl esters or butyl esters is also rather difficult. At higher temperatures and under pressure DBAEs are quantitatively hydrolyzed in acidic or alkaline media to the corresponding acids or their salts and the alcohols. The separated dibasic acids can then be characterized in several ways, e.g. melting point of their salts, boiling point of their methyl esters, acid numbers, etc.

2.0 METHODS OF APPROACH FOR ANALYSIS OF DIBASIC ACID ESTERS

In spite of the inertia of the diesters towards characteristic chemical reactions, the only logical approach for their analysis would be one of the following:

(a) Hydrolysis of the DBAE followed by identification and quantitative determination of the dibasic acid and corresponding alcohol formed.

(b) Trans-esterification and characterization of the volatile methyl ester of the dibasic acid.

(c) Formation of hydroxamates from the methyl ester of the dibasic acid and characterization by melting point determination.

Because of difficulties in direct trans-esterification of the original diester and due to the fact the hydroxamate formation can be carried out most efficiently only from the methyl ester of the acid, the formation of which depends upon hydrolysis, the most important step for analysis of the diester is its hydrolysis. Thus method (a) will be in most cases the simplest method of approach for qualitative and quantitative determination of a given DBAE.

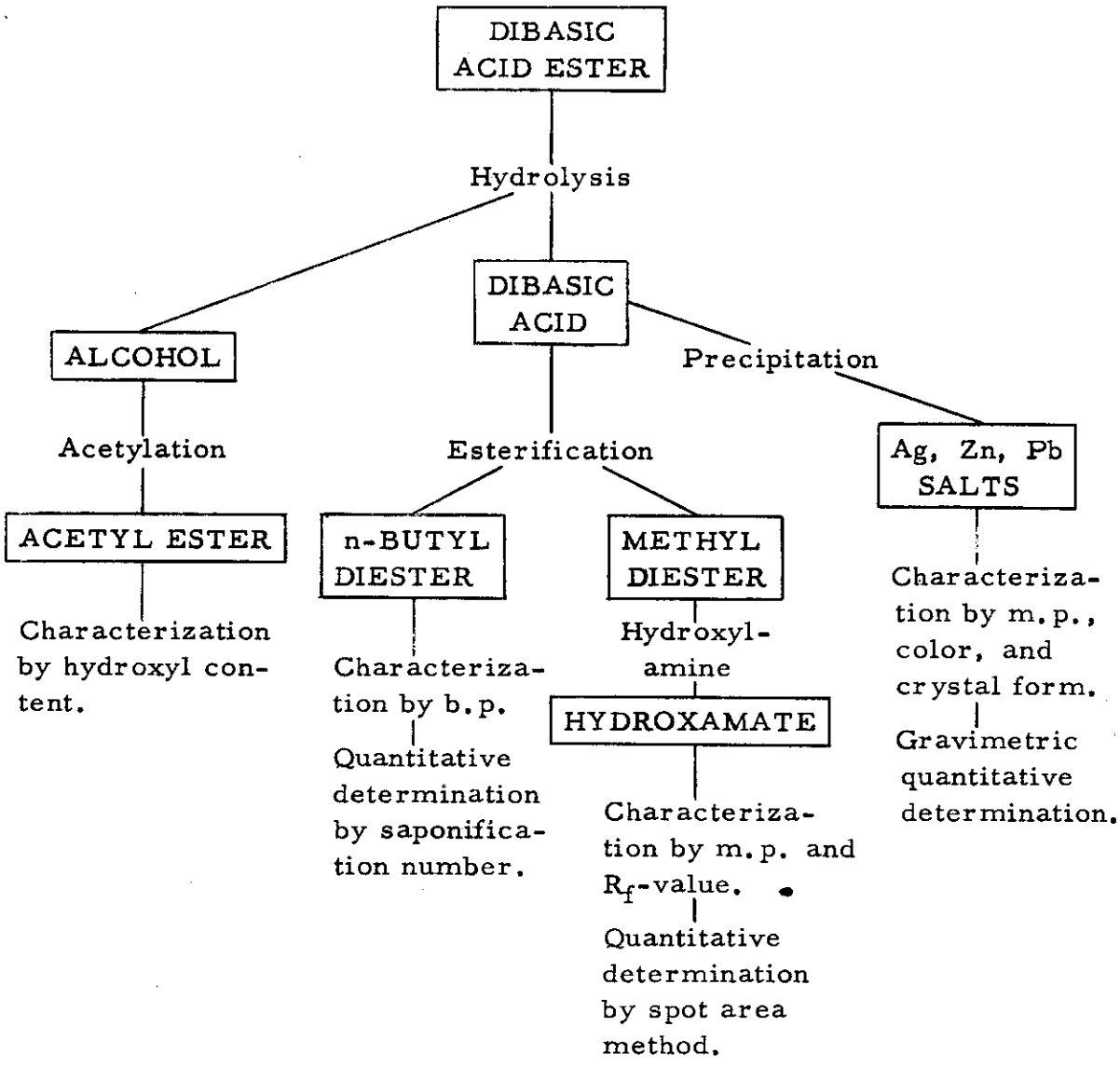
2.1 FEASIBILITY OF THE HYDROLYTIC METHOD

The hydrolytic method for identification and determination of dibasic acid esters is feasible in cases where either a single DBAE is present or two DBAEs with the same acid base but different alcohol components. In these cases determination of the dibasic acids and alcohols and their correlation to each other will be possible, providing no other hydrolyzable ester is present at the same time.

Several methods for identification of the hydrolyzed diester are possible and are presented schematically below. However, in cases where several DBAEs or other hydrolyzable compounds are present at the same time, the hydrolysis produces a series of dibasic acids and alcohols, and the correct correlation of these components to each other is complicated. In this situation identification of the individual diesters prior to the hydrolysis will be necessary.

2.1.1 Single Dibasic Acid Esters

The method of approach for determination of a single DBAE is summarized in the following schematic diagram:



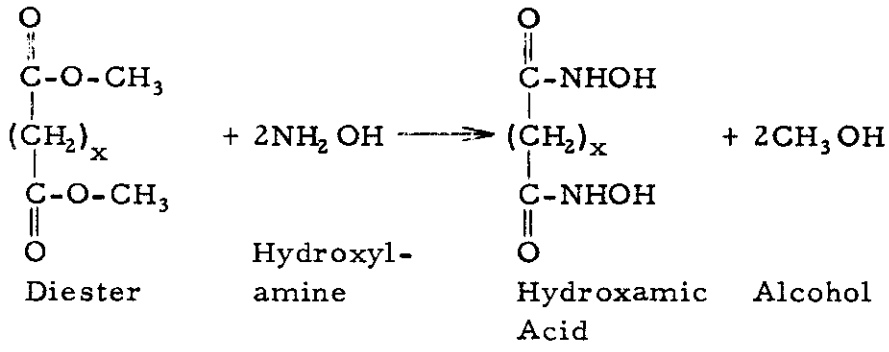
In this case the DBAE is hydrolyzed and the dibasic acid and alcohol are characterized and determined quantitatively. The alcohol can be characterized sufficiently in most cases by determining the percent hydroxyl groups present and by the boiling point. The dicarboxylic acid can be determined in several ways:

(a) Gravimetric determination by precipitating the acid as the Ag, Zn, or Pb salt. This method can be used to a certain extent for quantitative separation and determination of several different dicarboxylic acids.

(b) Titration of the free acid with alcoholic KOH.

(c) Formation of the n-butyl diester and distillation of the diester. The n-butyl esters of dibasic acids show characteristic boiling points. Hydrolysis of the fractionated n-butyl diesters may be used as a means for their quantitative determination.

(d) Formation of the methyl diester and use of this ester for the formation of acid hydroxamates with hydroxylamine in ether, according to the reaction:



The hydroxamates show characteristic melting points for different acids and can be chromatographed on paper, giving characteristic R_f-values. The spots on the paper can be detected readily by color reaction with ferric ion, e.g. ferric chloride or preferably ferric perchlorate. Characteristic pink or red-brown colored spots are formed with different mono- and dibasic acid esters. Although this method is not always conclusively applicable, particularly with mixtures of several DBAEs, it is one of the more feasible methods for quantitative determination of DBAEs after their qualitative nature has been determined by other means.

2.1.2 Mixture of Dibasic Acid Esters

Whenever a mixture of several DBAEs is present in a synthetic lube-oil, characterization of the individual diesters by the hydrolytic method described above becomes complicated because the hydrolysis produces a series of dibasic acids and alcohols. Although it is possible to determine qualitatively and quantitatively the type of dicarboxylic acids and possibly also the type of alcohols, it is difficult to correlate the different alcohols found to the corresponding acids. This in turn complicates quantitative evaluation of the mixture of diesters.

In this case qualitative identification of the unhydrolyzed dibasic acid esters is necessary. Once the qualitative nature of the mixture of DBAEs is known, correlation of the different acids and alcohols found in the hydrolyzate is possible and the quantitative evaluation is simplified. Qualitative identification of the unhydrolyzed esters, however, is difficult because of the lack of specific simple reactions, e.g. color reactions, precipitation reactions, etc. During the previous year's program the feasibility of column and paper partition chromatography was investigated, and it was found that the paper chromatographic technique in particular is applicable not only to the hydrolyzed dibasic acid but also to the unhydrolyzed diester (see 141, p. 159-60). Thus the paper chromatographic technique was developed further for identification of individual diesters, whereas the column chromatographic technique proved more useful for separation of the entire group of diesters from other groups of base-oils, or for separation of the different dicarboxylic acids from each other in the hydrolyzed diester mixture. Detecting the diester spots on the paper was the only major difficulty in using the paper chromatographic technique; the inertness of the compounds made it impossible to employ the usual type of chemical reactions to reveal the location of the diester spots directly on the paper.

2.2 DETECTION OF DIBASIC ACID ESTERS IN BASE-OILS

2.2.1 Detection With Hydroxylamine or With Fat-Staining Dyes

Because of their chemical inertness the unhydrolyzed DBAEs cannot be detected readily in the base-oil itself. It is therefore necessary to hydrolyze the diester and then identify the corresponding dibasic

acid, e.g. by precipitation as a heavy metal salt, or by color reaction as hydroxamate with ferric chloride. The latter reaction has also been tried as a means to detect diester spots on paper strips. Although this technique gives good results with dibasic acids, it is not feasible with the higher molecular weight diesters themselves because these diesters do not trans-esterify easily and do not split on the paper with hydroxylamine as compared with the methyl diesters (see Par. 2.0, p.4). If the chromatogram is developed on acetylcellulose paper, hydroxylamine attacks the acetyl groups in the cellulose much more readily than it attacks the diester on the paper, and thus by subsequent treatment with ferric chloride the whole paper strip becomes a hydroxamate derivative, turns yellow-brown, and masks the diester spots. Therefore other means for detection have been sought. In a limited way coloration of the diester with organic stains such as Sudan III and Sudan IV showed some promise, but this technique did not prove to be completely satisfactory.

Since DBAEs exhibit some similarities to certain fats like glycerides, e.g. the formation of fatty spots, it was conceivable that methods used in the analysis of fatty glycerides could possibly also be applied to the analysis of DBAEs. This lead to investigation of fluorescent dyes for detection of unhydrolyzed DBAEs on acetylcellulose paper.

2.2.2 Detection of Dibasic Acid Esters With Fluorescent Dyes

The use of fluorescent dyes for the identification of compounds on paper chromatograms (in this case called fluorograms) was introduced by Kaufman and Budwig (29, 30, 32) for the paper chromatographic analysis of fatty acids and fatty glycerides. Later this method was also introduced for the detection and identification of unsaturated fatty acids (31), lacquers, poly-oils (32), and other compounds when using paper chromatographic techniques.

There is a series of such fluorescent indicators which are suitable for the detection of fatty materials and fatty acids and which therefore seemed potentially useful for the detection of DBAEs. Table I, p. 9 , summarizes the different dyes investigated for detection of DBAEs on acetylcellulose paper, and the appearance of the paper and diester spots after application of the dye by spraying (0.1% aqueous solutions of the dye were used).

TABLE I

Fluorescent Indicators For Detection
of Dibasic Acid Esters On Paper Chromatograms

Fluorescent Indicator	Appearance of Paper and Diester in Visible Light	Appearance in UV-Light		Remarks
		Background	Diester	
Quinine	Colorless	Blue	Blue	No distinction.
Acridine Orange	Orange	Light yellow	Light orange	Slight distinction. Good for acids.
Anthracene	Colorless	Blue	Bluish-red	Poor distinction.
Fluoresceine	Yellow	Greenish-yellow	Orange-yellow	Fades quickly-easily quenched.
Rhodamine B	Crimson-red	Wine-red	Carmine-red	Good distinction.
Fluorol G	Brownish-yellow	Yellow-green	Orange-green	Fair distinction.
Chlorophyll	Brownish-green	Yellow-green	Yellow-green	No distinction.
Nile Blue A	Blue	Blue	Blue-violet	Poor distinction.

There are numerous other fluorescent dyes known in the literature which have potential value as specific indicators for the DBAEs; these will have to be found in the course of further investigation. It seems, however, that for use with DBAEs the most suitable indicators will be certain types of diphenyl polyenes, e.g. different types of stilbenes, and a number of ketones such as benzophenone and its derivatives. It is also visualized that a mixture of different fluorescent indicators could provide a spray reagent which would differentiate between the DBAE spot and

the background with stronger contrast than would a single indicator. However, for initial investigations dyes have been employed which are similar to those applied by Kaufman and Budwig (loc. cit.) for detection of glycerides and higher molecular weight fatty acids. The following fluorescent indicators have been tested with DBAEs: quinine sulfate, acridine orange, Rhodamine B, Nile Blue A, anthracene, Anthranole, fluoresceine, chlorophyll, Fluorol G, Fluorol GR, and some mixtures thereof.

Although several of these dyes showed distinct fluorescence on the ester spots when compared to the background, it was found that the indicator of choice from this particular group was Rhodamine B. Spraying the paper on only one side with a 0.1% aqueous solution of Rhodamine B showed that the dye was readily taken up by the DBAE and therefore appeared on the opposite side of the paper as a pink or red spot which fluoresced under UV-light with a brilliant purple-red color. The remainder of the paper, being hydrophobic, repelled the aqueous dye solution, which was blotted off to a great extent or washed away by a short rinsing with water in a Petri dish. The intensity of fluorescence increased overnight and did not diminish in intensity after at least a week; after this time the DBAE slowly migrates and dissipates in the paper and the spots become indistinct. Another advantage in the use of Rhodamine B rests in the fact that it can be used simultaneously for the detection of silicate esters and silicone compounds, both of which quench the fluorescence when viewed in UV-light, causing dark blue spots or voids to appear on the paper, which fluoresces bright rose (see Par. 2.2.1. p.53).

It is obvious of course that among the numerous fluorescent dyes, such as those compiled in Forster's study on luminescence (18), or in the tables of Bandow (8), or Ley and Engelhardt (18), there may be even more suitable compounds available for detection and differentiation between different types of base-oil compounds. The screening of such indicators will be a part of the future program. For determination of the characteristic R_f-values of DBAEs as well as for investigation of silicone and silicate esters, however, the use of Rhodamine B is adequate and shows sufficient ability to differentiate between these two basic groups of compounds.

3.0 SEPARATION OF DIBASIC ACID ESTERS ON ACETYLCELLULOSE PAPER

Having an adequate fluorescent indicator on hand, the problem of separating the different DBAEs from each other by partition paper chromatography could be attacked. A large number of runs with different DBAEs, using different solvent combinations, were carried out. Application of a 5% benzene solution of the diester to the acetylated paper was carried out with a micro-pipet in the same manner as that described with antioxidants (see 141, p. 122), and the paper strips were cut either square or similar to the technique used for determination of antioxidants (see Par. 2.2.1, p. 85 of this report). Development of the chromatogram was carried out using the ascending technique rather than the descending technique because of the shorter time involved. After marking the front and drying, the strips were fastened in a frame and sprayed only on the back side with 0.1% aqueous solution of Rhodamine B, left for a few minutes, rinsed for ten seconds in distilled water, and blotted. The position of the DBAEs appears in UV-light as bright purple-red spots or arcs, which were outlined on the paper with a pencil.

For the preparation of lipophilic acetylcellulose chromatographic paper, see APPENDIX A, p. 116.

3.1 SOLVENT COMBINATIONS

After it was found that DBAEs could be moved as spots as acetylated paper, the next problem was development of a solvent combination which on the one hand could separate the whole group of DBAEs from the silicones and silicate esters and on the other hand would permit separation of possible mixtures of several DBAEs. In other words the solvent combination should cause distinctive differences in R_f-values of the DBAEs, which would allow characterization of the individual DBAE, since the fluorescent indicator does not discriminate color-wise between different DBAEs. Although among the various solvent combinations investigated experimentally an ideal solvent combination has not as yet been found, to date the most suitable solvent combination for separation of di-octyl-sebacate, di-octyl-adipate, and di-octyl-phthalate has been found to be methanol:acetone:water (in various proportions) which gives sufficiently distinctive R_f-values to the DBAEs for their separation and characterization. The results of runs with these solvent combinations are included in Table II, p. 12, and Table IV, p. 15,16.

Other solvent combinations have also been investigated in order to include other DBAEs than just the di-octyl esters mentioned previously. The results of these investigations are summarized in Table IV, p. 15,16.

TABLE II

Partition Chromatographic Separation of
Dibasic Acid Esters on Acetylcellulose Paper
(Indicator: Rhodamine B)

Diester	Solvent Combination *	R_f-Value
Di-n-butyl sebacate	I	0.79
"	II	0.15
"	III	0.95
"	IV	0.62
"	V	1.00
"	VI	1.00
Di-2-ethylhexyl adipate	I	0.49; 0.46
"	II	0.17
"	III	0.96
"	IV	0.53
"	V	1.00
"	VI	1.00
Di-n-butyl phthalate	I	1.00
"	II	0.35
"	III	1.00
"	IV	1.00
"	V	1.00
"	VI	1.00

* Solvent Combinations:

I - MeOH:Acetone:Water (3:1:1, v/v)
II - MeOH:Water (1:1, v/v)
III - MeOH:Acetone:Water (6:1:1, v/v)
IV - MeOH:Acetone:Water (12:3:5, v/v)
V - BuAc:Pyridine:Water (6:30:60, v/v)
VI - BuAc:Pyridine:Water (6:30:42, v/v)

3.2 SEPARATION OF DIBASIC ACID ESTERS FROM ANTIOXIDANTS OR OTHER BASE-OIL COMPONENTS

Since in the compounded lube-oil other components such as antioxidants and base-oils like silicones or polyglycols are usually present, it was necessary to determine whether these components would interfere with the separation and identification of DBAEs. Mixtures of different DBAEs with various antioxidants have been submitted to paper chromatographic separation and subsequently the fluorogram developed. It could be shown that the presence of such antioxidants as N-phenyl-alpha-naphthylamine, phenothiazine, and hindered phenols did not interfere with separation of the DBAEs. Using the solvent combination MeOH:Acetone:Water (12:3:5, v/v), the R_f-values of the mentioned antioxidants are much lower than those of the esters, and the antioxidants can be detected chemically prior to spraying dye on the fluorogram. If the antioxidants themselves fluoresce like N-phenyl-alpha-naphthylamine, the fluorescence of these compounds is not affected by spraying the fluorogram with Rhodamine B. A summary of several runs with DBAEs and antioxidants is presented in Table III, p.14.

As far as other principal base-oil constitutents are concerned, it was found that silicones and silicate esters will not interfere because of their low R_f-value. Free fatty acids can be distinguished by their blue-violet or greenish fluorescence and similarly mineral oils can be distinguished by their greenish-blue fluorescence, which is not altered by the presence of the Rhodamine B. Whether the presence of polyglycols or corrosion preventive compounds will interfere must still be investigated; however, it is expected that these compounds are not likely to interfere with the determination of DBAEs, if an adequate solvent combination is used.

3.3 FEASIBILITY OF REVERSED PHASE PAPER PARTITION CHROMATOGRAPHY FOR IDENTIFICATION AND SEPARATION OF DIBASIC ACID ESTERS

In order to prove the feasibility of the reversed phase paper partition chromatographic technique for identification and separation of DBAEs, it was necessary to test a large number of solvent combinations until the most usable combination or group of combinations was discovered. As will be discussed in succeeding paragraphs, it was noted that the DBAEs fell roughly into three R_f-value ranges, the group having the lowest

TABLE III

Separation of Dibasic Acid Esters
From Antioxidants on Acetylcellulose Paper
(Solvent Combination: MeOH:Acetone:Water, (12:3:5, v/v)

Mixture	R_f-Value of Diester	R_f-Value of Antioxidant	Fluorescence With Rhodamine B
Di-octyl-sebacate Phenothiazine (PT)	0.62	0.11	DBAE purple PT green
Di-octyl-adipate N-phenyl-alpha-naphthylamine (PANA)	0.51	0.16	DBAE purple PANA blue
Di-octyl-sebacate 2,6-ditertiary butyl-4-methyl-phenol (26Ph)	0.43	0.05	DBAE purple 26Ph none

R_f-values being the highest molecular weight compounds and the group having the highest R_f-values being the lowest molecular weight compounds, with a given solvent combination. Therefore it was necessary to find solvent combinations which would be able not only to separate the diesters into the three groups, but also the diesters within a single group. This required use of more than one solvent combination to establish definitely the identity of a single or a mixture of DBAE; one solvent combination would be used to establish to which group the DBAE(s)belonged, and a second solvent combination would be required to separate and permit identification of the DBAE(s) within the group. Table IV, p. 15-16, is a summation of all of the runs made with DBAEs in the effort to find those solvent combinations which would permit complete separation and identification of any possible mixture of DBAEs which might be encountered in the analysis of synthetic base-oils.

From results of the experiments presented in Table II, p. 12, and Table IV, p. 15-16, it can be concluded that paper partition chromatography is applicable and feasible for separation and identification of dibasic acid esters if it is carried out in reversed phase (see 141, p.124), using

TABLE IV

Summary of Paper Partition Chromatographic Runs With Dibasic Acid Esters
(Acetylated Whatman No. 1 Filter Paper; Indicator: Rhodamine B)

Run No.	Diester or Mixture	Spot Vol. (λ)	Solvent Combination	R_f-value*								Paper Width (cm.)	Cut**	Remarks
				DOA	DOS	DOP	DAA	DAS	DBS	DBP	DBSu			
1	DOA	2.5	MeOH:Ac:H_2O (12:3:7, v/v)	.35	-	-	-	-	-	-	-	3	C	Well defined.
2	DOS	"	"	-	.10	-	-	-	-	-	-	"	"	Tailing up to 0.28.
3	DOA-DOS	"	"	.32	.10	-	-	-	-	-	-	"	"	Overlapping; fanning.
4	DOA	"	"	.34	-	-	-	-	-	-	-	"	"	Well defined.
5	DOS	"	"	-	.08	-	-	-	-	-	-	"	"	Defined;fanning.
6	DOA-DOS	5	"	.30	.05	-	-	-	-	-	-	"	"	Fair separation.
7	DOA	2.5	"	.31	-	-	-	-	-	-	-	"	B	Defined spot.
8	DOS	2.5	"	-	.10	-	-	-	-	-	-	"	B	Defined arc; fanning.
9	DOA-DOS	5	"	.24	.06	-	-	-	-	-	-	"	B	Fair separation.
10	DOA	"	EtOH:Ac:H_2O (12:3:7, v/v)	.62	-	-	-	-	-	-	-	"	"	Defined wide arc.
11	DOS	"	"	-	.50	-	-	-	-	-	-	"	"	Elongated; irregular.
12	DOA-DOS	10	"	.44	.60	-	-	-	-	-	-	"	"	Overlapping; no sepn.
13	DOA	2.5	EtOH:Ac:H_2O (24:7:15, v/v)	.70	-	-	-	-	-	-	-	4	C	Defined sharp arc.
14	DOS	2	"	-	.66	-	-	-	-	-	-	"	"	Defined irregular arc.
15	DOA-DOS	5	"	?	?	-	-	-	-	-	-	"	"	Overlapping; no sepn.
16	DOA	2.5	MeOH:Ac:H_2O (12:3:6, v/v)	.45	-	-	-	-	-	-	-	3	"	Defined spot.
17	DOS	"	"	-	.21	-	-	-	-	-	-	"	"	Diffuse from 0.1-0.4.
18	DOA	5	EtOH:Ac:H_2O (12:3:6, v/v)	.80	-	-	-	-	-	-	-	4	D	Defined spot.
19	DOS	"	"	-	.70	-	-	-	-	-	-	"	"	Elongated; fanning.
20	DOA-DOS	10	"	.80	.66	-	-	-	-	-	-	"	"	Overlapping; no sepn.
21	DOA	2.5	MeOH:Ac:H_2O (12:3:5, v/v)	.57	-	-	-	-	-	-	-	4	D	Defined but wide.
22	DOS	"	"	-	.37	-	-	-	-	-	-	"	"	Elongated; fanning.
23	DOP	"	"	-	-	.46	-	-	-	-	-	"	"	Defined; rather large.
24	DBS	"	"	-	-	-	-	-	.63	-	-	"	"	Well defined arc.
25	DBP	"	"	-	-	-	-	-	-	.63	-	"	"	Defined spot.
26	DOA	"	MeOH:Ac:H_2O (37:9:23, v/v)	.18	-	-	-	-	-	-	-	3	A	Fuzzy; tailing.
27	DOS	"	"	-	.03	-	-	-	-	-	-	"	"	"
28	DOA	"	MeOH:Ac:H_2O (37:9:22, v/v)	.28	-	-	-	-	-	-	-	"	"	Well defined.
29	DOS	"	"	-	.07	-	-	-	-	-	-	"	"	Elongated.
30	DOA-DOS	"	"	.25	.07	-	-	-	-	-	-	"	"	Good separation.
31	DOA-DOS	"	MeOH:Ac:H_2O (39:9:22, v/v)	.26	.10	-	-	-	-	-	-	"	B	Overlapping.
32	DOA	"	MeOH:Ac:H_2O (37:9:21, v/v)	.34	-	-	-	-	-	-	-	"	D	Defined spot.
33	DOS	"	"	-	.12	-	-	-	-	-	-	"	"	Defined spot; fanning.
34	DOP	"	"	-	-	.30	-	-	-	-	-	"	"	Defined spot.
35	DOA-DOS	"	"	.34	.08	-	-	-	-	-	-	"	"	Good separation.
36	DAA	"	"	-	-	-	.52	-	-	-	-	"	"	Defined spot.
37	DOP-DAA	"	"	-	-	.36	.54	-	-	-	-	"	"	Good separation.
38	DBP	"	"	-	-	-	-	-	-	.52	-	"	"	Defined spot.
39	DBS	"	"	-	-	-	-	-	.47	-	-	"	"	"
40	DAS	"	"	-	-	-	-	.49	-	-	-	"	"	"
41	DBSu	"	"	-	-	-	-	-	-	-	.53	"	"	Defined spot; faint.

TABLE IV concluded on following page.

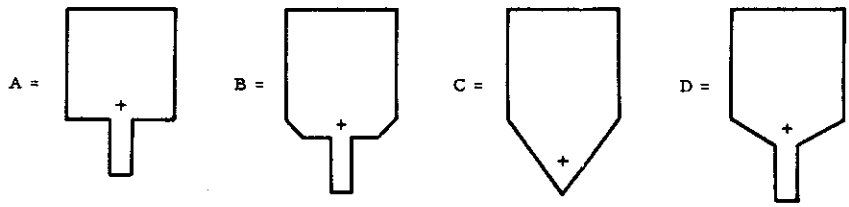
TABLE IV - Continued

Summary of Paper Partition Chromatographic Runs With Dibasic Acid Esters
(Acetylated Whatman No. 1 Filter Paper; Indicator: Rhodamine B)

Run No.	Diester or Mixture	Spot Vol. (λ)	Solvent Combination	R_f-value*								Paper Width (cm.)	Cut**	Remarks
				DOA	DOS	DOP	DAA	DAS	DBS	DBP	DBSu			
42	DOA	2.5	MeOH:Ac:H_2O (37:10:21, v/v)	.38	-	-	-	-	-	-	-	3	B	Well defined.
43	DOS	"	"	-	.08	-	-	-	-	-	-	"	"	Fanning.
44	DOP	"	"	-	-	.32	-	-	-	-	-	"	"	Defined spot.
45	DOA-DOS	"	"	.35	.14	-	-	-	-	-	-	"	"	Overlapping; poor sepn.
46	DOP-DOS	"	"	-	.15	.32	-	-	-	-	-	"	"	DOS fanning; poor sepn.
47	DBP	"	"	-	-	-	-	-	-	.50	-	"	"	Defined spots; faint.
48	DOA	"	MeOH:Ac:H_2O (37:8:21, v/v)	.30	-	-	-	-	-	-	-	"	B	Well defined.
49	DOS	"	"	-	.10	-	-	-	-	-	-	"	"	Fanning.
50	DOA-DOS	"	"	.28	.10	-	-	-	-	-	-	"	"	Fair separation.
51	DBP	"	"	-	-	-	-	-	-	.45	-	"	"	Faint.
52	DOA	"	MeOH:Ac:H_2O (37:8:24, v/v)	.16	-	-	-	-	-	-	-	3	"	Defined; elongated.
53	DOS	"	"	-	.06	-	-	-	-	-	-	"	"	Well defined.
54	DOA-DOS	"	"	.22	.03	-	-	-	-	-	-	"	"	Very good separation.
55	DOP-DAA	"	"	-	-	.21	.43	-	-	-	-	"	"	Good separation.
56	DBP	"	"	-	-	-	-	-	-	.44	-	"	"	Defined spots.
57	DAS	"	MeOH:Ac:H_2O (4:1:4, v/v)	-	-	-	-	.08	-	-	-	"	D	Defined spots.
58	DAA	"	"	-	-	-	.18	-	-	-	-	"	"	"
59	DBS	"	"	-	-	-	-	-	.11	-	-	"	"	Well defined.
60	DAA-DBS	"	"	-	-	-	.20	-	.12	-	-	"	"	Good separation.
61	DBP	"	"	-	-	-	-	-	-	.19	-	"	"	Faint.
62***	DOA	"	MeOH:Ac:H_2O (37:9:22, v/v)	.19	-	-	-	-	-	-	-	4	D	Blurred; good sepn.
63***	DOS	"	"	-	.07	-	-	-	-	-	-	"	"	"
64***	DOA-DOS	"	"	.22	.03	-	-	-	-	-	-	"	"	"
65***	DAA	"	"	-	-	-	.38	-	-	-	-	"	"	"
66	DOP	"	"	-	-	0.16	-	-	-	-	-	"	"	"

* Abbreviations used for dibasic acid esters:
DOA = di-(2-ethylhexyl)-adipate ("Flexol A26", Carbide & Carbon)
DOS = di-(2-ethylhexyl)-sebacate ("Plexol 201", Rohm & Haas)
DOP = di-(2-ethylhexyl)-phthalate ("Flexol DOP", Carbide & Carbon)
DAA = di-(iso-amyl)-adipate ("Plexol 268", Rohm & Haas)
DAS = di-(sec. amyl)-sebacate ("Plexol 202", Rohm & Haas)
DBS = di-(n-butyl)-sebacate (Eastman)
DBP = di-(n-butyl)-phthalate (Eastman)
DBSu = di-(n-butyl)-succinate (Eastman)

** Type of Cut:



*** Descending run; all other runs are ascending.

fluorescent dyes to locate the diester spots. With the use of different solvent combinations it is possible to use this method for the following operations:

(a) Qualitative separation of DBAEs as a group from other groups of compounds such as silicate esters and silicone oils. These separations are discussed in more detail in Par. 3.0, p.60 .

(b) Separation and identification of individual diesters by their R_f-values, using the most suitable solvent combination.

(c) Separation and identification of mixtures of two or more esters by subsequent development with one or more solvent combinations.

Methods (b) and (c) will be discussed in detail in the following paragraphs. The presented methods employ Rhodamine B as indicator for detecting the spots or arcs on the paper. It is conceivable that other fluorescent dyes may prove to be more sensitive and eventually more selective.

Practical application of these methods to commercial grade DBAEs used in compounding synthetic lube-oils encounters complications because of impurities present in some of the DBAEs. Thus, for example, the "tailing" and fanning of di-octyl-sebacate spots on the paper with most solvent combinations is due more to impurities than to its higher molecular weight. Isomers and also polymers which could conceivably be present have slightly different R_f-values than the diester and thus move at a different rate with the solvent combination, causing formation of a long streak rather than a well-defined spot. This fact also demonstrates a limitation of paper partition chromatography as a separation method, in that compounds which consist of a mixture of polymers of the same basic molecular unit with different degrees of polymerization will not be separated into a well defined spot; rather they will appear as an elongated streak which can extend over the entire length of the chromatogram, thus completely overlapping other compounds present, preventing their identification.

For this reason most of the solvent combinations have been investigated for their ability to separate di-octyl-adipate and di-octyl-sebacate mixtures, because not only are these two DBAEs most commonly employed in synthetic lubricants, but also because the R_f-values of these compounds are relatively close and the fanning of the sebacate ester makes

separation rather difficult. If a solvent combination can separate these two compounds, then other DBAEs can also be separated as well, since most other DBAEs have similar or higher R_f-values than di-octyl-adipate.

The solvent combinations which proved to be most satisfactory were those used in Runs 32-41, 42-47, 52-56, and 57-61, Table IV, p. 15:

(a) Methanol:Acetone:Water (37:9:21, v/v)
(b) Methanol:Acetone:Water (37:10:21, v/v)
(c) Methanol:Acetone:Water (37:8:24, v/v)
(d) Methanol:Acetone:Water (4:1:4, v/v)

These solvent combinations can be used both for separation of DBAEs into different sub-groups and for identification of certain DBAEs as specific compounds, as discussed in detail in the following section.

3.4 IDENTIFICATION OF INDIVIDUAL DIBASIC ACID ESTERS

Using one or a combination of two of the four most efficient solvent combinations presented in Par. 3.3, p. 13, individual DBAEs can be identified with sufficient accuracy to indicate further steps in the analytical procedure. Using, for example, the solvent combination (a) methanol: acetone: water (37:9:21, v/v), the different DBAEs have the R_f-values presented in Table V, p.19. This solvent combination distinguishes between three possible groups of DBAEs:

(a) An R_f-value of about 0.12 indicates very definitely the presence of di-octyl-sebacate (DOS).

(b) An R_f-value of 0.30-0.34 can indicate either di-octyl-adipate (DOA) or di-octyl-phthalate (DOP).

(c) An R_f-value of 0.47-0.52 can indicate the presence of one of four different DBAEs.

Figure 1, p. 20, presents a drawing of the actual paper chromatograms obtained with DBAEs on acetylcellulose paper with the solvent combination MeOH:Ac:H_2O (37:9:21, v/v). The figure demonstrates clearly separation of the various DBAEs into three distinct R_f-value groups.

TABLE V

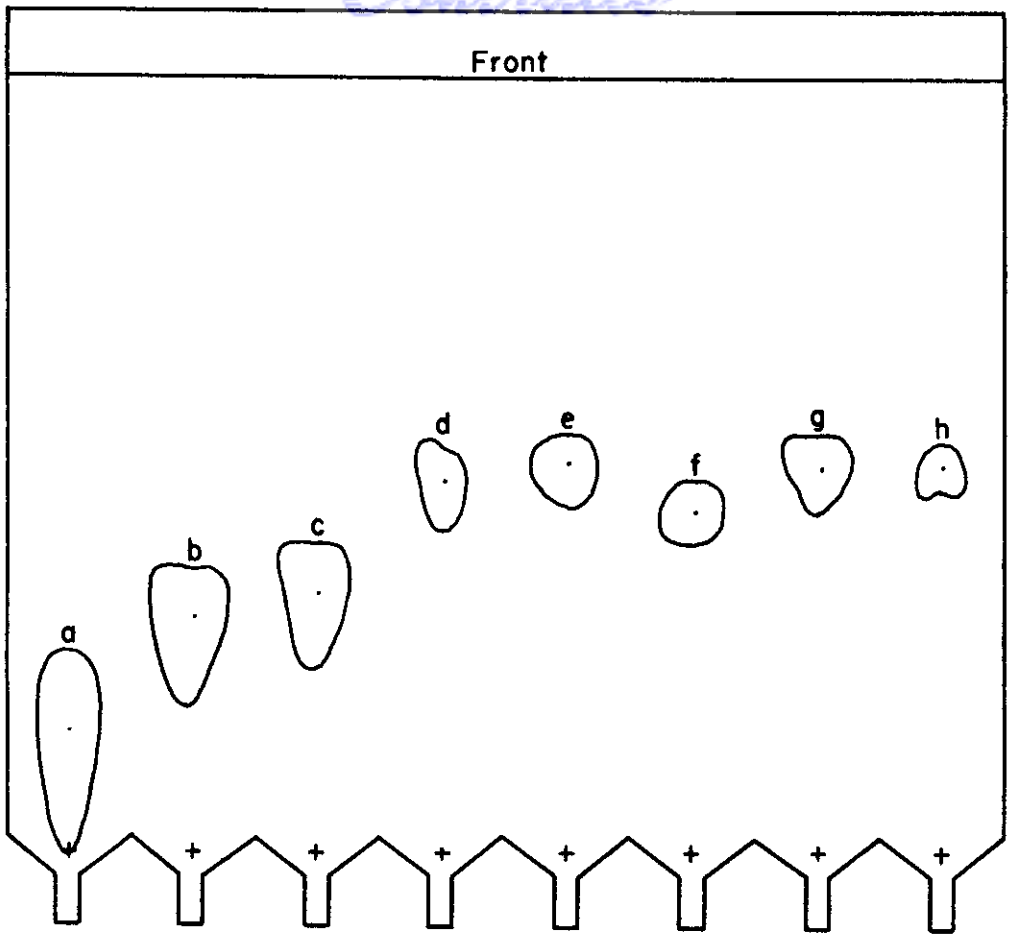
R_f-Values of Different Dibasic Acid Esters on Acetylcellulose Paper With Solvent Combination MeOH:Ac:H_2O (37:9:21, v/v)

Diester	R_f-Value
Di-octyl-Sebacate	0.12
Di-octyl-Phthalate	0.30
Di-octyl-Adipate	0.34
Di-n-butyl-Sebacate	0.47
Di-isoamyl-Adipate	0.49
Di-n-butyl-Phthalate	0.52

In order to distinguish between DOA and DOP a second chromatogram is developed using a solvent combination of MeOH:Ac:H_2O (37:10:21, v/v). With this combination DOA has an R_f-value of 0.38 and DOP has a value of 0.32. These two values are far enough apart to be feasible for characterization of the two diesters, even though they are not far enough apart to permit clear-cut separation of the two compounds. Figure 2, p. 21, illustrates the appearance of the paper chromatograms of these diesters.

If the initial run shows diesters in the R_f-value range of 0.47-0.52, these could be any of the diesters di-isoamyl-adipate (DAA), di-isoamyl-sebacate (DAS), di-n-butyl-sebacate (DBS), or di-n-butyl-phthalate (DBP). A further run with solvent combination MeOH:Ac:H_2O (4:1:4, v/v) would clarify the situation, in that the following R_f-values will define two of the four esters, DAS and DBS; DAA and DBP have R_f-values which do not permit their characterization by this paper chromatographic technique:

Diester	R_f-Value
DAS	0.08
DBS	0.11
DAA	0.18
DBP	0.19



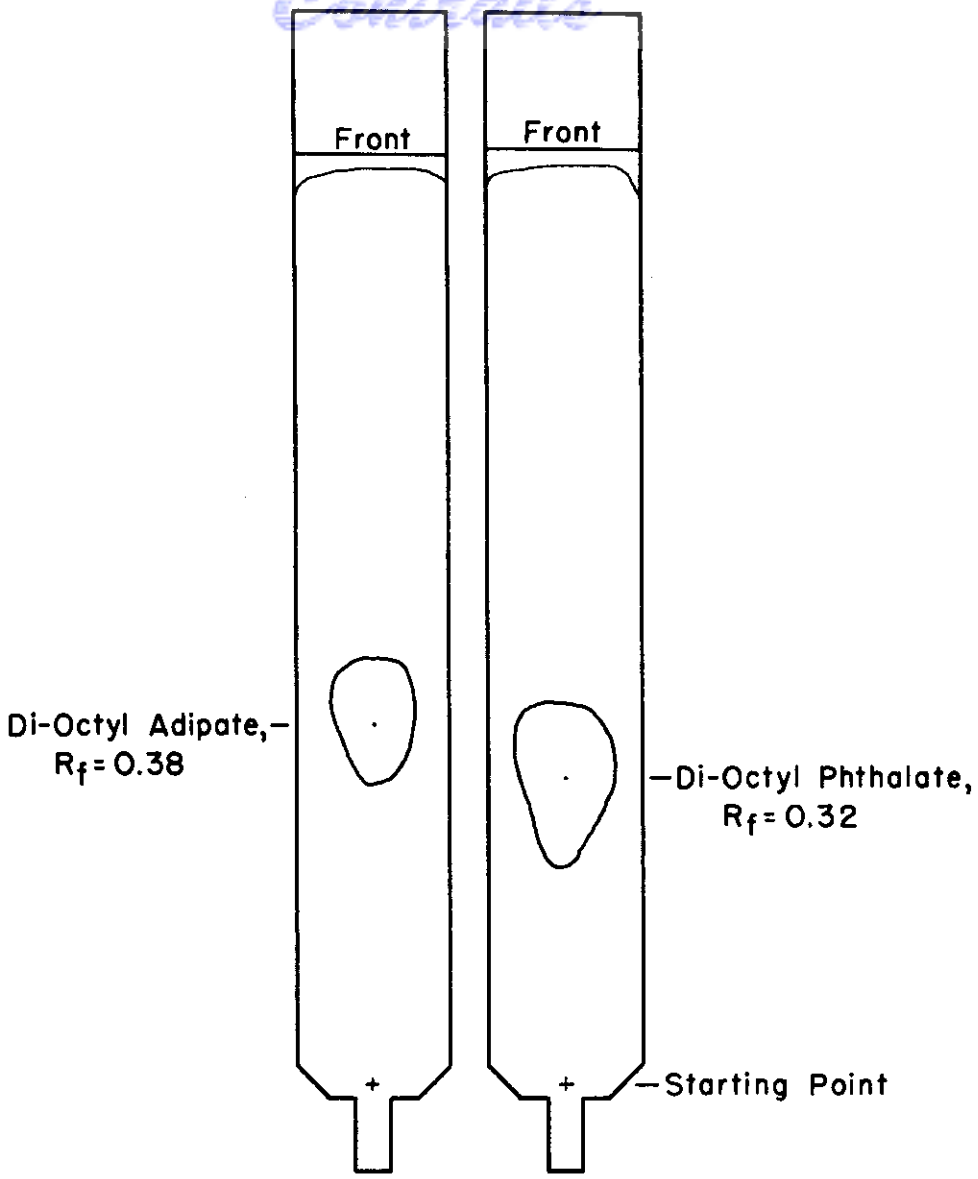
Key: a = Di-Octyl Sebacate, R_f = 0.12
b = " Phthalate, R_f = 0.30
c = " Adipate, R_f = 0.34
d = Di-isoAmyl Sebacate, R_f = 0.49
e = " Adipate, R_f = 0.52
f = Di-n-Butyl Sebacate, R_f = 0.47
g = " Phthalate, R_f = 0.52
h = " Succinate, R_f = 0.53

5λ spots of oil (5% in benzene).

Ascending run at 25°C.

Indicator: Rhodamine B

Figure 1. Chromatograms of Individual Dibasic Acid Esters on Acetylcellulose Paper With Solvent Combination MeOH:Acetone: Water (37:9:21, v/v) (1/2 Actual Size).



Solvent Combination: Methanol:Acetone:Water (37:10:21, v/v).

2.5λ spots of oil (5% in benzene).

Ascending runs at 25°C.

Indicator: Rhodamine B.

Figure 2. Chromatograms Demonstrating Characterization of Di-Octyl Adipate and Di-Octyl Phthalate on Acetylcellulose Paper (2/3 Actual Size).

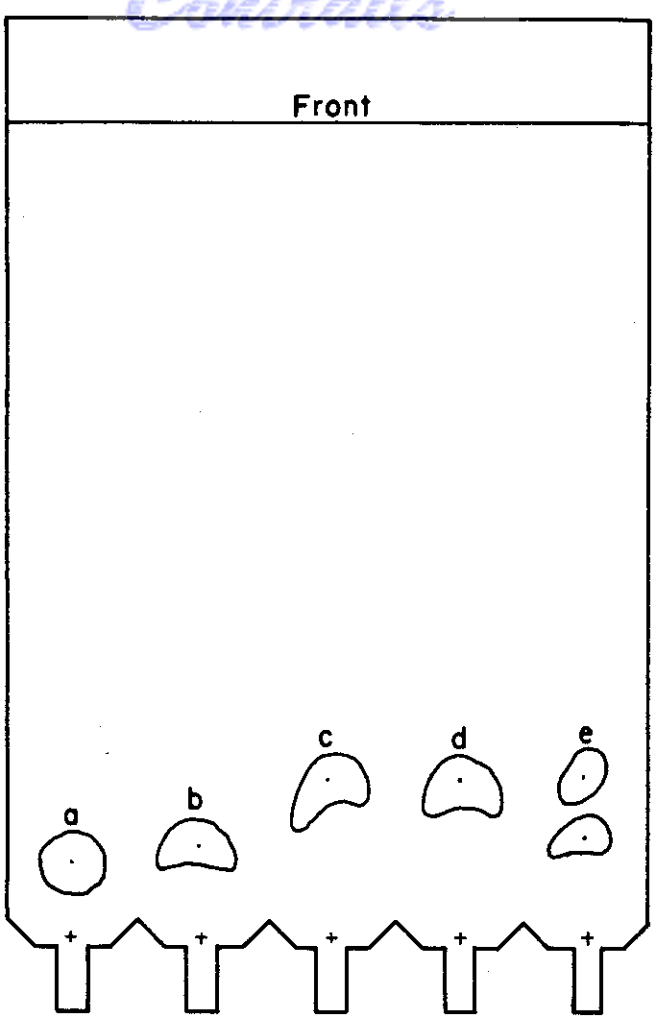
Figure 3, p. 23, presents drawings of actual runs with these individual DBAEs along with a separation of DBS and DAA to prove the feasibility of this solvent combination for separating these esters. When a spot is located near R_f 0.18-0.19, it could be either DAA or DBP, as was mentioned previously. In this case the only practical means for identifying the diester is by wet chemical reaction, rather than by further paper chromatography. The phthalate diester can be detected quite simply by the following reaction, to which the adipate diester does not respond:

A few milligrams of the diester, which has been isolated from the base-oil and other components by column chromatography (see Par. 3.3, p. 78), is heated in a microcrucible with freshly sublimed resorcinol and a few drops of pure sulfuric acid at 130°C. for five minutes. When the reaction is complete, the crucible and contents are placed in 50 ml. of distilled water to dissolve the reaction mixture. The solution is then made alkaline with sodium hydroxide, and, if a phthalic acid diester was present in the oil, a bright fluorescence (yellow) will appear. This fluorescence becomes particularly bright (light green) under ultraviolet light. A blank should be employed to avoid any error which could arise from heating the reaction mixture in excess of 130°C. (138).

If DBP is shown to be absent from the oil, it may be assumed that the oil appearing at R_f 0.18-0.19 is DAA. If DBP is found to be present through the above test, it is reasonably safe to assume that the oil does not contain a mixture of the two diesters and that the only diester present is DBP. Additional corroboration of these findings can be made if, in a second run with the same solvent combination but without spraying with indicator, the area in which the DBAE spot is located (which can be closely defined from the previously developed strip) is cut from the paper and the diester eluted with a solvent such as benzene or alcohol. After elution the diester can be hydrolyzed with HCl, the dibasic acid and the alcohol extracted, the acid transformed into its hydroxamate, and the R_f-value of the hydroxamate determined by appropriate paper chromatographic techniques.

3.5 SEPARATION OF MIXTURES OF DIBASIC ACID ESTERS

The methods presented in the preceding paragraph can also be applied in principle for identification of a mixture of two or more DBAEs, using different solvent combinations in the same manner as discussed above. In Par. 3.3, p. 13, the feasibility of identifying individual compounds and separating mixtures of DBAEs has been discussed, and



Key: a = DAS = Di-Isoamyl Sebacate, R_f = 0.08.
b = DBS = Di-n-Butyl Sebacate, R_f = 0.11.
c = DAA = Di-Isoamyl Adipate, R_f = 0.18.
d = DBP = Di-n-Butyl Phthalate, R_f = 0.19.
e = Mixture of DBS, R_f = 0.12, and DAA, R_f = 0.20.

2.5λ spots of oil (5% in benzene). The mixture was 2.5λ of a 1:1 solution of DBS and DAA (5% in benzene).

Ascending run at 25°C.

Indicator: Rhodamine B.

Figure 3. Chromatograms Showing Characterization and Separation of Dibasic Acid Esters on Acetylcellulose Paper With Solvent Combination MeOH:Acetone:Water (4:1:4, v/v) (4/7 Actual Size).

four solvent combinations have been presented which can be employed to effect these separations for almost any combination of DBAEs.

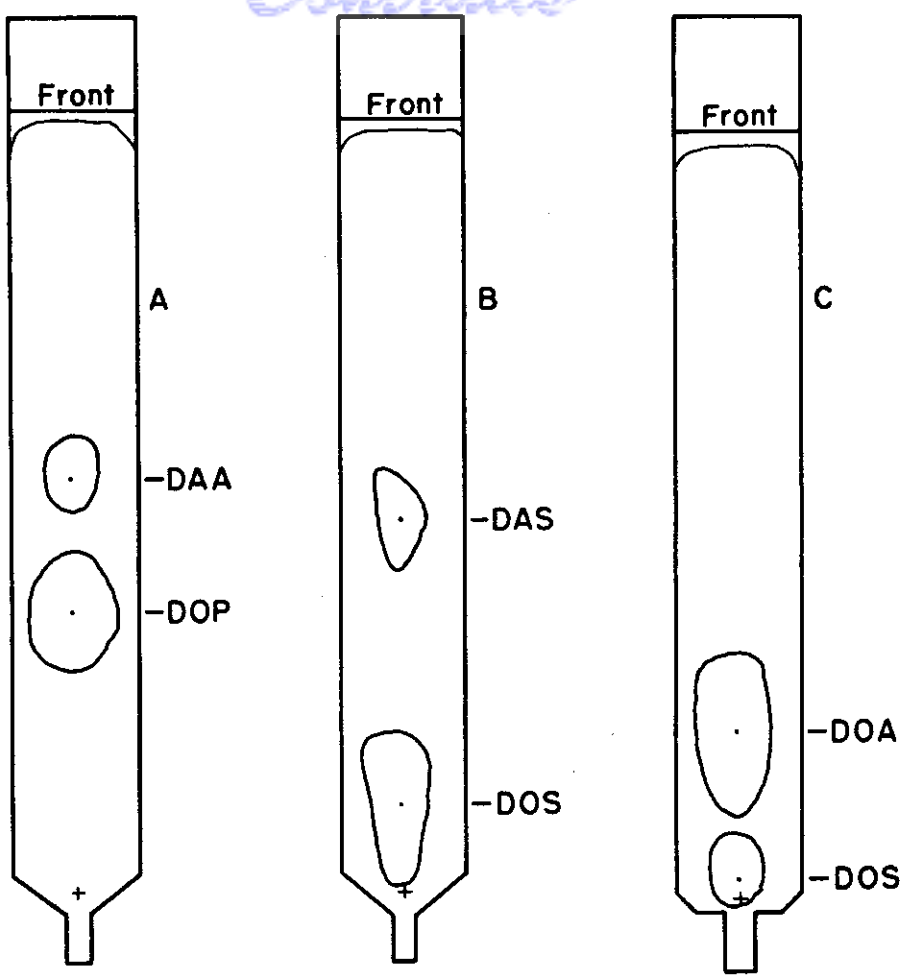
Figure 4, p. 25, presents drawings of some typical DBAE mixture separations. These separations demonstrate conclusively the feasibility of the technique. It will be noted on inspection of the drawings that the different solvent combinations discussed in the preceding section have been utilized. Were a given DBAE mixture to be run with each of the solvent combinations, only one of the combinations would separate the mixture. The other combinations either would not move the DBAEs at all, or would carry them too far, stretching them out over a large area and causing them to overlap, thus preventing identification. Figure 5, p. 26, demonstrates the effect of varying the solvent combination on separation of the mixture DOA-DOS.

With the possibility of locating the spots of DBAEs with Rhodamine B, the possibility of employing two-dimensional paper fluorograms can now be considered. Using two different solvent combinations in the two directions of development, a closer differentiation among different DBAE as well as possibly a separation between silicone oils and silicate esters may be feasible thus avoiding a series of runs on other paper strips. Preliminary investigations in this direction will be part of future investigations. In the field of esters this technique would be useful for distinction between monobasic and dibasic acid esters, if such compounds should be present simultaneously. It should also be possible to detect and identify on the same chromatogram antioxidants and different base-oil compounds simultaneously, the former by color development, the latter by development of the fluorogram.

4.0 QUANTITATIVE DETERMINATION OF DIBASIC ACID ESTERS BY PAPER CHROMATOGRAPHY

Attention has been given to the question whether paper partition chromatography would be feasible for quantitative estimation of DBAEs by the spot area method or by measurement of the optical density (intensity of fluorescence), similar to the methods used for quantitative determination of antioxidants (see Par. 4.0, p. 97). The results of these investigations have shown that such a method is not feasible for quantitative determination of DBAEs for the following reasons:

(a) The spot area method cannot be applied because spots of DBAEs (and for that matter also spots of silicones and silicate esters) steadily increase their area by diffusion in the paper both during



Solvent Combinations:

A = Methanol: Acetone: Water (37:9:21, v/v).
B = " " " "
C = " " " (37:8:24, v/v).

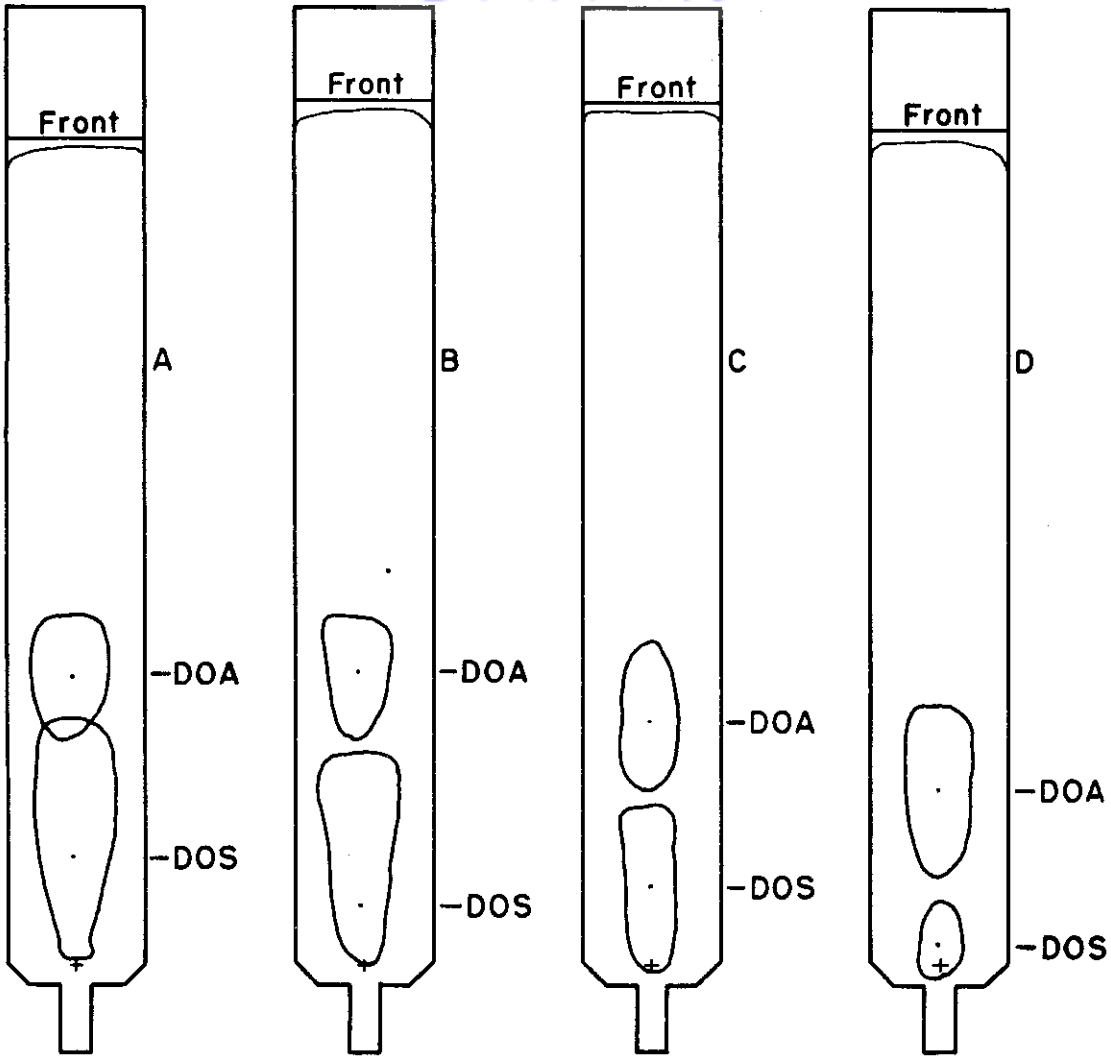
2.5λ spots of a 1:1 solution of each oil mixture (5% in benzene).

Ascending runs at 25°C.

Indicator: Rhodamine B.

Abbreviations: DOA = Di-Octyl Adipate.
DOS = Di-Octyl Sebacate.
DOP = Di-Octyl Phthalate.
DAA = Di-Isoamyl Adipate.
DAS = Di-Isoamyl Sebacate.

Figure 4. Some Typical Chromatograms Showing the Separation of Mixtures of Dibasic Acid Esters With Various Solvent Combinations On Acetylcellulose Paper (5/9 Actual Size).



Solvent Combinations:

A = Methanol:Acetone:Water (37:10:21, v/v).
B = " " " (37:9:21, v/v).
C = " " " (37:8:21, v/v).
D = " " " (37:8:24, v/v).

2.5λ spot of a 1:1 solution of the oils (5% in benzene).

Ascending runs at 25°C.

Indicator: Rhodamine B.

Figure 5. Chromatograms Showing the Effect of Solvent Combination Composition on Separation of a Mixture of Di-Octyl Adipate (DOA) and Di-Octyl Sebacate (DOS) on Acetylcellulose Paper.

and after drying. Therefore there is no constant quantitative relationship between the area of a spot and its concentration, because some compounds diffuse more rapidly at a given temperature than others.

(b) The intensity of fluorescence would within certain concentration limits obey the Beer-Lambert Law, but on the one hand it would be difficult to maintain these concentration limits in a practical analysis, and on the other hand quantitative measurement of fluorescent light requires more elaborate apparatus.

Consequently paper partition chromatography is useful only for qualitative identification of DBAEs per se or in mixtures. Once the compound is identified, quantitative determination can be achieved by other means as, for example:

(a) Quantitative determination of the corresponding dibasic acid by gravimetric methods as salts (e.g. silver salts), after hydrolysis of the diester.

(b) Titrimetric determination of the dibasic acid.

(c) Paper chromatographic determination of the corresponding hydroxamic acid spot by the spot area method or by the optical density method.

(d) Colorimeteric determination of the hydroxamic acid with $FeCl_3$.

Method (c) would make use of paper partition chromatography (see also Par. 4.0, p. 97).

SECTION B

SILICATE ESTERS AND SILICONE OILS

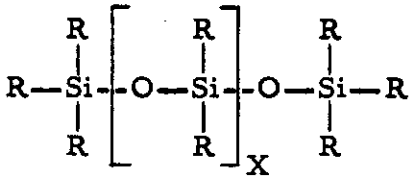
1.0 INTRODUCTION

One of the more important recent developments in the field of lubrication is the increasingly widespread use of silicone oils and silicate ester base-oil fluids. These are silicon-containing compounds having low volatility at elevated temperatures, low viscosity at low temperatures, excellent viscosity-temperature properties, and extreme resistance to chemical attack. Because of the latter property, it is difficult to formulate simple means for identifying and determining these compounds. Nevertheless several methods have been developed to characterize these compounds in synthetic lubricants and to distinguish between them, employing both chemical and paper chromatographic techniques.

1.1 CHEMICAL STRUCTURE AND PROPERTIES OF SILICONE OILS AND SILICATE ESTERS

1.1.1 Silicone Oils

Silicone fluids are polymers with the following chemical structure, the basic unit of the molecule being called a siloxane:



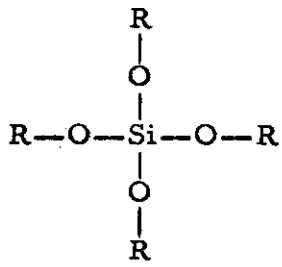
When the R groups are methyls, dimethyl polysiloxanes result, where x may vary from 1 to 2000 or more; these are the Dow Corning 200 Fluids. R may be an aromatic radical, such as a phenyl (Dow Corning 550 Fluid), or the two Rs on the silicon may be mixed, one being alkyl and the other aromatic. Mixed polymers are also possible, wherein dimethylsiloxane may be polymerized with either diphenylsiloxane or a mixed siloxane such as methylphenylsiloxane. Thus the combination possibilities for these polymers are numerous (62).

The silicone compounds derive their great chemical and thermal stability from the presence of Si-O and Si-C bonds in the molecule. The energy in the Si-O bond is much higher than that in the C-C bond in hydrocarbons, and the Si-C bond is similarly strong and stable, due to the polar bonding and symmetrical electron configuration in the polymer. Since silicone oils cannot be polymerized further because the ends of each chain are completed with tri-alkyl silane groups, they are chemically and thermally inert. Heating to 200° C. in air for a prolonged period has no effect, and higher temperatures result only in very slow oxidation; analytical combustions must be performed in pure oxygen at a temperature well in excess of 600°C.

Methyl silicones are the most stable of the silicones; any increase in length of the alkyl groups immediately increases the susceptibility of the silicone to oxidative attack. Phenyl silicones, while relatively inert, are also more readily attacked than the methyl silicones. Phenyl silicones burn with a very sooty flame, as would be expected from the aromatic groups in the molecule. The phenyl groups of aryl silicone oils may be split away from the silicon atoms by heating with aqueous acids or bromine water in a sealed tube. Chlorination, fluorination, bromination, or iodination of the alkyl or aryl groups of a silicone oil is possible, the introduction of halogens increasing the oxidation resistance and decreasing the flammability of the oils. Most silicone oils are soluble to some extent in chlorinated hydrocarbon and non-polar solvents, but are much less soluble in polar solvents (81, 77).

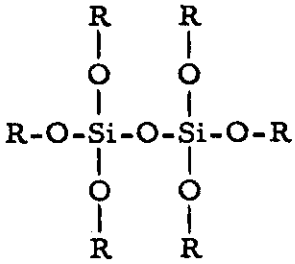
1.1.2 Silicate Esters

Silicate esters, in contrast to the silicone oils, are more related to inorganic silicates, are not polymeric materials, and are more susceptible to chemical attack. They might be looked upon as organic-substituted derivatives of orthosilicic acid, H_4SiO_4, having the type-formula



where R is usually an alkyl group, such as 2-ethylbutyl or 2-ethylhexyl. To date no aryl-substituted orthosilicates have been noted in the literature, yet there is reason to expect that such compounds could serve useful purposes in the lubrication field; substituted phenols are excellent high-temperature-resistant, low melting point fluids which might conceivably form orthosilicate esters of value.

A second type of silicate ester encountered in synthetic lubricants is of the general formula:



where R is again an alkyl group, such as 2-ethylbutyl or 2-ethylhexyl. While not a direct derivative of orthosilicic acid, this compound cannot be classed as a silicone because it has no Si-C bonds. It is called an alcoxy disiloxane (for example, hexa-(2-ethylhexoxy)-disiloxane) and undergoes all the reactions of orthosilicate esters, being even more easily oxidized than orthosilicate esters.

Silicate esters in general are insoluble in water, but are quite soluble in almost all common organic solvents, whether polar or non-polar. They can be hydrolyzed by water, but the reaction rate is decreased as the size of the alkyl chains increases; this rate can be increased by acid catalysis. The esters are attacked readily by aqueous acids, bases, and oxidizing agents, thereby providing ample means for both qualitative and quantitative determination (98).

1.2 GENERAL APPROACH FOR ANALYSIS OF SILICATE ESTERS AND SILICONE OILS

Detection of silicone oils and/or silicate esters in a lubricant is a rather simple problem. Strong oxidizing action, such as Na_2O_2 fusion, breaks the Si-C or Si-O-C bonds, thereby converting the silicon in these compounds into a form easily detectable by color reaction. If the presence of silicon in the base-oil is established, the next step is to

determine whether one or the other or both classes of compound are in the lubricant, and the correct amounts of each. The simplest means would be selective solvent extraction of one of the oils from the other. However, as will be pointed out in following paragraphs, the solubility characteristics of silicone oils and silicate esters are so similar that a satisfactory solvent separation method could not be formulated. Therefore several color reactions had to be developed to differentiate qualitatively between the two types of compound.

If qualitative tests prove that both silicone oils and silicate esters are present in the lubricant (this possibility is quite likely with these compounds), the next problem is complete separation of the two types, in order to identify the individual compounds in each class and to determine the amount of each compound. When solvent extraction proved a useless avenue of approach, selective adsorption on silica or alumina gel columns was attempted in the manner of standard column chromatographic separations of petroleum components. This approach also proved ineffective, due to the weak adsorption of these compounds on silica or alumina gel.

Paper partition chromatography offered promise for the qualitative separation and identification of individual silicone oils and silicate esters, and was proven to be a feasible method. All details of the technique have not been worked out completely, but it is expected that this method will become part of the final analytical scheme because of its simplicity, reproducibility, and accuracy.

While paper chromatography was a means for qualitative analysis of these compounds, it could not be employed for quantitative determinations for reasons discussed previously (see Par. 4.0, p. 24). However, column partition chromatography could be used to separate these compounds quantitatively; therefore, column packing materials were sought which would function not as adsorptive media, but rather as inert support materials for the oil sample and for a solvent combination which would effect the separation by partition. Columns of acetylcellulose powder (in analogy to acetylcellulose paper used for paper strip qualitative separations) were investigated first. These columns were moderately successful, but they possessed a number of disadvantages. Several other materials have been tested; silica gel (working in this new capacity) has shown the greatest promise of success, and animal charcoal will be tested in the future program. During the research on qualitative separation of dibasic acid esters from silicone oils and silicate esters

(see Par. 3.0, p.60) it was found that with a given solvent combination silicate esters are much more mobile than silicone oils. It therefore seems probable that a solvent combination can be developed which will quantitatively elute silicate esters, while leaving silicone oils in the column.

If column chromatography proves to be a satisfactory means for separating silicone oils from silicate esters, quantitative determination of the individual compounds will probably have to be performed by non-chromatographic means. This implies hydrolysis of the silicate esters with determination of silica and the alcohol, and high temperature oxygen combustion of the silicone oils. Qualitative tests, of course, will already have shown whether more than one silicone oil or silicate ester is to be considered in the quantitative determination.

2.0 IDENTIFICATION OF SILICON-CONTAINING COMPOUNDS IN SYNTHETIC LUBRICANTS AND GREASES

2.1 SODIUM PEROXIDE FUSION METHOD FOR DETECTION OF SILICON

Two methods were tested for detecting the presence of silicon-containing compounds (including silicone oils, silicate esters, silica gel, bentones, etc.) in synthetic lubricants or greases: (a) $NaF-H_2SO_4$ digestion, forming volatile SiF_4, and (b) $Na_2O_2-Na_2CO_3$ fusion, forming an inorganic silicate which may be detected with ammonium molybdate, benzidine, and NH_3.

The digestion method consists in heating approximately a milliliter of the oil in a Pt crucible with several crystals of NaF and several drops of con H_2SO_4. The SiF_4 generated is detected by placing a moistened asphalt-covered glass rod in the vapors. A white precipitate on the rod indicates the presence of Si-containing compounds. While usable, this method is not so adequate as the fusion method; therefore the limits of sensitivity were not determined (92 through 96).

The fusion method for detecting silicon-containing compounds in oils or greases consists of the following: a reaction paste made up of approximately 0.1g. anhydrous Na_2CO_3, 0.1g. Na_2O_2, and 0.01g. oil or grease is mixed thoroughly with a spatula in a spot plate depression. A 1/8" diameter loop is formed at the end of a Pt wire, and the wire is cleaned by repeated dipping in dilute HCl and heating in a Bunsen burner

flame until no color is imparted to the flame. The loop is dipped into the reaction paste and heated cautiously in the flame until all reaction has ceased. Color and density of the smoke evolved during the fusion are noted. The wire loop is dipped repeatedly into the paste and fused each time until a 1/16" thick bead is formed in the loop. Finally the bead is heated several minutes until it becomes water-clear. After cooling the loop is unwound, the bead is dropped into a small Pt crucible, 2-3 ml. H_2O is added and the crucible is heated until the bead has dissolved. A 1" square piece of ashless filter paper is completely moistened with the solution from the fusion, and a drop of NH_4 -molybdate solution (15% aqueous) is added to the paper. The paper is warmed to evaporate excess moisture (but not dried completely), and a small drop of benzidine (0.5% in glacial HAc) is placed over the molybdate spot. After a moment the paper is placed in an NH_3 atmosphere. Appearance of a blue to dark blue spot indicates the presence of silicon.

Table VI, p. 34-35, shows results obtained using the Na_2O_2 fusion method. The method is accurate for a silicon content in the lube-oil or grease down to about 1% (which corresponds to 5% Bentone-34 or 3% silica gel). WADC lubricant MLO-9717, which contains 0.001% Silicone DC-200, gives a faint test for silicon, but the test is too questionable to be definitive. However, considering that actually less than 0.001g. of the oil is used in making the bead, the test may be considered extremely sensitive. The method thereby provides a reliable means for (a) identifying the presence of Si in a synthetic oil, and (b) assisting in tracing the course taken by silicon-containing compounds during separations.

Additional information about a sample of oil may be obtained while making the test: aromatic compounds (Silicone DC-550, mineral oil) give a dense carbon-black smoke during the fusion, whereas non-aromatic compounds fuse with a minimum of smoke.

2.2 DIFFERENTIATION BETWEEN SILICATE ESTERS AND SILICONE OILS

2.2.1 Sodium Borate Reaction

The usual test for short-chain orthosilicate esters consists in heating the sample with $Na_2B_4O_7$ and con. H_2SO_4, whereby volatile borates are formed which impart a green color when passed through a burner flame.

TABLE VI

Detection of Silicon-Containing Compounds in Synthetic Oils And Greases by Sodium Peroxide Fusion

WADC Spec. No.	Compound or Composition of Grease or Oil	Action on Fusion	Benzidine Test	Appearance of spot.
None	Tetra(2-ethylhexyl)orthosilicate	-	Pos.	Dark Blue
None	Hexa(2-ethylbutoxy)disiloxane	-	"	"
None	Hexa(2-ethylhexoxy)disiloxane	-	"	"
None	Silicone DC-200, 5cs.	-	"	"
None	Silicone DC-550	Black smoke	"	"
MLO-53-446	Chlorinated Silicone	-	"	"
MLO-8200	93% Hexa(2-ethylbutoxy)disiloxane 5% Silicone XF-371(100,000cs.) 2% DODPA and Qz*	-	"	"
MLO-53-291	Exact Composition Unknown: Orthosilicate Ester--Acryloid--Ester--Dilauryl-selenide	-	"	"
MLO-54-540	Exact Composition Unknown: Orthosilicate Ester--Acryloid-Ester	-	"	"
MLO-53-5277	89% Tetra(2-ethylbutoxy)silicate 10% Silicone DC-200(100,000cs.) 1% PANA*	-	"	"
MLG-9301	86% Silicone DC-550 14% Urea-type Gelling Agent	Black smoke	"	"
MLG-4369	30% Silicone Oil 60% Diester Oil Lithium Stearate	-	"	"
MLG-4135	74.5% Silicone Oil 25.2% Lithium Stearate Inhibitor	Black smoke	"	"

TABLE VI - Continued

Detection of Silicon-Containing Compounds in Synthetic Oils And Greases by Sodium Peroxide Fusion

WADC Spec. No.	Compound or Composition of Grease or Oil	Action on Fusion	Benzidine Test	Appearance of spot
MLG-53-185	78% Dipropylene glycol dipelargonate 20% Bentone-34 1% Hydrogenated Fish Oil 1% Petronate L	-	Pos.	Dark Blue
TYPE I0300**	95% Mineral Oil 5% Bentone-34	Black smoke	"	Blue
TYPE I017c3**	79% Mineral Oil 15% Phthalocyanine 3% Silica Gel 2% Ionol (26Ph)* 1% Sorbitan Mono-oleate	Black smoke	"	"
MLO-9717	92.4% Diester Oils 6.3% Acryloid HF-825 1.0% Tricresyl Phosphate 0.3% PT* 0.001% Silicone DC-200	-	Neg.	Spot turns faint blue, but fades.
MLO-53-371	95% Ucon Lubricant LB-65 5% Polyester	-	"	Yellow
TYPE ID000**	91% Mineral Oil 9% Aluminum Stearate	Black smoke	"	"
None	Mineral Oil	Black smoke	"	"
None	Di-2-ethylhexyl-adipate	-	"	"
None	Ucon Lubricant LB-525	-	"	"

*Abbreviations for antioxidants:

DODPA = Di-octyl-diphenylamine
Qz = Quinizarin
PANA = Phenyl-alpha-naphthylamine
26Ph=2,6-Ditertiarybutyl-4-methylphenol
PT = Phenothiazine

** Grease compounded at Denver Research Institute. For classification numbering system, see 141, pp. 5-8.

Orthosilicates in lubricants have longer-chain groups which do not form volatile borates; however it was noted that with these longer-chain compounds the reaction mixture gives a deep red to maroon color with silicate esters, whereas silicones do not produce any color, thus providing a means for distinguishing between these two classes of base-oils. The test consists of adding several crystals of $Na_2B_4O_7.10H_2O$, a few drops of the oil, and a few drops of con. H_2SO_4 to a test tube, and placing the tube in a water bath for 15 minutes.

Table VII, p. 37, summarizes results obtained using this technique. It may be noted that several synthetic lube-oils were tested, and that no interference was caused by the presence of other components in the lube-oil.

2.2.2 Potassium Dichromate-Nitric Acid Reaction

A second reaction to differentiate between silicate esters and silicones consists in mixing equal volumes (1 to 2 ml.) of lube-oil or grease, 2% aqueous $K_2Cr_2O_7$, and con. HNO_3 in a large test tube, heating to boiling, and keeping hot for about two minutes. In the presence of silicate esters, the aqueous layer turns light blue, due to reduction of chromium to the chromous state in oxidizing the alcohol after hydrolyzing the ester. However, if excessive amounts of oxidizable additives are present in the oil, the aqueous layer will turn blue, whether silicate esters are present or not; therefore this test can be misleading and should be used only in connection with other tests (95).

Table VIII, p. 38, illustrates the effectiveness of this reaction with a number of silicones, silicate esters, and lubricants containing silicate esters. One precaution should be mentioned: the volume of HNO_3 should be no more than the volume of the aq. $K_2Cr_2O_7$ (actually slightly less is preferred); otherwise the silicate esters react rather violently.

2.2.3 Substituted Benzophenone Reaction

An excellent color reaction (96) for detecting silicones consists in heating 1/2 to 1 ml. of oil with 0.05-0.1g. of anhydrous $AlCl_3$ in a test tube over a micro-burner until the reaction becomes self-sustaining. After reaction has ceased, the tube is cooled and 2 ml. of a 2% benzene

TABLE VII

Differentiation Between Silicone Oils And Silicate Esters With $Na_2B_4O_7.10H_2O$ And H_2SO_4

WADC Spec. No.	Compound or Composition of Grease or Oil	Appearance of Reaction Mixture
None	Blank (no oil added)	Clear
None	Silicone DC-200, 5cs.	Colorless
None	Silicone DC-550	Colorless
MLO-53-446	Chlorinated Silicone	Colorless
None	Tetra(2-ethylhexyl)orthosilicate	Red. Darkens to maroon on heating.
None	Hexa(2-ethylbutoxy)disiloxane	"
None	Hexa(2-ethylhexoxy)disiloxane	"
MLO-8200	93% Hexa(2-ethylbutoxy)disiloxane 5% Silicone XF-371 (100,000cs.) 2% DODPA and Qz*	Red and pink. Darkens on heating.
MLO-53-5277	89% Tetra(2-ethylbutoxy)silicate 10% Silicone DC-200 (100,000cs) 1% PANA*	Red, but only with prolonged heating.
MLO-54-540	Exact Composition Unknown: Orthosilicate Ester-- Acryloid--Ester	Red.

* Abbreviations for antioxidants:

DODPA = Di-octyl-diphenylamine.
Qz = Quinizarin.
PANA = Phenyl-alpha-naphthylamine.

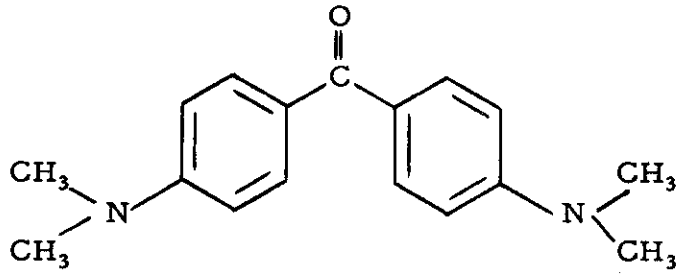
TABLE VIII

Differentiation Between Silicone Oils And Silicate Esters With $K_2Cr_2O_7$ And HNO_3

WADC Spec. No.	Compound or Composition of Grease or Oil	Color of Aqueous Layer	Remarks
None	Blank (no oil added)	Orange	-
None	Silicone DC-200 (5cs.)	Yellow	-
None	Silicone DC-550	Orange	-
None	Mineral Oil	Orange	-
None	95% Di-2-ethylhexyl-sebacate 5% Ionol (26Ph)*	Orange	Aq. layer turns blue overnight due to phenol.
MLG-9301	86% Silicone DC-550 14% Urea-type Gelling Agent	Orange	-
None	Tetra(2-ethylhexyl)-orthosilicate	Lt. Blue	Requires several min. heating.
None	Hexa(2-ethylhexoxy)disiloxane	Lt.Blue	-
None	Hexa(2-ethylbutoxy)disiloxane	Lt. Blue	Reaction self-sustaining.
MLO-53-291	Exact Composition Unknown: Orthosilicate Ester--Acryloid--Ester--Dilauryl-Selenide	Lt. Blue	-
MLO-53-5277	89% Tetra(2-ethylbutoxy)-silicate 10% Silicone DC-200(100,000cs.) 1% PANA*	Dark green	Reaction self-sustaining.
MLO-8200	93% Hexa(2-ethylbutoxy)-disiloxane 5% Silicone XF-371 (100,000cs.) 2% DODPA and Qz*	Dark green	Further heat gives blue aq. layer and wine-red oil layer.
MLO-54-540	Exact Composition Unknown: Orthosilicate Ester--Acryloid--Ester	Lt. Blue	-

* Abbreviations for antioxidants:
26Ph = 2,6-Ditertiarybutyl-4-methylphenol. Qz = Quinizarin.
PANA = Phenyl-alpha-naphthylamine. DODPA = Di-octyl-diphenylamine.

solution of N, N, N', N', -tetramethyl-4, 4'-diaminobenzophenone



is added. Alkyl and chlorinated silicones immediately give a bright orange precipitate; aryl silicones develop this precipitate after about 15 to 30 minutes. Silicate esters and disiloxanes give a wine-red solution. On diluting the reaction mixture with about 5 ml. of water, the chlorinated silicone gives a chartreuse-green precipitate, the aryl silicone gives a royal-blue water soluble dye (which is ether insoluble), and alkyl silicones, silicate esters, and disiloxanes white precipitates. Table IX, p. 40, summarizes these results. With this reaction it is therefore possible to distinguish silicones from silicate esters, and to distinguish between three classes of silicones themselves.

3.0 IDENTIFICATION OF INDIVIDUAL SILICATE ESTERS AND SILICONE OILS

In previous paragraphs (Par. 2.0, p. 32) it has been shown how test tube color reactions may be employed to indicate the presence of silicate esters or silicone oils as groups, and how color reactions will differentiate between alkyl, aryl, and chlorinated silicones. These reactions may be used as a guide in the final analysis of a base-oil mixture, but they do not provide a means for identifying individual compounds but rather only groups of compounds. Qualitative identification of individual silicate esters may be accomplished by either of two techniques:

(a) Paper partition chromatography.

(b) Hydrolysis of the ester and identification of silica and the alcoholic component of the ester.

While both of these alternatives offer good promise of success at least for qualitative identifications, paper chromatography would be the method of choice because of its simplicity, accuracy, and reproducibility.

TABLE IX

Differentiation Between Silicone Oils and Silicate Esters
With N, N, N', N'-Tetramethyl-4, 4'-Diamino-Benzophenone

WADC Spec. No.	Compound or Composition of Grease or Oil	Color After Reaction	Color After Dilution With H_2O
None	Blank (no oil added)	Yellow	Yellow
MLO-53-446	Chlorinated Silicone	Orange ppt.	Green ppt.
None	Silicone DC-200(5cs.)(alkyl)	"	White ppt.
None	Silicone DC-550 (aryl)	" (after 30 min.)	Blue soln.
None	Hexa(2-ethylhexoxy) disiloxane	Wine-red soln.	Cream-colored ppt.
None	Tetra(2-ethylhexyl) orthosilicate	"	"
None	Di-2-ethylhexyl-adipate	"	Orange ppt.

Identification of the higher alcohols after hydrolysis would probably be performed by paper chromatography or by acetylation, and silica by wet chemical analysis. The difference in time involved in carrying out the two methods would also make chromatography of the ester itself the more desirable method.

3.1 PAPER PARTITION CHROMATOGRAPHY OF SILICATE ESTERS

In the following SECTION C (Par. 2.2, p. 52) the paper chromatographic technique for separation of silicate esters and silicone oils is discussed in detail. It is pointed out in the discussion and in Table XIII, p. 59 , that with some solvent combinations silicone oils are completely immobile, remaining on the starting point, while silicate esters of the types tested in these laboratories can be quite mobile. With such solvent combinations as MeOH:Water, EtOH:Water, tetrahydrofuran:water, and pyridine:water, it is probable that silicate esters can be moved along the

paper away from silicone oils, and identified by their R_f-values. Acetyl-cellulose paper would be employed in these determinations, and the spots of silicate esters on the paper would undoubtedly have to be detected with a fluorescent, fat-staining type dye, such as Rhodamine-B, which has been used to date for these compounds.

In the work discussed in SECTION C tetra-(2-ethylhexyl)-ortho-silicate (TOS) was more mobile than either hexa-(2-ethylbutoxy)-disiloxane (HBDS) or hexa-(2-ethylhexoxy)-disiloxane (HHDS), all three compounds showing an appreciable R_f-value when the solvent combination was strongly on the organic side. Based on this work, it is felt that a solvent combination which will separate these compounds can be developed.

3.2 HYDROLYSIS OF SILICATE ESTERS AND IDENTIFICATION OF THE ALCOHOL COMPONENT

The most logical point for attack on the silicate esters is the oxygen to carbon linkage. This is due to the fact that these compounds are readily hydrolyzed by agents such as HAc, both glacial and dilute, and by most dilute acids and alkalis (see Par. 4.0, p.42). In addition they are oxidized easily by $K_2Cr_2O_7$ and HNO_3 (see Par. 2.2.2, p. 36) to silica and the aldehyde or acid of the alkyl group on the ester. Both of these reactions are possible means for qualitative identification of individual silicate esters, either in the event that paper chromatography does not prove to be feasible for this identification or to act as a further check on results of the paper chromatographic technique.

Identification of silicate esters by hydrolysis must depend upon identification of the alcohol hydrolyzed from the ester, and on a positive test for silicon by the peroxide fusion procedure (see Par. 2.1, p. 32). Establishment of identity of the alcohol could be accomplished by several means:

(a) Paper chromatographic identification by R_f-value and possibly by color reaction.

(b) By formation of a solid derivative, such as the 3,5-dinitrobenzoate, phenyl urethan, or alpha-naphthylurethan, and determination of the melting point of this derivative.

(c) By esterifying with acetic anhydride or acetyl chloride, and determining the boiling point of the ester.

Each of these tests is an accurate, relatively simple method to establish identity of the alcohol, and thereby identity of the silicate ester itself.

However, in the event a mixture of two esters occurs, such as TOS with HHDS, then it will be necessary to provide such reaction conditions during the hydrolysis that only one of the esters is hydrolyzed at a time. This seems to be a practical solution, since during the experimental work it has been observed that TOS is much more susceptible to hydrolysis and oxidation than are the disiloxane esters (see also Par. 4.2 p. 43). However, it is unlikely that this time-consuming procedure will be necessary if paper chromatographic techniques prove to be feasible for these esters.

3.3 COLOR REACTIONS FOR SILICONE OILS

As was indicated in Par. 2.2.3, p. 36, the substituted benzophenone reaction provides a series of color reactions which will distinguish between the groups of silicate esters and silicone oils and also between the silicone oils themselves. Employing this reaction as described in the above paragraph, chlorinated silicones give a chartreuse green precipitate, aryl silicones give a bright blue water-soluble dye, and alkyl silicones give a white precipitate.

It is unlikely that mixtures of silicone oils would appear in a lubricant or grease, but if they were to be present, column separation techniques would probably be necessary to separate the silicones from one another, at least partially, in order to obtain a successful qualitative identification of the types present in the lube-oil. This is a feasible separation technique, as has been indicated by work in England, employing animal charcoal columns (64). Paper chromatographic studies under the present contract have shown that the aryl silicone is the most mobile of the three types of silicones, but the difference in mobilities does not seem to be sufficient to expect that paper chromatographic techniques could be employed for separation of silicones themselves.

4.0 QUANTITATIVE DETERMINATION OF SILICATE ESTERS BY HYDROLYSIS

For analysis of orthosilicate esters, it was believed that hydrolysis with the accompanying determination of silica and/or alcohol would be

the simplest and most accurate method. Accordingly, runs were made using various acidic or alkaline reaction conditions to hydrolyze the ester, and the amount of silica and/or alcohol determined.

4.1 EXPERIMENTAL PROCEDURE

The general procedure consisted of mixing the sample oil with the hydrolyzing media in a round-bottom flask, bringing to reflux temperature, and holding there for the desired amount of time. At the end of the run the flask was cooled and the contents extracted with ether. The ether phase was decanted and evaporated in an air stream, and the liquid remaining in the reaction flask was made alkaline with NaOH. The reaction mixture was extracted with ether a number of times, and the ether added to the first ether extract for evaporation. The residue, after evaporation of the ether, was distilled and a rough cut taken between 150 and 200° C. For preliminary determinations any material distilling in this temperature range was considered to be 2-ethylhexanol-1. In later runs the alcohol was determined by acetylation and hydrolysis; that is, free alcohol formed during hydrolysis of the silicate ester was first acetylated and, together with alcohol from the silicate ester which had esterified with the HAc hydrolyzing agent, was then determined by alkaline hydrolysis and back titration (see Par. 4.2.3, p.47).

The residue remaining in the flask after the ether extractions was air dried, then dried to a powder on a hot plate, and finally placed in a muffle furnace for two hours at 800°C. After removing from the furnace and cooling, the ash was weighed as SiO_2 .

4.2 EXPERIMENTAL RESULTS

Results of the hydrolysis runs are summarized in Table X, p. 44-45. Silica was usually determined because of its simplicity and accuracy, compared to the difficulty of distilling the small amount of alcohol generated in the hydrolysis reaction, approximately 5 ml. of liquid. The silica value gave an indication as to the degree of hydrolysis. Later, alcohol determinations were made by the acetylation method in an attempt to obtain an accurate check on the degree of hydrolysis as indicated by the silica values.

TABLE X

Quantitative Determination of Silicate Esters By Hydrolysis

Run No.	Silicate Ester*	Hydrolyzing Agents	Volume of Agents (ml.)	Time (hrs.)	Theoretical SiO_2 Recovered (%)	Theoretical Alcohol Recovered** (%)	Remarks
1	TOS***	H_2O HCl	100 0.1	71/2	2.6	-	-
2	TOS	H_2O HCl	100 1	191/2	18.6	-	-
3	TOS	H_2O HCl	20 2	18	30.2	-	-
4	TOS	H_2O KOH	100 3 g.	18	26.8	42.0	Alcohol determined by distillation.
5	TOS	H_2O KOH	25 10 g.	16	100+	98.0	"
6	TOS	H_2O H_2SO_4	20 2	-	-	-	Charred on heating.
7	TOS	HAc	20	2	85.6	100+	Alcohol determined by distillation.
8	TOS	H_2O HAc	10 20	2	62.8	-	-
9	TOS	H_2O EtOH HAc	5 3 20	1	67.6	-	-
10	HHDS***	HAc	25	1	0.0	-	No indication of silicic acid.
11	HHDS	HAc	20	1	0.0	-	"
12	HHDS	H_2O HAc	5 20	2	0.0	-	Polymer-like material formed.
13	HHDS	HAc	20	3	0.0	-	"

TABLE X - Continued

Quantitative Determination of Silicate Esters By Hydrolysis

Run No.	Silicate Ester*	Hydrolyzing Agents	Volume of Agents (ml.)	Time (hrs.)	Theoretical SiO_2 Recovered (%)	Theoretical Alcohol Recovered** (%)	Remarks
14	TOS	H_2O HAc	0.5	2	73.0	-	-
15	TOS	HAc	20	2	91.8	-	Silica recovery improved.
16	TOS	HAc	20	3	96.4	-	-
17	TOS	HAc	20	4	94.3	-	-
18	TOS	HAc	20	3	95.4	-	-
19	TOS	HAc	20	3	95.4	-	Trace moisture added:no effect.
20	HHDS	HAc	20	3	0.0	-	No hydrolysis.
21	TOS	HAc	20	3	96.5	80.4	Alcohol determined by acetylation.
22	TOS	HAc	20	3	95.6	84.0	"

* Five ml. of ester were used for each run, excepting the first two runs, when ten ml. were used.

** Alcohol recovery is based on pure 2-ethylhexanol-1.

***Abbreviations:
TOS = Tetra(2-ethylhexyl)orthosilicate.
HHDS = Hexa(2-ethylhexoxy)disiloxane.

4.2.1 Tetra(2-ethylhexyl)orthosilicate(TOS)

The SiO_2 values obtained from hydrolysis of TOS with dilute HCl indicate poor hydrolysis even with long heating periods (Runs 1, 2, and 3, Table X, p. 44). KOH also gave inconsistant hydrolysis yields despite long heating times (Runs 4 and 5). Evidently in Run 5 KOH hydrolysis formed a compound of silicon (possibly a polymer) which was not decomposed to SiO_2 by the usual HCl digestion and ashing used in determining silica. Only one run (Run 6) was made using H_2SO_4, due to charring of the organic part of the ester. Run 7 with glacial HAc gave the highest yield of SiO_2 obtained up to that time. The alcohol yield was high due to difficulties encountered during distillation of the alcohol. It was then decided to determine whether hydrolysis using glacial or dilute HAc would improve the yield of SiO_2. When Runs 8 and 9 are compared to Runs 15-19, it appears that glacial HAc gives the better results. Runs 15, 16, and 17 show that a reflux time of about three hours gives a maximum silica yield.

It will be noted in the table that the average silica yield for six glacial HAc hydrolyses is about 96% of theoretical. The reasons for this inability of the method to attain closer to 100% yields could be due to a number of causes:

(a) Experimental errors inherent in the method, due to excessive numbers of manipulations, such as numerous extractions, transfer of the SiO_2, weighing, etc.

(b) Possible establishment of an equilibrium condition (which is typical of most hydrolysis reactions), whereby no further hydrolysis is possible without removing some of the products formed in the reaction.

(c) Possible formation of silicon compounds, such as polymers, which defy further hydrolysis, and even resist the drastic conditions imposed by con. HCl digestion and ashing.

(d) Impurities in the starting material, in this case possibly 2-ethylhexanol-1. This is a distinct likelihood, since on distillation of the original TOS a small percentage of the oil distilled at a much lower temperature than that of the ester, near that of the above alcohol.

4.2.2 Hexa(2-ethylhexoxy)disiloxane (HHDS)

Runs 10 through 13 show that even with reaction conditions similar to those which hydrolyze TOS there is no visible trace of hydrolysis of HHDS, as evidenced by the lack of silica gel formation. This is further corroborated by Run 20, which shows no hydrolysis using 20 ml. of HAc with three hours of refluxing; these conditions give maximum yields of silica from TOS.

In summation it seems likely that this hydrolysis technique could be used to distinguish between the two types of silicate esters, by effecting hydrolysis of only one of the compounds when mixtures of the two materials occur. The latter case will have to be verified, of course, by further tests. It is visualized that, if a mixture of the two types of esters does occur, first TOS and similar compounds would be hydrolyzed by the above procedure, and that the disiloxane-type compounds could then be separated in the ether extraction, the alcohol from the TOS removed possibly by distillation, and the remaining disiloxane compounds hydrolyzed by much more drastic hydrolysis conditions.

4.2.3 Determination of Alcohol by Acetylation

Runs 21 and 22 show the amount of alcohol and silica recovered from TOS using optimum reaction conditions. The alcohol obtained from the reaction mixture by ether extraction was determined by acetylation. This determination consists in heating the extracted alcohol with acetic anhydride-pyridine (1:3, v/v) in a closed flask on a steam bath for one hour. After cooling, water is added to hydrolyze unreacted acetic anhydride, and the acetic acid thus formed is titrated with alcoholic NaOH to a phenolphthalein end point. Next excess alcoholic NaOH is added to the same flask to hydrolyze all of the acetate ester formed both during the acetylation and during the original hydrolysis of the silicate ester with HAc. The mixture is boiled gently for 15 minutes, cooled, and excess alkali is titrated with standard HCl to give the total alcohol present. A blank run is made to reduce error in the method.

It appears from the results that HAc gives the best hydrolysis as shown by the silica values obtained; however, the use of HAc has one disadvantage in that some ester formation between the HAc and the liberated alcohol takes place, thus complicating the determination of alcohol by imposing a second hydrolysis and titration into the acetylation procedure. If hydrolysis with a mineral acid such as HCl or H_2SO_4

could be developed to give results comparable to those obtained with HAc, one would avoid the disadvantageous formation of a secondary ester with the hydrolyzing agent, and the acetylation method for determination of the alcohol would consist of only one titration, thus eliminating several sources of experimental error. This improved technique would permit the use of both the silica determination and the alcohol determination as cross-checks on the accuracy of the hydrolytic method.

Having once established the feasibility of hydrolysis with non-esterifying hydrolytic agents, then the procedure would have to be checked with TOS, HHDS, various silicone oils, and mixtures of all three components. This assumes, of course, that these compounds cannot be separated quantitatively; however, at the present time it appears likely that silicate esters can be separated from silicone oils by column chromatography, and that orthosilicate esters can be separated from disiloxanes (see Par. 3.0, p.60). If these separations prove successful, there will be no need to work with mixtures of base-oils during the determination of silica and alcohol by the above technique.

5.0 QUANTITATIVE DETERMINATION OF SILICONE OILS

Quantitative determination of silicone oils found in base-oil mixtures will depend upon two factors: (a) accuracy of determination desired, and (b) accuracy of separation which can be achieved between silicone oils from other groups of oils and from one another (see Par. 2.0, p.68 ; and Par. 3.0, p.72). If maximum accuracy is necessary for evaluation of the lube-oil, then high-temperature combustion in oxygen is mandatory for these extremely inert compounds. However, if maximum accuracy is not necessary, then reasonably accurate results can be achieved simply by determination of the weight of oil eluted from a column separation, followed by qualitative identification of the silicone oil eluted. The simpler method is, of course, most likely the method of choice when the laboratory is not equipped with necessary combustion apparatus.

Quantitative column separation of the group of silicone oils from other groups of base-oils is a feasible procedure, as will be pointed out in the following two Sections of this report. Both paper chromatographic techniques and column separations of DBAEs from silicate esters and silicone oils show that with some solvent combinations the mobility of

silicone oils is zero, while the other groups of compounds are moved a considerable distance on the paper or in the column. This means that it should be possible to isolate the group of silicone oils quantitatively from other base-oils possibly present in a lube-oil. Once the oils are isolated, their weight may be determined, and their identity established by color reactions discussed previously (see Par. 2.2.3, p. 36; and Par. 3.3, p. 42). These reactions merely distinguish the type of silicone oils into alkyl, aryl, or chlorinated groups.

If further identification of the oil is required, the above-mentioned combustion techniques must be used, or possibly another type of column separation. Work performed in England (64) has shown that it is possible to separate a single silicone oil into its various molecular weight species on animal charcoal columns with a gradient-type solvent combination. Since the mobilities of the silicone oils are different according to their degree of polymerization and their molecular weight, one could then expect that some degree of separation of the three types of silicone oils would be achieved by further column chromatographic analysis. This, of course, will have to be verified by future experimental work. It is visualized that if this column separation technique is proven feasible, it would be possible to separate (to a certain extent at least) a mixture of two silicones. A mixture of three or more silicone oils would be very difficult to separate, unless there were very large differences in their average molecular weights.

Combustion at high temperature in oxygen is a routine procedure which requires the use of rather elaborate apparatus, but which could assist materially in accurate quantitative determinations of silicone oils. However, it would still be necessary to employ accurate separation techniques to obtain samples of pure silicones. If the separation technique cannot be developed, oxygen combustion would also be useless except for determination of pure silicone oils, but not for mixtures.

Determination of silicone oils by combustion would include analysis for hydrogen and carbon in the combustion gases, and silica as residue in the combustion tube. Oxygen would be obtained by difference. The ratio carbon/silicon, C/Si, would give a direct clue to identity of the silicone oil, aromatic silicones with phenyl groups having a large value for this ratio, chlorinated alkyl silicones having an intermediate value, and alkyl (methyl) silicones having a low value. It is obvious that if the sample does not contain a pure compound, the C/Si ratio would be useful only to a small extent in predicting the composition of a mixture.

SECTION C

QUALITATIVE SEPARATION OF DIBASIC ACID ESTERS, SILICONE OILS, AND SILICATE ESTERS

1.0 INTRODUCTION

The problem of separating DBAEs (dibasic acid esters), silicone oils, and silicate esters could be approached from two directions:

(a) The DBAE could be hydrolyzed into its alcoholic and acidic components under conditions which would not affect the silicone oil or silicate ester. The two components could then be recovered, identified, and determined quantitatively, having separated out the silicon compounds during the procedure.

(b) The DBAE could be isolated intact from the silicon compounds by a procedure which would not affect the latter, such as vacuum distillation, selective solvent extraction, or adsorption. Identification of the diester would be dependent on measurement of one of its physical properties, or on utilization of chemical reaction to give characteristic compounds or colors, or on paper chromatographic determination, etc.

A number of difficulties present themselves with the first approach: (1) the entire procedure would require a large amount of manipulation and time; (2) if a mixture of two or more DBAEs were present, both would be hydrolyzed and positive identification of the two or more esters would be difficult to establish; (3) simple, characteristic reactions for long chain alcohols are not entirely reliable; (4) quantitative measurement of the ester would be difficult, due to the nature of the reactions involved; and (5) from hydrolytic reactions observed in these laboratories with DBAEs and silicate esters, it appears that it would be difficult to achieve reaction conditions which would split the DBAE but not the silicate ester.

The hydrolytic method has already been found accurate when working with mixtures of mineral oil-di-n-butyl-sebacate (141, p.159), but the possible presence of silicate esters in the base-oil precludes exclusive use of the method. Even if qualitative tests show an absence of silicon in the base-oil, the hydrolytic technique may not be employed safely, due to the difficulties which could arise when two or more diesters

are present in the base-oil. Therefore it was necessary to seek other means for isolating and determining DBAEs in base-oils.

Approach (b), above, offers several advantages over the hydrolytic method: (1) the diester (or diesters) are recovered unchanged, leaving no doubt about the exact compounds in the oil; (2) the number and complexity of manipulations would probably be reduced, resulting in reduction of time and error; and (3) if a technique were available to detect the DBAE directly, only one identification operation would be required, as compared with two for the hydrolytic method.

It seemed logical, therefore, that approach (b) above should be exploited from the standpoint of the contractual specifications, whereby the least elaborate, most time-saving, non-optical methods of analysis were to be employed. Selective solvent extraction and partition chromatography, both paper strip and column, meet the requirements of the contract and of approach (b); therefore these were chosen as the most likely means for effecting separation and identification of DBAEs, silicone oils, and silicate esters.

2.0 SEPARATION OF SILICONE OILS AND SILICATE ESTERS

2.1 SOLUBILITY STUDIES

Having established qualitative means for identifying silicone oils and silicate esters (see Par. 2.0, p. 32), the next step was to find satisfactory means for separating these base-oils quantitatively from each other and from other base-oils such as mineral oil, dibasic acid esters, etc. Solubility differences offered the most convenient means for such separations; therefore the solubility properties of two silicone oils (Silicone DC-200 (5cs.) (alkyl) and Silicone DC-550 (aryl)) and two silicate esters (tetra(2-ethylhexyl) orthosilicate and hexa-(2-ethylhexoxy)disiloxane) were studied with some thirty pure solvents and ten solvent mixtures. The solvents employed were: acetone, five alcohols, three esters, dioxane, methylethylketone, diethylether, n-hexane, cyclohexane, ethylidine chloride, chloroform, carbon tetrachloride, benzene, pyridine, carbon disulfide, acetic acid, tetrahydrofuran, aniline, toluene, xylene, petroleum ether, ligroine, 2-picoline, ethanolamine, and piperidine. Solvent mixtures employed were pyridine:water, ethanol: water, isopropanol:water, and isopropanol:acetic acid, in several different ratios for each combination.

Results of this study showed that the four compounds were soluble in all of the solvents except acetic acid, aniline, and ethanolamine. There were several solvents (methanol, ethanol, pyridine, 2-picoline), where one compound or the other was sparingly soluble but the solubility was large enough in each case that no quantitative separation could be achieved. Hence solvent mixtures were tried as a possible means for these separations. Again no satisfactory separations could be achieved because of similarities in solubility properties of the four compounds. Even when centrifugation had separated them from certain solvent mixtures, the silicones would diffuse so rapidly into the solvent, that separation of the two phases could not be accomplished.

It was thought that the compounds might conceivably be separated by centrifugation with a material such as water in which neither type of oil was soluble and which possessed a density intermediate between the two types of compound. Several such separations were obtained, in which the silicone sank to the bottom of the tube and the silicate ester floated on top of the intermediate water layer; however, the silicone would diffuse up into the water before separation could be effected. Therefore, other means for separating these compounds were sought.

It should be pointed out that higher molecular weight silicones could undoubtedly be separated by solvent extraction from silicate esters, but the method would be of no value when low viscosity, low molecular weight silicones are encountered in lube-oils.

2.2 PAPER CHROMATOGRAPHIC SEPARATION OF SILICATE ESTERS AND SILICONE OILS

Since solvent extraction methods did not offer a ready solution to the problem of silicone and silicate ester separation, paper chromatographic techniques were immediately investigated. Paper chromatography had been employed most successfully for determination of antioxidants in synthetic lubricants (see Part II, p. 83), so that its potential for separation and identification of groups of base-oils, and even individual compounds in a group, was considered high. This technique permits working with a compound in its original form without extensive chemical manipulations, thereby offering a satisfactory means for fulfilling contractual requirements whereby complicated procedures and optical methods must be avoided.

Because of the nature of the base-oils it was, of course, necessary that a lipophilic paper be employed, such as acetylcellulose. Other types of lipophilic paper like silicone or vaseline treated papers could not be used because they would contaminate the oil sample. Cellulose, on the other hand, could be esterified to yield a non-contaminating, lipophilic carrier for the chromatogram. While acetylcellulose was employed in these experiments, it is felt that a paper such as butyrylcellulose or phthalylcellulose could give more definitive results. However, the time available was not sufficient for preparing and testing these various types of paper.

Preparation of acetylcellulose paper has been described and illustrated in detail (141, pp. 148-50) and is reproduced in APPENDIX A of this report. Details of the paper chromatographic technique have been presented in the above report (141). Application of this technique to the separation of DBAEs from silicone oils and silicate esters is given in succeeding paragraphs.

2.2.1 Detection of the Compounds on the Paper

Detection of DBAEs on the paper chromatogram has been discussed previously (see Par. 2.2, p. 7). It was felt that similarities in chemical structure and solubility properties of the DBAEs and silicate esters suggested that those fluorescent indicators employed for detecting the diesters might also be employed to detect silicate esters and perhaps silicone oils. DBAEs were detected by spraying the acetylcellulose paper strip on one side with a 0.1% aqueous solution of Rhodamine B, the dye staining the diester spot but not the rest of the paper, thus causing a bright red fluorescent spot to appear on the opposite side of the paper.

The same technique was applied to silicone and silicate ester spots with six indicators which fluoresce in UV light. Alkyl, aryl, and chlorinated silicones and two silicate esters were tested with each dye. It was noted that, as with the DBAEs, the indicators did not give characteristic colors according to the compound, but simply fluoresced with their natural color on the spot of oil; therefore, only the presence of oily compounds could be detected. Other chemical reactions or physical constants, such as the R_f-value, would have to be used to identify individual compounds. Results obtained with these dyes are tabulated in Table XI, p. 54.

TABLE XI

Detection Of Silicone Oils And Silicate Esters
With Fluorescent Indicators By Spraying Technique

Fluorescent Indicator (0.1% aq.)	Appearance of Spot			
	Visual		UV-Light	
	Spot	Background	Spot	Background
Quinine HCl	White	White	Blue	Blue
Fluoresceine	Pink	Pink	Purple	Yellow-green
Acridine Orange	White	Lt. Orange	Purple	Yellow
Nile Blue A	Lt. Blue	Dk. Blue	Lt. Blue	Dk. Blue
Rhodamine B	Lt. Pink	Dk. Pink	Purple	Br. Rose
Acridine Orange-Rhodamine B (1:1, v/v)	Pink	Rose	Purple	Rose
Parasheen (0.1% in benzene)	White	Lt. Yellow	Purple	Yellow

Of the fluorescent indicators tested Nile Blue A gave spots which had the highest contrast to the background visually and under UV-light. It is interesting to note that the silicones and silicates esters both quench fluorescence of the dyes, leaving purple voids in the brightly fluorescent background of the dye.

A second detection technique was attempted in an effort to force the dye into the oil spot to give bright fluorescent spots, analogous to those formed with DBAEs: the paper strip was placed on the surface of the aqueous dye solution in a covered Petri dish, and allowed to stand overnite. The paper, being water-repellant, floated, and several interesting phenomena occurred; the results of these tests are tabulated in Table XII, p. 55. Except with Nile Blue A, this experiment confirmed the quenching effect of the compounds. Nile Blue A was the best reagent, either visually or in UV-light, forming light pinkspots against a very dark background. However, this technique suffers because of the long period of time involved in having to wait overnight to obtain well-defined spots. In addition it is a poor reagent for detecting DBAEs. Therefore Rhodamine B was selected for detection of these compounds, because it gives good

TABLE XII

Detection Of Silicone Oils And Silicate Esters
With Fluorescent Indicators By Immersion Technique

Fluorescent Indicator (0.1% aq.)	Appearance of Spot			
	Visual		UV-Light	
	Spot	Background	Spot	Background
Fluoresceine	Pink	Pink	Purple	Yellow (poor contrast)
Acridine Orange	White	Orange	Purple	Yellow-Orange
Nile Blue A	Rose	Dk. Blue	Pink	Black
Rhodamine B	Pink	Fuschia	Lt. Pink	Dk. Pink (poor contrast)

spots with DBAEs and good visual spots with silicones and silicates (runs discussed later show how this reagent works to advantage in detecting a mixture of organic esters and silicones).

Further tests showed that when working only with silicones and silicate esters, a 0.1% solution of either Rhodamine B or Nile Blue A in methanol:water (1:3, v/v) sprayed lightly on one side of the paper gave almost pure white spots against bright red or blue backgrounds.

The spraying technique with Rhodamine B to detect the spots of oil had to be modified slightly in order to detect both DBAEs and silicones on the same strip of paper. Projecting a light spray on one side of the paper only, followed immediately by drying at about 60°C. gave good contrast in the spots, the silicone appearing white against a pink background, and the DBAE dark pink against the background. The methanol:water (1:3, v/v) solution of the dye could not be used, as this caused the color to come thru the paper everywhere except on the silicone spot, thus masking the DBAE. The spray should be handled carefully, the good judgement of the operator being very important in this situation. Too heavy a spray will hide the diester, and too light a spray will fail to detect the silicone. Best results were obtained by spraying very lightly, inspecting the strip carefully after waiting a few

seconds for the dye to spread, spraying again very lightly, and repeating this process until the correct contrast was achieved. Drying time required was about ten minutes, but length of time or temperature of drying were not found to be critical.

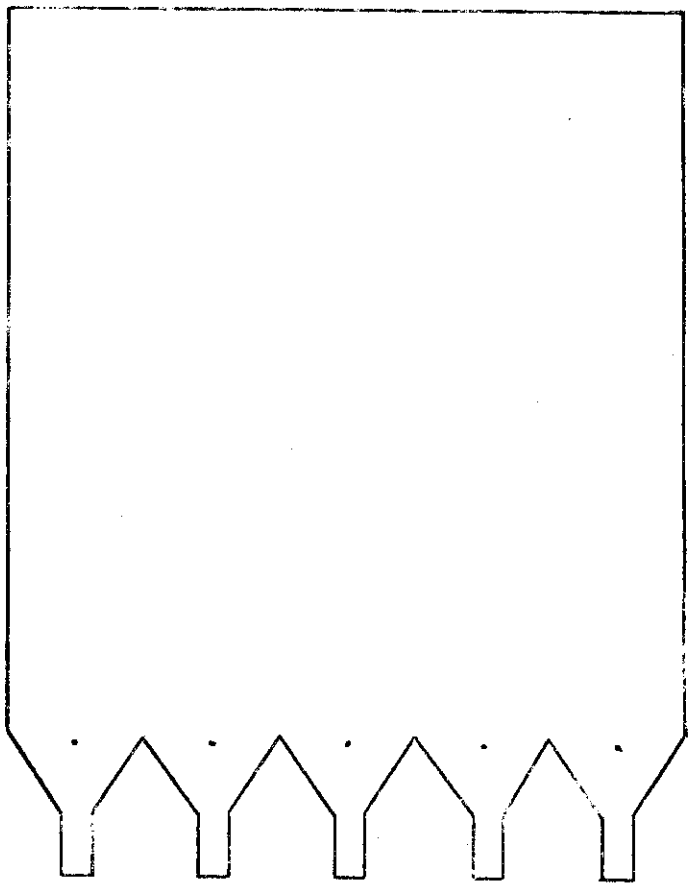
2.2.2 Development of Semi-Micro Scale Technique

As the testing program developed, it became obvious that for economy's sake the scale of the tests should be reduced to conserve time both on each actual run and on the time involved in making fresh supplies of acetylcellulose paper. Since it was necessary to check representative compounds singly on each strip (three silicone oils, two silicate esters and two DBAEs were used with each solvent combination), the scale was reduced by 2/3. The paper chromatographic runs were divided into three groups:

(a) Runs on small paper strips with silicone oils and silicate esters as individual compounds to determine their R_f-value with each solvent combination.

(b) Runs on small paper strips with mixtures of DBAEs and silicone oils and silicate esters, usually one DBAE with one silicone oil (to obtain clearly defined spots).

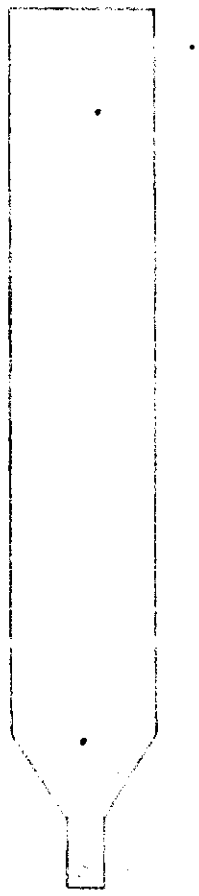
(c) Runs on larger paper strips to verify the most successful runs obtained on the small strips.



Each group of runs was performed on different size strips of acetylcellulose paper. The first group was run on paper shaped like the accompanying sketch (actual size). Starting points for each of the compounds are indicated by the

dots near the bottom of the sheet. With this shaped paper five individual R_f-values were obtained simultaneously.

The run is carried out in a glass jar wide and tall enough to accomodate the paper sheets (a 1000 ml. beaker can be used). 2.5 λ * spots of 5% benzene solutions of the oils are placed on the starting points on the paper. Solvent combination (about 30-50 ml.) is placed in the beaker, and the paper is suspended in the container on a wire so that the paper does not touch the surface of the liquid. The top is closed tightly to prevent escape of the solvent atmosphere (when using a beaker sheets of Parafilm, a reinforced paraffin sheeting, are stretched over the beaker). After an hour for saturation of the atmosphere and paper, the paper is lowered so that the five tails extend a few millimeters into the liquid. When the solvent front is near the top edge of the paper, the paper is removed, the front marked, and the paper dried at a temperature appropriate to the particular solvent combination. When dry, the spots are detected by spraying with 0.1% aqueous solution of Rhodamine-B on one side of the paper. The silicone and silicate ester spots appear as white voids in the pink background after drying. The R_f-value is calculated.



Runs for group (b) above, DBAEs with silicones or silicate esters, were made on paper strips similar to that sketched on the right (actual size). Runs were performed two strips at a time in a glass cylinder, 1-1/2" diameter by 7" high, closed with a rubber stopper. Wires through the stopper supported the papers and their clamps. The small circle at the tip is a hole into which a glass bead with a hook can be inserted to prevent the paper from curling. 2.5 λ spots of each oil (5% in benzene) are applied to the starting point, and the run is carried out as described in the previous paragraph. Whereas silicone oils and silicate esters give white spots on a pink background (or white spots surrounded by a pink circle), the DBAEs give a dark pink spot on a light pink or white background.

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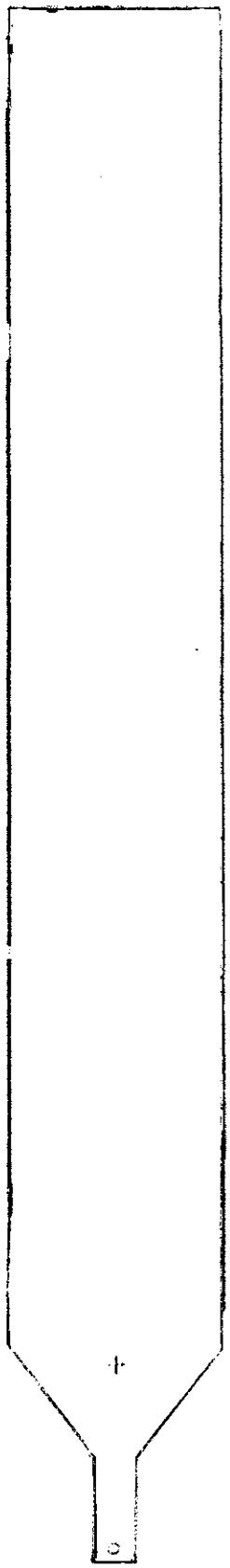
* λ = lambda = 0.001 milliliter

Runs for group (c) were performed on paper strips like that sketched in glass cylinders 2" diameter by 11" high. The procedure was the same as described above, except that the atmosphere and paper were saturated overnight instead of for one hour, as was done for the group (a) and (b) runs.



2.2.3 Determination of Optimum Solvent Combinations for Silicone Oils and Silicate Esters

These runs were carried out by the procedure described and illustrated on page 56. Purpose of this group of runs was three-fold: (1) to determine R_f-values for silicone oils and silicate esters with each solvent combination, (2) to find a solvent combination which would separate silicone oils from silicate esters, and (3) to determine relative mobilities of the oils so that DBAE separation experiments might be improved by using silicones or silicate esters of known mobility.

Of the silicone oils and silicate esters which were available, five were selected as representative of the types used in synthetic lubricants (the abbreviation in parentheses will be used throughout this report in referring to these compounds):

(1) MLO-53-446 = Chlorinated silicone (ClSil).
(2) Silicone DC-200(30,000cs) = Alkyl silicone (AlkSil).
(3) Silicone DC-550 = Aryl silicone (ArSil).
(4) Hexa(2-ethylhexoxy)disiloxane (HHDS).
(5) Tetra(2-ethylhexyl)orthosilicate (TOS).

R_f-values of these compounds with a number of solvent combinations are listed in Table XIII, p. 59. While the information does not appear in Table XIII, it must be pointed out that when the silicones are listed as having an R_f-value of 0.95, they actually are very diffuse spots, frequently possessing tails which spread out almost from the starting point. This is to be expected for polymeric materials such as silicones.

TABLE XIII

R_f-Values Of Silicone Oils And Silicate Esters With Various Solvent Combinations

Solvent Combination (v/v)*	Silicone Oil or Silicate Ester					Remarks
	ClSil	AlkSil	ArSil	HHDS	TOS	
MeOH:Bz (1:1)	1.00	1.00	1.00	1.00	1.00	-
" (2:1)	1.00	1.00	1.00	0.90	0.90	-
" (5:1)	0.95	0.95	0.95	0.75	0.85	Much tailing.
MeOH (pure)	0.00	0.00	1.00	0.65	0.80	"
n-BuOH:Bz(1:1)	0.95	0.90	1.00	1.00	1.00	Clear spots.
" (2:1)	0.95	1.00	1.00	1.00	1.00	"
" (5:1)	0.90	0.95	1.00	1.00	1.00	"
n-BuOH:Bz:H_2O(9:3:1)	0.95	0.95	1.00	1.00	1.00	"
MeOH:Pyr(1:1)	1.00	1.00	1.00	0.95	1.00	Diffuse spots.
" (2:1)	1.00	1.00	1.00	0.75	0.85	"
" (7:2)	0.00	0.00	0.70	0.60	0.80	"
EtOH:Pyr(1:1)	0.95	0.95	1.00	1.00	1.00	"
" (2:1)	0.95	0.95	1.00	1.00	1.00	"
" (5:1)	0.95	0.95	1.00	1.00	1.00	"
i-PrOH:Pyr(5:1)	1.00	1.00	1.00	1.00	1.00	Much tailing.
n-PrOH:Pyr(7:2)	0.95	0.95	1.00	1.00	1.00	Clear spots.
n-BuOH:Pyr(7:2)	0.95	0.95	1.00	1.00	1.00	"
n-BuOH:Pyr:H_2O(3:1:1)	0.00	0.00	1.00	1.00	1.00	"
MeOH:Ac (4:1)	0.00	0.00	1.00	0.75	0.90	Much tailing.
MeOH:Ac :H_2O(8:2:1)	0.00	0.00	0.00	0.00	0.00	"
" (12:3:5)	0.00	0.00	0.00	0.00	0.00	Clear spots.
BuAc:Pyr:H_2O(1:5:5)	0.00	0.00	0.00	0.00	0.00	"
" (2:10:5)	0.00	0.00	0.00	0.00	0.05	"
" (6:30:5)	0.00	0.00	1.00	1.00	1.00	HHDS tails.
EtAc:THF:H_2O(6:35:47)	0.00	0.00	0.00	0.00	0.00	Clear spots.
" (6:33:24)	0.00	0.00	0.10	0.35	0.40	Double front at R_f 0.45.
" (6:36:24)	0.00	0.00	0.00	0.30	0.40	"
" (6:48:24)	0.00	0.00	0.50	0.50	0.55	Double front at R_f 0.75.
BuAc:THF:H_2O(1:12:4)	0.95	0.95	0.95	0.95	0.95	Double front at R_f 0.95.

* Abbreviations for solvents:
Bz = Benzene
Pyr = Pyridine
Ac = Acetone
THF = Tetrahydrofuran

The data indicate that ArSil is much more mobile than AlkSil or ClSil. This silicone therefore was used most frequently to test column separations with diesters, since its greater capacity for moving with a given solvent combination was an indication whether the other silicones could be expected to move in a column. In addition the data indicate that TOS is slightly more mobile than HHDS, and can thus be expected to cause more difficulty in separations from DBAEs than HHDS. Therefore TOS was used as representative of the silicate esters in separation experiments.

Both of the silicate esters are more mobile than ArSil, indicating that silicate esters will be eluted during column partition separations ahead of silicones. As a result the group of silicate esters should be separable from silicone oils on columns under carefully controlled conditions. None of the runs gave sufficiently clear-cut results to predict a positive separation of silicones from silicate esters, although the solvent combinations MeOH-Acetone(4:1, v/v) and MeOH-Benzene (5:1, v/v) with slight modification might be useful in this regard.

It would appear from the data in Table XIII, p. 59, that tetrahydrofuran (THF) solvent combinations hold some promise; however, this is misleading because the THF forms a second solvent front, probably because it is being partitioned from the solvent combination itself. The oils move in this second front, giving misleading R_f-values. The R_f-value of the second solvent front depends upon the amount of THF in the solvent combination, the higher the percent of THF the greater the R_f-value of the front. Therefore, these runs have been disregarded.

3.0 PAPER CHROMATOGRAPHIC SEPARATION OF DIBASIC ACID ESTERS, SILICONE OILS, AND SILICATE ESTERS

3.1 EXPERIMENTAL RESULTS

Having determined in general the mobilities and functioning of silicone oils and silicate esters with a large number of solvent combinations, the next step was actual separation of these oils from DBAEs by paper partition chromatography. A total of 18 solvent combinations were tested, using the paper strips and procedure described for the group (b) runs on page 56. Two paper strips were used with each solvent combination, one having a mixture of tetra(2-ethylhexyl)orthosilicate (TOS) with di-(2-ethylhexyl)-adipate (DOA),

and the other having a mixture of Silicone DC-550 (ArSil) with di-(2-ethylhexyl)-sebacate (DOS).

Preliminary runs had shown that DOA possessed an R_f-value which was about average for all diester compounds tested, and DOS had an R_f-value which was the lowest of the diesters tested and only slightly higher than that of TOS. Therefore the entire separation procedure depended on the ability of a solvent combination to separate DOS from TOS, other diesters being more mobile than DOS, and other silicones and silicate esters being less mobile than TOS. With DOS on one paper strip and TOS on the other, positive means for identifying the exact locations of the two oils was available; on a single paper strip the two spots could overlap to a degree where it would be impossible to distinguish them, and the run would be lost. Table XIV, p. 62, summarizes the results of these runs.

From inspection of the data in Table XIV and the paper chromatograms themselves, the most successful solvent combinations, listed in descending order, are:

(1) EtOH:Acetone:Water (12:3:7, v/v)
(2) EtOH:Water (12:6, v/v)
(3) MeOH:Methyl Ethyl Ketone:Water (24:5:10, v/v)
(4) n-PrOH:Water (12:20, v/v)
(5) MeOH:Acetone:Water (12:5:5, v/v)
(6) MeOH:Ethyl Acetate:Water (12:4:5, v/v)
(7) MeOH:i-PrOH:Water (12:3:5, v/v)

With any of these solvent combinations it is possible to identify the presence of the group of DBAEs and/or silicones and silicate esters in a 5 λ sample of oil or oil mixture of 5% concentration in benzene. Figure 6, p. 63, illustrates typical actual separations of these base-oils, using solvent combinations (1) and (3) above.

Several problems were encountered in carrying out these tests:

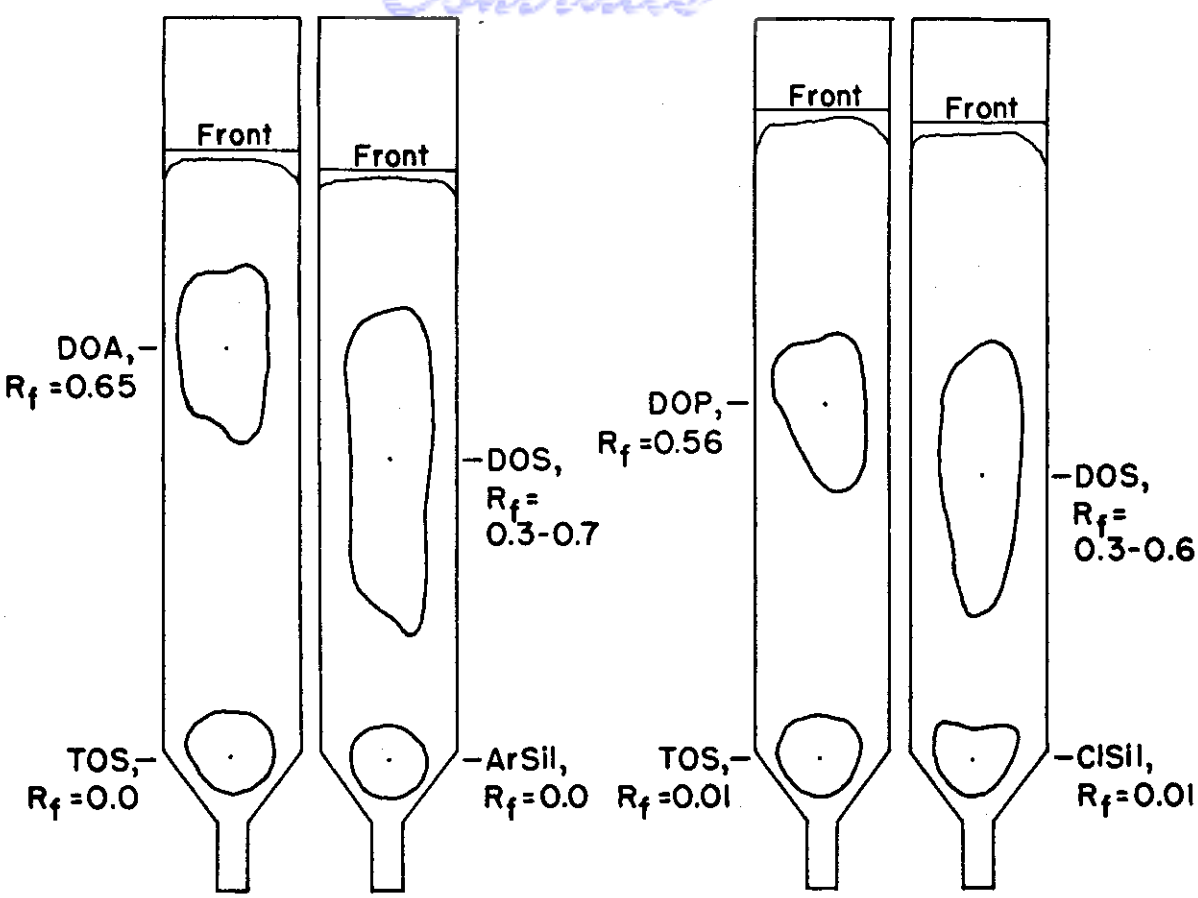
(a) It is almost impossible to prevent "tailing" of DOS.
(b) The amount of tailing and the R_f-value of DBAEs is strongly influenced by the type and amount of silicone oil or silicate ester present in the sample.
(c) Resins and oils inherently present in the acetylcellulose paper usually travel in the solvent front, but occasionally tail out from the front far enough to mask the exact location of the high R_f-value diester spots.

TABLE XIV

Separation Of Dibasic Acid Esters From Silicone Oils And Silicate Esters On Acetylcellulose Paper

Solvent Combination* (v/v)	R_f-value or R_f-range				Remarks
	DOA	DOS	ArSil	TOS	
MeOH:Ace:H_2O(12:3:5)	0.1-0.6	0.1-0.5	0.0	0.05	Much tailing.
" (12:4:5)	-	0.1-0.6	-	0.0	No separation.
" (12:5:5)	0.6	0.1-0.7	0.0	0.0	Fairly good separation.
" (12:6:5)	0.7	0.2-0.7	0.0	0.0-0.2	TOS moved slightly.
" (12:7:5)	0.8	0.2-0.9	0.0	0.0-0.4	Tailing; no separation.
MeOH:MEK:H_2O(12:2:5)	0.5	0.0-0.5	0.0	0.0	No separation.
" (24:5:10)	0.6	0.3-0.6	0.0	0.05	Very good separation.
" (12:3:5)	0.6	0.2-0.7	0.05	0.05	Fairly good separation.
" (12:4:5)	0.7	0.4-0.8	0.05	0.0-0.4	TOS moves too far.
MeOH:Diox:H_2O(12:3:5)	0.5	0.0-0.6	0.0	0.0	DOS tailed out.
" (12:4:5)	0.6	0.1-0.7	0.0	0.05	"
" (12:5:5)	0.7	0.2-0.8	0.0	0.0-0.3	No separation.
MeOH:BuAc:H_2O(12:3:5)	0.6	0.2-0.7	0.0	0.0-0.3	No separation.
" (12:3:6)	0.2-0.5	0.0-0.4	0.0	0.05	"
MeOH:EtAc:H_2O(12:3:5)	0.6	0.1-0.7	0.0	0.0	DOS tailed out.
" (12:4:5)	0.6	0.2-0.7	0.0	0.0	Fairly good separation.
" (12:5:5)	0.7	0.3-0.7	0.0	0.0-0.5	No separation.
" (12:5:7)	0.1-0.6	0.0-0.5	0.0	0.0	"
" (12:5:8)	0.4	0.0-0.5	0.0	0.1	"
" (12:7:7)	0.6	0.2-0.6	0.0	0.0-0.3	"
MeOH:i-PrOH:H_2O(12:3:5)	0.8	0.4-0.8	0.0	0.0-0.2	Good separation.
" (12:3:6)	0.5	0.1-0.5	0.0	0.0-0.1	No separation.
MeOH:n-BuOH:H_2O(12:3:10)	0.1	0.0	0.0	0.0	No separation.
EtOH:Ace:H_2O(12:3:5)	0.9-1.0	0.8-1.0	0.0	0.0-0.7	R_f-values too high.
" (12:3:7)	0.7	0.3-0.7	0.0	0.0	Excellent separation.
" (24:6:13)	0.9	0.5-0.9	0.0	0.05	"
EtOH:Ace:H_2O-HAc(12:3:7:1)	?	0.0-0.9	0.0	0.0-0.9	Tailing; no separation.
EtOH:MEK:H_2O(24:4:15)	0.8	0.4-0.8	0.0	0.0-0.4	No separation.
" (12:4:10)	0.2-0.5	0.0-0.4	0.0	0.0-0.1	"
EtOH:Bz:H_2O(12:3:5)	1.0	0.5-0.1	0.0-0.4	0.0-0.6	"
" (34:6:21)	0.1	0.01	0.0	0.0	"
" (36:7:20)	0.0-0.3	0.0-0.05	0.0	0.0	"
" (36:7:15)	0.0-1.0	0.6-0.8	0.0	0.0-0.5(?)	"
EtOH:Pyr:H_2O(12:3:15)	0.1	0.0	0.0	0.0	"
" (12:6:15)	0.1-0.4	0.0-0.1	0.0	0.0-0.1	"
EtOH:BuAc:H_2O(12:3:5)	0.3-1.0	0.2-0.8	0.0	0.0-0.2	"
EtOH:EtAc:H_2O(12:3:10)	0.4	0.0-0.4	0.0	0.0-0.1	Clear spots; no sepn.
" (12:4:10)	0.5	0.1-0.6	0.0	0.0-0.4	"
" (13:4:10)	0.7	0.1-0.7	0.0	0.0-0.3	"
" (13:4:11)	0.6	0.1-0.6	0.0	0.0-0.4	"
" (13:4:12)	0.4	0.1-0.3	0.0	0.05	"
EtOH:n-BuOH:H_2O(12:3:10)	0.9	0.5-0.9	0.0	0.0-0.7	Much tailing.
" (12:3:13)	0.5	0.0-0.5	0.0	0.05	"
" (12:4:13)	0.7	0.2-0.7	0.0	0.0-0.2	"
" (12:5:13)	1.0	0.9	0.0	0.0-0.9	"
EtOH:i-PrOH:H_2O(12:3:10)	0.0(?)	0.0(?)	0.0	0.05	Much tailing.
" (12:5:10)	1.0	0.9	0.0	0.0-0.8	Much TOS tailing.
EtOH:H_2O(12:5)	0.8-1.0	0.7-1.0	0.0	0.0-0.7	Fair separation.
" (24:15)	0.5	0.0-0.6	0.0	0.05	No separation.
" (12:6)	0.8	0.4-1.0	0.0	0.05	Excellent separation.
n-PrOH:Ace:H_2O(12:3:7)	1.0	1.0	0.1	0.4-1.0	Very blurred.
" (12:3:10)	1.0	0.5-1.0	0.0	0.1-0.6	No separation.
" (12:3:15)	0.8	0.6-0.9	0.0	0.0-0.7	"
" (12:3:17)	0.7	0.4-0.7	0.0	0.0-0.5	"
" (12:3:21)	0.4	0.0-0.6	0.0	0.0-0.2	"
n-PrOH:H_2O(10:10)	1.0	1.0	0.0-0.5	0.0-0.4	Fairly good separation.
" (10:20)	0.4	0.0-0.4	0.0	0.0-0.2	No separation.
" (12:20)	1.0	1.0	0.05	0.05	Excellent separation.

* Abbreviations for solvents:
Ace = Acetone
MEK = Methyl Ethyl Ketone
Diox = Dioxane
Bz = Benzene
Pyr = Pyridine



Solvent combination:
EtOH:Acetone:H_2O (12:3:7, v/v)

Solvent combination:
MeOH:MeEtKetone:H_2O (24:5:10, v/v)

5λ of each oil (5% in benzene).

Ascending runs at 25°C.

Indicator: Rhodamine B.

Abbreviations:

DOA = Di-Octyl Adipate
DOS = Di-Octyl Sebacate
DOP = Di-Octyl Phthalate
ArSil = Aryl Silicone Oil
ClSil = Chlorinated Silicone Oil
TOS = Tetra(2-Ethylhexyl)orthosilicate

Figure 6. Semi-Micro Scale Chromatograms Illustrating Qualitative Separations of Dibasic Acid Esters From Silicone Oils and Silicate Esters On Acetylcellulose Paper (Actual Size).

(d) When using solvent combinations containing ketones, a small amount of acetylcellulose is dissolved and carried along through the paper strip or column. This is particularly bothersome when trying to recover the eluted oils from column separations.

It seems unlikely that the first two difficulties can be eliminated entirely. Figure 7, p.65 , shows how "tailing" and elongation causes overlapping of the spots of oil, preventing identification or separation of oil mixtures. However, in the case of column separations "tailing" is not too important; here the important criterion is complete separation of all DBAEs from silicone oils or silicate esters by the solvent combination, regardless of the amount of tailing that occurs.

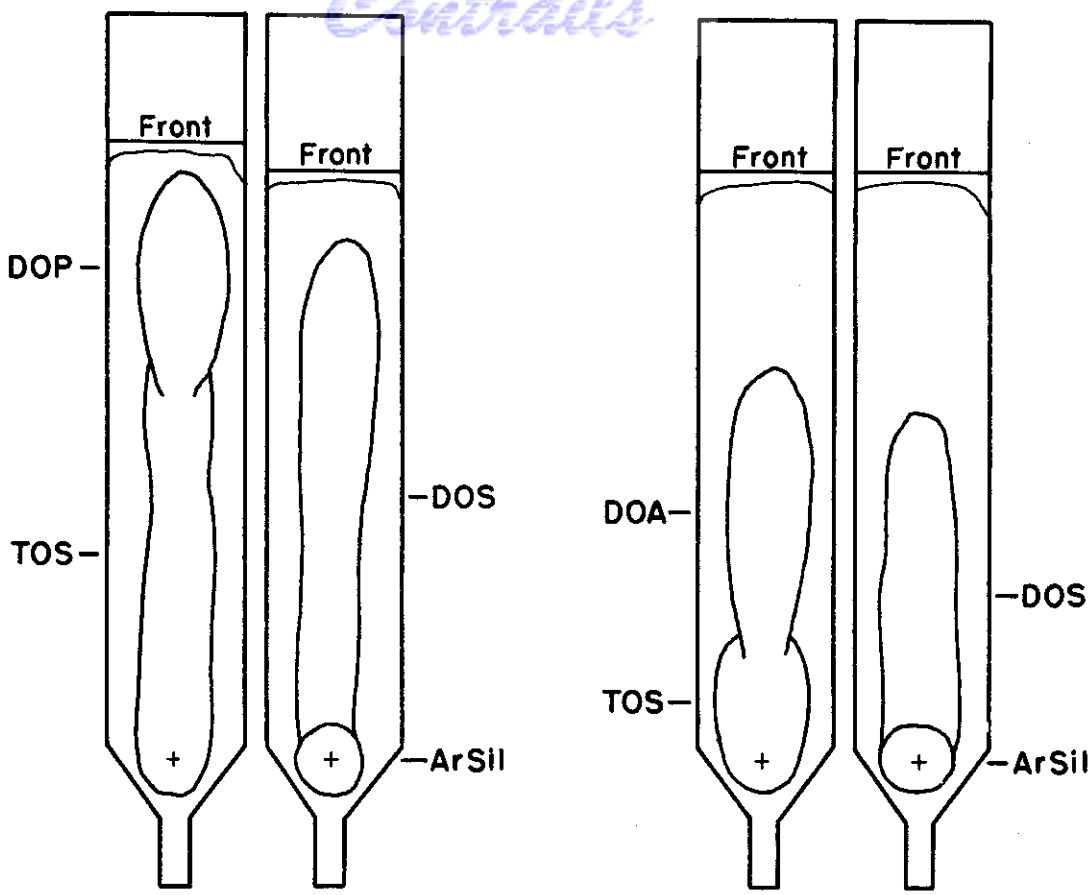
Elimination of oil and resins present in the paper is accomplished by thorough washing with ether and drying. A relatively large quantity of ether-soluble oils and resins is removed from acetylcellulose in this manner, giving much more easily interpreted chromatograms.

Elimination of dissolved acetylcellulose can be achieved, of course, by using solvent combinations which do not contain ketones. However, separation of the base-oils is more important in a column separation than addition of an extraction step at the end of a run; therefore, ketone-containing solvent combinations have been used for column separation experiments.

3.2 VERIFICATION OF RESULTS WITH MACRO-SCALE RUNS

Although several solvent combinations gave good separations on a semi-micro scale, it was necessary to check these combinations on the usual macro-size ascending strips, which are described and illustrated on page 58. It will be noted in Table XV, p.66 , that several solvent combinations which were optimum for small-scale chromatograms had to be shifted slightly toward the aqueous side to prevent movement of TOS. Whether this is due to saturating the paper and atmosphere overnight instead of one hour for the micro-scale runs is not known.

Table XV shows that DBAEs can be separated from silicone oils and silicate esters. Figure 8, p.67 , is a drawing of two actual paper chromatograms, demonstrating successful separations of these base-oil mixtures. The chromatogram sprayed with Rhodamine-B gives



Solvent combination:
Ethanol:Acetone:Water
(12:7:5, v/v)

Solvent combination:
n-Propanol:Acetone:Water
(12:3:21, v/v)

10λ spots of a 1:1 solution of each oil mixture (5% in benzene).

Ascending runs at 25°C.

Indicator: Rhodamine B.

Abbreviations: DOP = Di-Octyl Phthalate.
DOS = Di-Octyl Sebacate.
DOA = Di-Octyl Adipate.
TOS = Tetra(2-Ethylhexyl)orthosilicate.
ArSil= Aryl Silicone Oil.

Figure 7. Semi-Micro Scale Paper Chromatograms Showing Incomplete Separation of Base-Oils With "Tailing" and Elongation of the Spots.

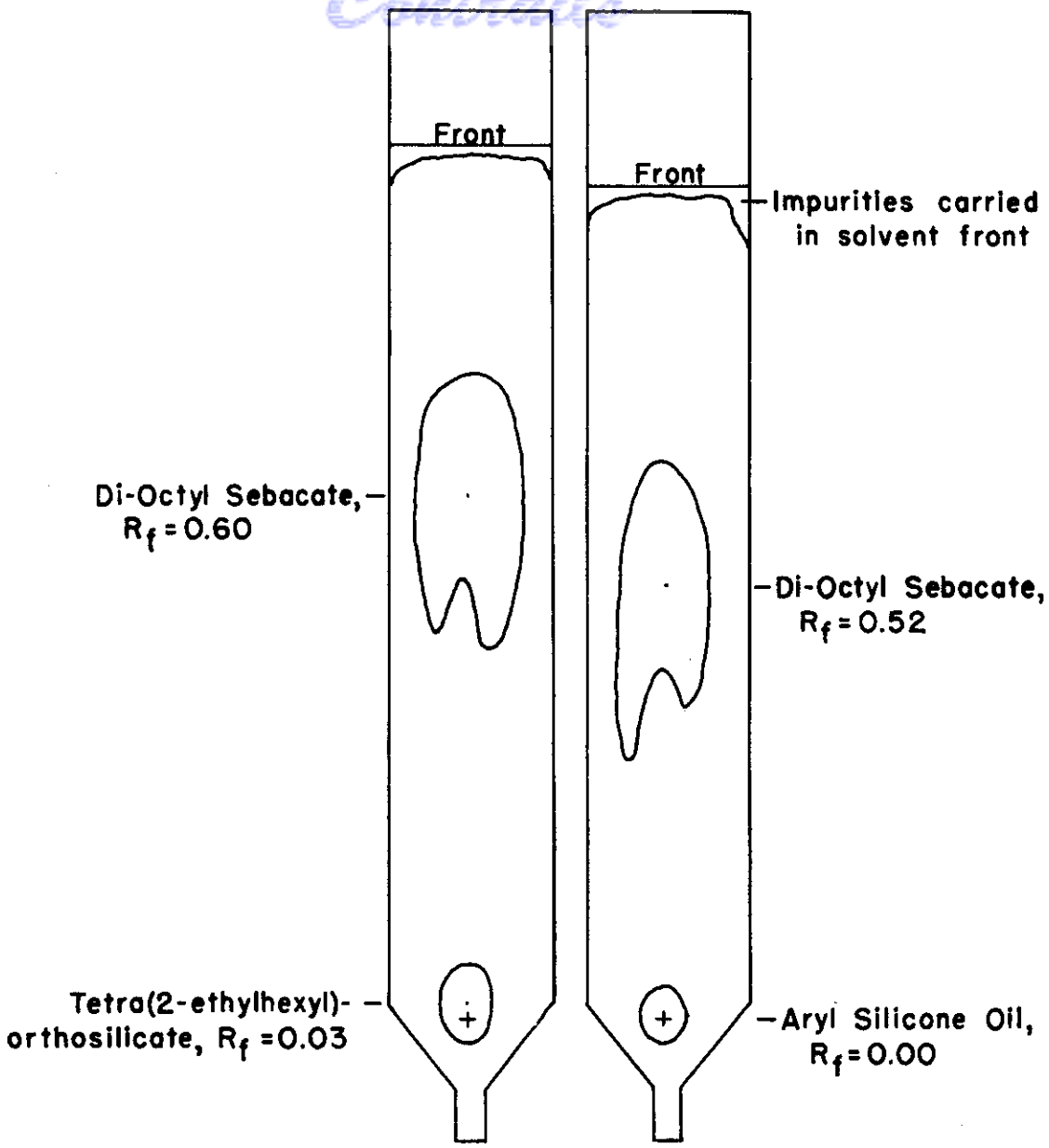
clear spots for the diesters, and the degree of tailing seems to be reduced with the larger paper strips. The final step in this phase of the program will be to determine whether DBAEs may be separated and detected when in the presence of other base-oils, such as mineral oil, polyglycols, etc.

TABLE XV

Macro-Scale Paper Chromatographic Separation
Of Diesters From Silicone Oils And Silicate Esters

Solvent Combination * (v/v)	Oil Mixture (5 λ spots)	R_f-Values	
		Diester	Silicone or Silicate Ester
EtOH:Ac :H_2O (12:3:7)	DOS-ArSil	0.57	0.00
" "	DOS-TOS	0.53	0.0-0.26
" (12:3:8)	DOS	0.50	-
" "	DOS-ArSil	0.52	0.00
" "	DOS-TOS	0.60	0.03
" (12:3:9)	TOS	-	0.00
" "	DOS	0.38	-
" "	DOS-TOS	0.36	0.00
" "	DOA-ArSil	0.62	0.00
MeOH:MEK:H_2O (24:5:10)	DOS-TOS	0.60	0.08
" "	DOS-HHDS	0.45	0.00
" "	DOP-ArSil	0.51	0.00
" "	DOA-ClSil	0.60	0.00
EtOH:H_2O (12:6)	DOS-TOS	0.40	0.10
" "	DOS-ArSil	0.85	0.00
" (12:7)	DOA-ArSil	0.70	0.00
" "	DOS-TOS	0.20	0.00

* Abbreviations for solvents:
Ac = Acetone
MEK = Methyl Ethyl Ketone



Solvent combination: Ethanol:Acetone:Water (12:3:8, v/v).

2.5λ of each oil (5% in benzene).

Ascending run at 25°C.

Indicator: Rhodamine B.

Figure 8. Chromatograms Demonstrating Qualitative Separations of Di-Octyl Sebacate From Tetra(2-ethylhexyl)orthosilicate and from an Aryl Silicone Oil on Acetylcellulose Paper (3/4 Actual Size).

SECTION D

QUANTITATIVE SEPARATION OF DIBASIC ACID ESTERS, SILICONE OILS, AND SILICATE ESTERS

1.0 INTRODUCTION

In the previous section it has been shown that diesters can be isolated by paper partition chromatography and identified qualitatively as a group from silicone oils and silicate esters. This qualitative technique required a relatively short period of time, a minimum of materials, no elaborate apparatus, and only minute amounts of oil sample. In a rough way the technique may also be used for order-of-magnitude estimations of amounts of oil. But for quantitative measurement of each oil present, it is necessary to use column chromatographic separation of the oil (the lack of feasibility of paper partition chromatography for quantitative estimation of diesters and oils in general is discussed in SECTION A, Par. 4.0, p. 24).

Several column separations of diesters and silicones were unsuccessfully attempted early in the research program, using silica gel and alumina gel columns with hydrocarbon solvents, in analogy to petroleum and shale oil chromatography. The diesters and silicones did not adsorb in the column and were eluted immediately with the hexane solvent. Therefore acetylcellulose powder was tried as filling for the column. Since the behavior of oils on acetylcellulose paper was known, it seemed logical that somewhat the same behavior could be expected in a column of the same material.

2.0 ACETYLCELLULOSE POWDER COLUMNS

2.1 PREPARATION OF ACETYLCELLULOSE POWDER COLUMNS

Acetylcellulose powder is prepared in the same manner as the paper (see APPENDIX A, p. 116, of this report), with a few modifications of the apparatus which depend on the quantity of powder to be acetylated. The powder columns, regardless of size, were prepared in one of three ways, the first and second methods being replaced when experimental results showed that the column was not functioning as expected.

The first columns were prepared simply by placing a small amount of cotton at the bottom of a plain glass column (no fritted glass disk), pouring

the powder in small increments into the tube, tapping the tube to settle the powder, and filling to the desired height or volume. A small disk of acetylcellulose paper was placed on top of the powder. In the case of a fritted glass chromatographic tube, a disk of paper instead of the cotton plug was placed on the frit at the bottom of the column. The weighed oil sample was then carefully poured onto the powder and allowed to absorb completely before pouring in solvent combination.

When experimental results showed this method of filling gave incomplete separations, a second technique was attempted which in effect duplicated more precisely the conditions met while running a paper strip separation. The column was filled with powder as before, but the oils were not added immediately. Instead enough solvent combination was poured onto the column to saturate it completely, thus duplicating the effect of saturating the atmosphere and paper with vapors of the solvent combination for paper strip separations. The oil sample was now added, allowed to absorb, and several grams of wetted powder were poured in, sealing the oil into the powder. While this technique improved percentage recoveries of the oils, refractive index values for the oils indicated very poor separation. Therefore a small amount of fluorescent dye was added to show visually what was happening in the column. This indicated the presence of a great many air pockets, which caused excessive channeling to the extent that in some parts of the column the silicone oil was carried by the final solvent to the tip of the column,while in other parts of the column the silicone was not moved downward at all.

To eliminate air pockets, a vacuum technique was attempted, in which the empty chromatographic tube was stoppered at the bottom, filled with solvent combination, a few grams of powder poured into the liquid, the slurry stirred, and vacuum applied until the solvent boiled, releasing air from the powder. Upon relieving the vacuum, solvent combination moved into the interstices in the powder. This procedure was repeated until the desired amount of powder had been added. While this technique eliminated air pockets, the rate of flow of solvents through the powder was so slow, despite application of 18 p.s.i. pressure, that the advantage of uniform packing was totally outbalanced by the loss of time. Since further improvement in the technique did not seem probable, except possibly by the use of filter-aids, other column packing materials were investigated.

2.2 DEVELOPMENT OF COLUMN SEPARATION TECHNIQUE

Ether extraction of acetylcellulose powder proved the presence of appreciable oil and resin which could contaminate the sample oils. Thereafter all acetylcellulose columns were washed three times with ether and dried before the oils or solvent combinations were added. The pre-wetted type column, designed to duplicate the conditions under which a paper strip separation is performed, has been described in the previous paragraph. Runs with columns prepared by this technique resulted in nearly quantitative recoveries of the oils; however, refractive index values proved that clean separations were not being obtained. Irregularities in the oil zones would account for poor refractive index values, i.e., the first oil is not completely eluted before the second oil starts to emerge, thus causing mixing of the two fractions.

This problem was analyzed by using a fluorescent dye in the oil mixture. A fluorescent dye consisting of Sudan III together with an olefin and aromatic dye dissolved in xylene* proved most useful. This dye remained with the silicone oil, thereby permitting direct observation of the movement of the silicone zone with various solvent combinations. The dye revealed that the silicone oil was uniformly distributed at the top of the column while most solvent combinations were passing through; however, the benzene solvent moved the fluorescent zone so irregularly that part of the zone was being eluted while other parts had moved only a few millimeters. This startling performance was the result of extreme channeling due to air pockets in the powder (which were clearly visible) and uneven packing. Therefore the method for preparing the column was changed to a vacuum technique already described above (Par. 2.1, p. 68).

2.3 RECOVERY OF OILS AFTER SEPARATIONS

The method for recovering sample oils during and after elution is a fairly standard one. From 100 to 350 ml. of solvent combination, depending on column size, is added to the space above the column carefully in order to avoid disturbing the surface of the powder. The solvent combination emerges from the column either by gravity or by pressure (affected by a tank of inert gas attached to the column through a ball joint union on the upper end of the tube). Ten milliliter test tubes in a rack or in the reel of an automatic fraction collector are used to collect the eluting liquid usually

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* This dye is available from Patent Chemical, Inc., 335 McLean Blvd., Patterson, N. J.

in 4 to 7 ml. portions.

When the meniscus of the solvent combination has almost entered the surface of the column, a hydrocarbon solvent in which the silicone oil is soluble (benzene was used in these experiments) is added to the tube. The elution continues as benzene forces solvent combination out of the column ahead of it. As soon as the junction between the two solvents appears at the tip of the column, as indicated by two phases in the collection tube or by the first droplet of fluorescent dye, a new collection tube is placed under the column tip and all succeeding fractions are collected in a second group. The first group of collection tubes should contain the diester, and the second group the silicone oil and any residual diester which was not eluted with the solvent combination.

As the tubes are filled they are placed in an oven at 70°C. overnight to evaporate organic solvents. The entire group of tubes is then placed in a 110°C. oven for an hour to remove traces of moisture. After removal from the oven and cooling, the appearance and estimated volume of oil in each tube are noted. This observation shows when and how the oils were eluted from the column. The absence of any trace of oil in those tubes immediately ahead of the benzene eluate is an indication that the solvent combination has eluted all of the DBAE.

The tubes are now extracted and washed with three successive 8 ml. portions of hexane, taking care to catch all traces of oil from inside and from the lip of each tube. Two groups of extractions are performed, one of the tubes containing solvent combination eluate and the other of the tubes containing benzene eluate, an average total of 50 tubes. The hexane extracts are placed in pear-shaped centrifuge tubes, centrifuged briefly to bring down any foreign matter such as flakes of acetylcellulose which might have been carried along with the hexane, and poured into weighed Petri dishes. The centrifuge tubes are rinsed with hexane to pick up residual oil, centrifuged, and the washings added to the Petri dishes. Part of the hexane is evaporated in an air stream and the remainder on a water bath. After 10 minutes drying at 110°C. the dishes are cooled and weighed. Percent recovery of each oil is calculated and refractive index values for each oil are taken at 25°C. to determine purity.

It must be understood that the above procedure has been employed only to study the separation process and to determine factors necessary to obtain successful separations. Once all conditions for successful separations are known, a simple procedure will be outlined, whereby to obtain

quantitative data on oils eluted from a column the operator need collect only two or three total fractions, evaporate them to dryness, extract the oil, transfer to a weighed container, dry again, and weigh.

2.4 EXPERIMENTAL RESULTS WITH ACETYLCELLULOSE POWDER COLUMNS

Table XVI, p. 73, summarizes all of the pertinent data for quantitative separation runs made with acetylcellulose powder columns, and most of the preceding discussion is based on the data in this table. Preliminary qualitative runs are not included. It is evident that complete separation of a DBAE from a silicone oil was not achieved, yet several runs (particularly Run 4) showed very promising results. Had the refractive index values for Run 4 been closer to the actual values, this might have been considered a satisfactory separation. In general all of the runs show at least a strong tendency toward separation, as shown by the very nearly pure diester eluted in Runs 6 and 7.

Fluorescent dye, 0.003g., was used in Run 8. It was because of this run that the vacuum packing technique to eliminate air pockets was tried. The resulting dense column (Run 9) could not be used for practical separations; therefore other types of column packing material were sought. This led to trials with silica gel, which proved superior to acetylcellulose in several ways, as discussed below.

3.0 SILICA GEL COLUMNS FOR SEPARATION OF BASE-OIL MIXTURES

Silica gel may be used in column chromatographic separations either to adsorb the material being chromatographed, or to act as a support for the sample oil and the solvent. In the first case the separation depends on differences in the adsorbability of compounds on silica gel, the more polar the compound, the greater its attraction to the surface of the gel. When a solvent which is more strongly adsorbed than the compound is added to the column, the compound is replaced by the solvent, and the compound is eluted by the solvent.

On the other hand, when silica gel is used as an inert support for the compound and solvent, solubility of the compounds in the solvent is the main governing force holding the compound in the column or eluting it from the column. When a substance is completely soluble, it is eluted immediately; when completely insoluble, it remains in the column indefinitely while the solvent passes by; and if it is only partially soluble it will be eluted at an

TABLE XVI

ATTEMPTED QUANTITATIVE SEPARATION OF A DIBASIC ACID ESTER FROM A SILICONE OIL ON ACETYLCELLULOSE COLUMNS

Run No.	Dimensions of Column (mm.)	Weight of Powder (g.)	Gas Pressure (p.s.i.)	Type Packing	Solvent Combination (v/v)	Volume of Solv. Comb. (ml.)	Final Solvent	Volume of Final Solvent (ml.)	Total Fractions Collected
1	19 d. x 140	19	None	Dry	EtOH:Acetone:Water (12:3:9)	100	Benzene	50	43
2	"	"	"	"	"	"	"	"	14
3	"	"	"	"	EtOH:Water(12:6)	"	"	"	28
4	"	"	"	Pre-wetted	"	200	"	100	69
5	"	"	"	"	EtOH:Acetone:Water (12:3:8)	"	"	"	52
6	19 d. x 150* 7 d. x 1160	22	13	"	"	"	"	"	56
7	27 d. x 220	40	5	"	"	"	"	125	65
8	"	"	"	"	EtOH:Water(12:6)	"	"	"	64
9	"	"	18	Vacuum	"	---	---	---	---

TABLE XVI - Continued

Run No.	Oil or Mixture Added	Total Wt. Oils Added (g.)	DOA Recovered (%)	ArSil Recovered (%)	Total Oil Recovered (%)	n_D^{25} Diester Fraction **	n_D^{25} Silicone Fraction **	Remarks
1	DOA-ArSil	2	14	130	77	---	---	No Separation.
2	DOA	3	63.4% in Solvent Comb., 12.4% in Benzene	---	75.8	1.4453	---	Solvent Combination not staisfactory.
3	DOA	2.5	40.1% in Solvent Comb., 53.9% in Benzene	---	94.0	1.4453	---	Not satisfactory.
4	DOA-ArSil	4	99.2	98.2	98.7	1.4542	1.4832	Refractive index values showing mixing.
5	DOA-ArSil	4	91.3	103.6	97.4	1.4603	1.4780	"
6	"	4	34.4	163.9	99.4	1.4460	1.4734	No separation.
7	"	2	85.1	110.3	97.7	1.4463	1.4880	Silicone is not pure.
8	"	2	108.0	87.6	97.8	1.4503	1.4940	Not satisfactory.
9	"	2	---	---	---	---	---	Flow rate too slow- no run made.

* This column had a short wide section at top of tube.

** n_D^{25} DOA = 1.4453; n_D^{25} ArSil = 1.5024

intermediate time, according to the solubility and the amount of solvent employed. In this situation the adsorption capabilities of the silica gel are excluded, and correct choice of solvents becomes most important in the separations.

Any one of a number of materials would probably function equally as well as silica gel, such as alumina gel, animal charcoal, etc. The important criterion for any column packing material used as a support is that it be chemically inert both to the solvent and to the substances being chromatographed, and that it have uniform size to provide minute spaces for passage of solvent through the column. Acetylcellulose powder failed to meet this latter requirement, forming such a dense column that movement of solvent through it was almost impossible. A number of advantages over acetylcellulose powder may be found in using silica gel:

(a) Acetylcellulose powder is so fine that flow rate is nearly zero in columns prepared by the vacuum technique. The larger, uniform mesh size of silica gel prevents this.

(b) No preparation is required with silica gel. Both the gel and powder can be washed, dried, and re-used a number of times.

(c) Silica gel is a more uniform product chemically. Small variations in time, temperature, etc., during acetylation result in variations of the acetyl content of the cellulose from batch to batch.

(d) Silica gel permits use of a greater variety of solvent combinations, particularly those which contain acetylcellulose-dissolving ketones.

(e) Silica gel columns after a run may be dried and removed from the tube more easily than acetylcellulose.

3.1 PREPARATION OF SILICA GEL COLUMNS

The silica gel used in these columns was Davison Chemical Corporation Type 22-08-09-216, thru 200 Mesh.

After experience gained in preparation of acetylcellulose columns (see Par. 2.1, p. 68), it was comparatively simple to prepare silica gel columns which would function satisfactorily. Preliminary experiments established that the gel, like acetylcellulose, readily formed air pockets which seriously interferred with smooth movement of solvent through the column. The vacuum technique, whereby gel was poured into solvent

combination already in the column, vacuum applied to remove air from the gel, and the vacuum released to force solvent into the pores of the gel, functioned most satisfactorily during the initial ten runs. This technique had disadvantages, however, in that the used silica gel had to be removed from the column, and a fresh portion of gel employed for each run.

If residual oils from the preceding run were washed from a used column, there was no reason to change the gel, providing the gel functioned satisfactorily during subsequent runs. As will be pointed out in the experimental results, washing with ether removed all residual oils and left the gel ready for the next run. Drying was accomplished by passing dry air through the gel at a pressure of about 5 p.s.i. for about an hour after the last liquid ether emerged from the tip of the column. The next run was started by pouring the desired solvent combination onto the gel. The solvents being more polar than ether displaced adsorbed ether from the gel, the last traces of ether being eluted from the column. It was found that as the solvent front descended through the column, it apparently forced almost all air out and left a negligible number of air pockets. Pressure was employed when longer or larger columns were used. With this technique it was possible to save much time in preparing the columns, with no sacrifice of accuracy or reproducibility.

A third technique for preparing silica gel columns for separation runs consisted of pouring the gel into the glass tube in a slow stream with continuous tapping to settle the gel. When the desired amount had been added, the sample oil was poured in (without pre-wetting the gel with solvent) and permitted to absorb completely into the gel. The oil had been diluted slightly (about 50-50) in benzene to carry it deeper into the gel to give better dispersion and to prevent formation of a gummy mass on the surface. The run was started immediately by adding solvent combination to the dry column. This technique resulted in very poor separation of the oil mixture, because the dry silica gel partitioned the solvent combination into an alcohol front followed by a solvent combination front. The alcohol front carried part of both oils, whereas the alcohol-water solvent combination would not; therefore part of the oil mixture was eluted unseparated in the first few milliliters of eluate until the front containing the solvent combination reached the tip of the column. At that time the oil which the solvent combination should carry started to emerge pure from the column, and the insoluble oil remained behind. Thus quantitative results could not be obtained with this technique. This run is listed as Run 4 in Table XVII, p. 79.

3.2 EXPERIMENTAL PROCEDURE

To make a separation run the first step is preparation of the column (see previous paragraph). If a fresh column is required, it should be prepared by the vacuum technique mentioned in the preparation of acetylcellulose powder columns. This consists of stoppering the bottom of a chromatographic tube (usually with a rubber tube and pinchclamp) and filling the tube with solvent combination to a height slightly higher than the expected height of the silica gel packing. A few grams of gel are poured into the liquid, the slurry stirred with a glass rod, and vacuum applied by closing the ball joint at the top of the tube and attaching the end of the joint to a low vacuum source. In this manner air and gases are released from the gel and boil out. Upon relieving the vacuum, solvent combination is forced into the space vacated by the gases. This procedure is repeated until the desired amount of gel has been added. Finally the stopper is removed and excess solvent above the gel is allowed to flow from the tube. When the surface of the solvent reaches the surface of the gel, the column is ready to receive the sample oil.

When the column was used in a previous run and has been washed with ether and dried by passing air through the gel (see Par. 3.1, p. 74), the solvent combination is poured gently onto the surface of the gel and allowed to percolate through, forcing adsorbed ether out of the column. Liquid ether emerges from the tip of the tube. When the last traces of ether have been eluted and the column is saturated with solvent, the surface of the solvent is allowed to sink to the surface of the gel, and the oil sample is poured into the column from the weighing tube.

When the sample oil has disappeared into the gel, about five grams of clean gel are poured into the column, a few milliters of solvent combination added, and the slurry stirred gently to remove air bubbles. This procedure seals the oil in the gel, preventing its rising upward in the column under the weight of the solvent, due to the lower density of the oil. When the stirred gel has settled and the solvent has reached the surface, the run is ready to start by adding the measured volume of solvent combination.

Large columns or elongated columns cause the flow rate of the solvent combination to be very slow, and it is necessary to apply pressure to drive the liquid through at a reasonable rate. This pressure may be supplied through a good regulator from a tank of inert gas, such as nitrogen, carbon dioxide, or air. The ball joint must be clamped to maintain pressure in the

system. Usually a maximum pressure of 12 p.s.i. is sufficient even for the longest columns tested (see Table XVII, p.79 , for actual size of columns). For average columns of 200 to 250 mm. length containing 60 to 100 grams of silica gel, a pressure of 2 to 4 p.s.i. is adequate. These pressures will give a flow rate of about 10 ml. per hour; this figure varies, of course, with the size and shape of the column, weight of gel, and pressure.

The oil sample is weighed in any standard weighing tube, preferably one having a pouring spout on the lip. When mixtures of oils are to be submitted to the column, they are intimately mixed by agitation in the weighing tube before being added to the column. Because of viscosity of the oils, the weighing tube is allowed to drain into the column for about fifteen minutes; the weighing tube is re-weighed, and the weight of oils taken is determined by difference.

Collection of the eluting solvents, evaporation of the solvents, and determination of weight of eluted oil has already been discussed (see Par. 2.3, p. 70). Refractive index has been employed as an index of purity of the eluted oils, comparing the reading with refractive index values of the original starting oils taken at 25°C.

It must be noted that the above method for collecting the eluting solvents in small portions in test tubes was used only to study the separation process in detail to determine those factors which are necessary to obtain accurate, reproducible results. When all of the necessary conditions for obtaining successful separation runs are determined, a simple, concise procedure will be outlined for the ultimate scheme of analysis which will include the collection of only a few large fractions corresponding to different groups of base-oils or different individual compounds. Table XVII, p. 79, shows that separation Run 13 was made collecting only two fractions, the alcohol-water solvent combination and the benzene-ether combination. Use of this type of fraction collecting eliminated errors resulting from handling many small test tubes, with a recovery of 99.3% of the oil sample. Run 16 in the same table was made collecting three alcohol-water solvent combinations in three 100 ml. fractions with the remaining fractions collected in small test tubes. Recovery of the DBAE for this run was 100.2%; this again demonstrates that collection of larger samples will be feasible for the final scheme of analysis. For experimental purposes, however, it is necessary that the small fractions be collected, despite the sacrifice in time and accuracy.

3.3 EXPERIMENTAL RESULTS OF SILICA GEL COLUMN SEPARATIONS

Table XVII, p. 79, summarizes data from all of the silica gel column separation runs. Initial runs were performed with the oil mixture di-(2-ethylhexyl) adipate (DOA) and Silicone DC-550 (ArSil), an aromatic silicone; the remainder of the runs were concerned with separation of the difficultly separated mixture, di-(2-ethylhexyl) sebacate (DOS) and tetra-(2-ethylhexyl)-orthosilicate (TOS). As already expained earlier (see Par. 2.2, p. 52) the reason for selecting this latter mixture was that qualitative paper partition chromatography had shown that with respect to a given solvent combination DOS was the least mobile diester tested, and TOS was the most mobile of the silicate esters and silicone oils, being only slightly less mobile than DOS. Therefore, to effect a complete separation of these two substances would insure the fact that diesters commonly employed in synthetic lubricants could be separated from silicate esters and silicone oils.

There are a large number of variables encountered in a column separation, such as size and shape of column, weight of gel, preparation of the column, solvent combination, volume of solvent combination, etc. Time would not permit complete investigation of each of these parameters, so that it is possible that further improvements in the method can be made. However, under the conditions of the most recent separation runs, it is possible to say that the DOS-TOS mixture, and therefore any diester and silicate ester or silicone oil mixture employed in these studies, can be separated quantitatively within the limits of experimental error. Studies of some of the individual variables in column separations are discussed in the following paragraphs.

3.3.1 Effect of Column Dimensions and Weight of Silica Gel

Three types of column shapes have been investigated, short wide columns (Runs 1-8 and 14-16), long narrow columns (Runs 9 and 10), and an intermediate shape having a short wide top and a narrow lower section but which was about as long as the narrow column (Runs 11-13).

Direct comparison of the effect of column dimensions may be made with reference to Runs 7 and 9 in Table XVII, p. 79. These were made using DOS as the sample oil, holding all other variables constant and varying the column shape. In Run 7 the capacity of the chromatographic tube was 50% greater than the tube in Run 9; therefore the weight of oil and volume of solvent combination in Run 9 were reduced by one third. The long narrow column (Run 9) showed 98.2% of the diester in the alcohol fraction with a total oil recovery of 98.8%, while the short wide column (Run 7) showed 97.6% of the diester in the alcohol with a total recovery of 99.3%. These results indicate no significant

TABLE XVII

QUANTITATIVE SEPARATION OF DIBASIC ACID ESTERS FROM SILICATE ESTERS AND SILICONE OILS ON SILICA GEL COLUMNS

Run No.	Dimensions of Column (mm.)	Wt. Silica Gel (g.)	Pressure (psi)	Type of Packing	Solvent Combination (v/v)	Vol. Soln. Comb. (ml.)	Final Solvent	Volume Final Solvent (ml.)	Total Fractions	Oil or Mixture added	Total Wt. Oils added (g.)	Diester Recovered (%)	Silicone or Silicate Recovered (%)	Total Oil Recovered (%)	n_D^{25} Alcohol Fractions *	n_D^{25} Benzene Fractions *	Remarks
1	27d. x 175	50	2	Vacuum	EtOH:H_2O(12:7)	200	Benzene	100	47	DOA ArSil	1.997	61.7	135.3	98.5	1.4465	1.4805	Solvent contains too much H_2O to move DOA.
2	27d. x 200	60	"	"	EtOH:H_2O(24:11)	250	"	"	65	DOA ArSil	1.954	98.9	95.2	97.0	1.4475	1.4937	Good separation.
3	27d. x 200	"	"	"	EtOH:Ac:H_2O(4:1:2)	300	"	"	68	DOA ArSil	2.001	----	95.9	----	1.4471	1.4930	Lost ester fractions by accident.
4	"	"	"	Dry	EtOH:H_2O(24:11)	250	"	"	55	DOA ArSil	2.060	99.4	47.3	73.4	1.4494	1.4943	Dry column technique mixes the oils.
5	"	"	"	Vacuum	"	"	"	"	64	DOS	1.989	Alcohol 45.7 Benzene 53.1	----	98.8	1.4493	1.4508	Solvent contains too much H_2O to carry DOS.
6	"	"	"	"	"	"	"	"	66	TOS	2.003	----	Alcohol 1.3 Benzene 96.3	97.6	too little to measure.	1.4368	Alcohol fraction is probably impurity from TOS, such as octyl-alcohol.
7	"	75	"	"	EtOH:H_2O(3:1)	"	"	"	60	DOS	2.488	Alcohol 97.6 Benzene 1.7	----	99.3	1.4492	too little to measure	Benzene fraction probably contains impurities from DOS.
8	"	"	"	"	"	"	"	"	53	TOS	2.516	----	Alcohol 3.7 Benzene 79.6	83.3	1.4380	1.4371	Not all TOS eluted from Column.
9	Upper 27d. x 50 Lower 7d. x 1380	50	12	"	"	190	"	"	54	DOS	1.632	Alcohol 98.2 Benzene 0.6	----	98.8	1.4492	too little to measure	Benzene fraction probably contains impurities from DOS.
10	"	"	"	No gel change.	"	190	"	75	51	DOS	1.621	Alcohol 99.2 Benzene 0.9	----	100.1	1.4489	"	"
11	Upper 27d. x 20 Middle 15d. x 400 Lower 6d. x 880	65	14	Fresh column; vacuum	"	250	Benzene Ether	100 50	59	TOS	2.014	----	Alcohol 3.3 Benzene 91.4	94.7	1.4387	1.4369	Alcohol fraction probably contains impurities from TOS.
12	"	60	8	No gel change	EtOH:H_2O(24:9)	275	"	125 50	58	DOS-TOS	4.012	93.3	----	----	1.4489	----	Benzene fraction lost by counter malfunction.
13	"	"	12	"	EtOH:H_2O(3:1)	250	"	100 50	2	DOS-TOS	3.894	70.6	128	99.3	1.4487	1.4401	Pure DOS recovered but separation not complete.
14	27d. x 230	100	4	Fresh column;vacuum	In Order: EtOH:H_2O(24:9) EtOH:H_2O(24:8) EtOH:H_2O(24:7)	100 100 100	"	100 50	72	DOS-TOS	4.019	In Order: 23.4 30.6 33.2 87.2 Total	108.5	97.9	In Order: 1.4489 1.4481 1.4480	1.4393	Improved separation, but more solvent needed to elute all DOS.
15	"	"	"	No gel change	" " "	100 150 125	Ether	100	74	DOS-TOS	4.028	In Order: 24.6 47.3 15.1 87.0 Total	78.2(?)	82.7(?)	In Order: 1.4484 1.4484 1.4481	1.4381	Part of TOS lost by spillage. Run about same as previous.
16	"	"	"	"	"	100 200 125	Benzene Ether	100 75	30	DOS-TOS	4.012	In Order: 22.0 57.6 20.6 100.2 Total	95.2	98.3	In Order: 1.4482 1.4481 1.4474	1.4381	Good separation. Refractive index values are fairly close.

* Refractive Index Values: n_D^{25} DOA = 1.4453; DOS = 1.4489; ArSil = 1.5024; TOS = 1.4363.

difference caused by different column shapes.

Comparison of Runs 8 and 11 using TOS corroborate the above comparison. In Run 8 the alcohol fraction contained 3.7% of the sample, while in Run 11 the alcohol fraction contained 3.3% (part of the TOS was not eluted because of insufficient final solvent in Run 8, but the results on the alcohol fraction are adequate to draw this conclusion). Even though weights of gel and the solvent combination were slightly different, Runs 13 and 14 also show that the separation of DOS and TOS is not influenced to any extent by column shape. One would expect the longer column to give better separations, but the experimental results do not bear out this assumption.

As a result of these runs it was felt that no superiority for one column shape or the other was established; therefore short columns are recommended for subsequent work, since the flow rate through them is higher. Also the pressure required for a short column is considerably lower than that needed for a long column.

These experiments brought out an interesting fact: some of the starting materials for synthetic lubricants are not pure, a situation which at times results in considerable confusion in interpreting results. Those runs in Table XVII, p. 79, in which a single oil is submitted to the column will illustrate this point. DOS as received has a light yellow color. When runs with this oil were completed, the alcohol fraction, containing the diester, yielded about 98% of a nearly water-white oil. The benzene fraction from these runs yielded about 1% of a bright orange-yellow oil. The refractive index of the eluted diester was slightly lower than that of the yellow starting oil. There was not enough of the orange-yellow oil to permit a refractive index reading; but because of its behavior in the column, it is felt that this oil must be a different compound from the diester. The reflection of this situation on separation of DOS and TOS means that DOS will be separated from TOS, but the TOS will be contaminated by the impurity from DOS.

Precisely the same situation exists with TOS; in these runs, about 3% of the starting oil is always eluted in the alcohol fraction. In a previous section (Par. 4.2, p.43) it has been mentioned that TOS is not a pure material, distillation showing that there is probably some 2-ethylhexanol-1 contamination in the TOS. This 2-ethylhexanol-1 is eluted in the alcohol fraction, and contaminates the diester during separation runs. It is therefore necessary to prove the feasibility of the quantitative technique by using

purified oils; however, for practical analysis of synthetic lube-oils which are undoubtedly compounded from technical-grade oils, the errors introduced by these impurities must be considered when determining the accuracy of the analysis.

3.3.2 Determination of Optimum Solvent Combination

Qualitative paper partition chromatography of DBAEs, silicate esters, and silicone oils indicated those solvent combinations which would most likely separate diesters from other base-oil compounds (see Par. 3.0, p. 60). Attempted quantitative separations on acetylcellulose powder columns added further information on solvent combinations for these separations (see Par. 2.4, p. 72). By the time silica gel column separations were started it was felt that an ethanol:water solvent combination would effect clean separations of the two groups of compounds.

Initial runs with DOS-ArSil mixtures confirmed the usefulness of the ethanol:water (24:11, v/v) combination (Run 2, Table XVII, p. 79). However, with DOS it became evident that the solvent combination would have to be modified by increasing the alcohol content (Run 5). Ethanol:water (3:1, v/v) moved DOS through the column effectively (Runs 7, 9, and 10), while holding TOS in the column (Runs 8 and 11). Therefore separations were attempted with this solvent combination and with a combination containing slightly less alcohol (24:9, v/v) (Runs 12 and 13). Run 12 was made at lower pressure and required four days to complete, but due to difficulties with the automatic fraction collector, part of this run was lost. However the alcohol fraction was recovered and showed that the separation was good. The excessive time required for the run eliminated this technique for practical analysis, however, and less polar solvent combinations with more rapid elution rates were sought. Run 13 employed these new conditions, but did not separate the compounds completely.

It was felt that to exceed the concentration of ethanol in the solvent combination much beyond 3:1 would cause excessive movement of the silicate ester; therefore, the "solvent gradient" method was tried for elution of the diester. This method consists in changing the concentration of the solvent combination during the analysis. In this case, the first solvent combination was ethanol:water (24:9, v/v), followed by 24:8 and 24:7. The first solvent moves DOS slightly down the column without moving TOS; the second solvent moves DOS considerably faster, while moving TOS only slightly; and the third solvent moves both oils, which by this time are far apart in the column,

at an increased rate. Results using this technique are given in the table as Runs 14, 15, and 16.

Run 16 shows that with this solvent gradient technique and with increased amounts of solvent combination a good separation of DOS from TOS has been achieved. Refractive index of the ethanol:water (24:7, v/v) fraction drops to 1.4474, indicating a small amount of mixing of the final portions of DOS with the first traces of TOS coming down the column; this however is not serious.

PART II

QUALITATIVE AND QUANTITATIVE DETERMINATION OF ANTIOXIDANTS

1.0 INTRODUCTION

In the course of the previous year's investigation on analysis of antioxidants in synthetic lubricants and greases (141), it was shown that, among the simpler laboratory methods not employing elaborate optical instruments, the paper chromatographic technique was feasible for qualitative separation and identification of antioxidants, and could be used successfully for quantitative determination of antioxidants with an accuracy of approximately 4% by measurement of the spot areas. Although the general feasibility of this method for analysis of amine-type and phenol-type AOs* was established at that time, it was intended to corroborate further these previous results by including new AOs used at the present time as additives in aircraft lube-oils, and by demonstrating the qualitative and quantitative analysis of these AOs in actual lube-oil samples supplied by WADC.

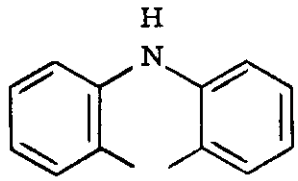
The first problem in using the paper chromatographic technique is selection or development of a solvent combination which is suitable for the large variety of AOs encountered in synthetic lubricants. Such a solvent combination should on the one hand be useful for the separation of different groups of AOs and on the other hand permit the separation of the AOs in a given group, with reasonable R_f-values. The fact that the new AOs, quinizarin (Qz) and p,p'-dioctyldiphenylamine (DODPA), showed R_f-values very close to those of some of the earlier AOs made it necessary to develop new solvent combinations. Because the para positions of DODPA are blocked, this compound could not be detected in the same manner as other amines, i.e., by reaction with diazotized sulfanilic acid; therefore another color reaction had to be found for qualitative detection of this amine in the oil and on the developed paper chromatogram.

2.0 AMINE-TYPE ANTIOXIDANTS

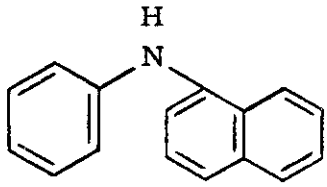
In addition to the amine-type AOs investigated in the first year's program another amine, p,p'-dioctyldiphenylamine, was included. Hence

* AO=Antioxidant

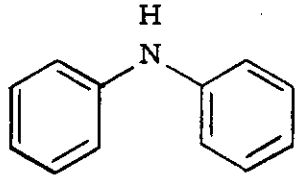
the following primary and secondary aromatic amines have been submitted to paper chromatographic separation:



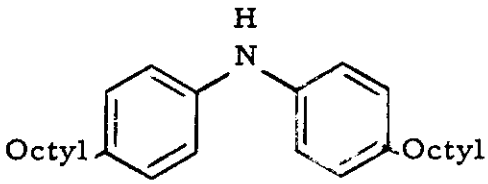
(1) Phenothiazine (PT)



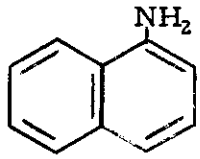
(2) N-Phenyl-alpha-naphthylamine (PANA)



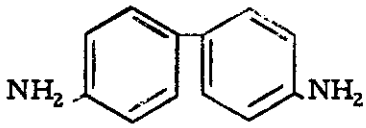
(3) Diphenylamine (DPA)



(4) p,p'-dioctyldiphenyl-amine (DODPA)



(5) Alpha-naphthyl-amine (ANA)



(6) Benzidine (Bz)

2.1 QUALITATIVE IDENTIFICATION

In the course of the investigation it appeared necessary to have, if possible, a general qualitative color reaction for the entire group of amine-type AOs, which could be applied directly to the original oil. Primary identification for the entire group of amine-type AOs could provide short-cuts during the different chromatographic runs. The following general procedures are feasible: extraction of the AO from the base-oil in acidic solution (preferably HCl) and identification of the extracted amine by one of the following tests:

(a) $FeCl_3$ gives a yellow-green compound which fluoresces green in UV-light.

(b) An alcoholic solution of the amine, placed on filter paper as a spot, is colored characteristically when exposed to chlorine gas.

(c) Iodo-chlorplatinate precipitates the amine.

(d) Dropwise addition of con. HNO_3 to a con. HCl solution of the amines gives an indigo blue color with most secondary amines.

(e) Addition of diazotized sulfanilic acid to the neutral or slightly alkaline solution produces characteristic colored diazo dyes with some primary and secondary amines.

(f) o-Toluidine in the presence of bromine gives characteristic greenish or indigo blue colors.

The diazotization reaction, which has been used successfully to date for qualitative identification and spot detection of most amine-type AOs, could not be used with DODPA because the octyl groups in the para positions hinder the coupling reaction with diazo compounds, yielding a very faint colored product or giving no color reaction. It appears therefore that the simplest and most effective qualitative detection reaction is extraction of the oil with a mixture of alcoholic con. HCl and color development by dropwise addition of con. HNO_3.

2.2 PAPER CHROMATOGRAPHIC SEPARATION OF INDIVIDUAL COMPOUNDS

It was intended to find a solvent combination which would permit separation of the different amine-type AOs from the base-oils, as well as allow the eventual separation of different amines among themselves (in case more than one amine-type AO should be present). Paper chromatographic separation of the first group of amine-type AOs was feasible using either normal paper and a solvent combination of the alcohol:water type, or acetylcellulose paper with butyl acetate:pyridine:water mixtures. The inclusion of DODPA, however, made it necessary to investigate other solvent combinations, since on normal paper the R_f-value of DODPA was too high. It therefore appeared that the best separation could be achieved with a chromatogram on acetylcellulose paper with butyl acetate: pyridine:water solvent combination.

2.2.1 Solvent Combinations

To determine the most effective solvent combination a total of eight different combinations have been tried with single compounds and mixtures of amine-type and phenol-type AOs. A total of more than 70 separation runs with these solvent combinations have been carried out during this phase of the program. A summary of most of these runs is given in Table XVIII, pp. 86, 87.

TABLE XVIII

SUMMARY OF RUNS WITH ANTIOXIDANTS ON ACETYLCELLULOSE PAPER

Solvent Combination*	Solvent Ratio (v/v)	Type Run	Temp. (°C)	Time (hrs.)	R_f - VALUES** Amine-Type AOs* PT	PANA	ANA	DPA	DODPA	Bz	Phenol-Type AOs* 24Ph	26Ph	Qz	Components In Mixture	Comments
BuAcPyr Water	6:30:60	Desc.	1.7	3.0	--	--	--	--	--	--	0.21(5)	0.07	--	None	Poor sepn. of mix.
"	"	"	25	2.5	--	--	--	--	--	--	0.18(4)	--	--	None	Quant. run.
"	"	"	25	1.7	--	--	0.20(4)	--	--	--	0.26(6)	--	--	None	Quant. run.
"	"	"	25	2.5	--	--	--	--	--	--	0.26	0.13	--	None	Qual. run.
"	"	"	26	2.0	0.20	0.15	0.19(4)	--	--	0.38	0.27(7)	0.16	--	None	Qual. & Quant. run.
"	"	Asc.	25	3.0	0.26(M)	0.19(M)	--	--	0.01(M)	--	--	--	--	PT-PANA-DODPA	Good arc of Pt.
"	"	"	25	5.5	--	--	0.22(M)	0.21(M)	--	0.39(M)	--	--	--	ANA-DPA-Bz	No sepn. ANA-DPA.
"	"	"	25	6.5	--	0.16	--	--	--	--	0.26(M)	0.14(M)	0.24	24Ph-26Ph	Good sepn phenols.
"	"	"	25	6.5	--	--	--	--	--	--	0.22(M)	--	0.21(M)	24Ph-Qz	No sepn. of M.
"	"	"	25	6.5	0.20(M)	0.15(M)	--	--	--	--	--	--	0.22(M)	PT-PANA-Qz	No sepn. of Pt-Qz.
"	"	"	25	6.5	--	0.14(M)	??(M)	??(M)	--	--	--	--	--	PANA-ANA-DPA	No sepn. of ANA-DPA.
"	"	"	25	6.5	0.23(M)	0.16(M)	--	--	--	0.37(M)	--	--	--	PT-PANA-Bz	Excellent sepn.
"	"	"	25	6.5	??(M)	0.15(M)	??(M)	??(M)	--	0.37(M)	??(M)	??(M)	--	Seven AOs	Only Bz Positive.
"	"	"	25	3.2	--	--	--	--	--	--	--	--	0.27	None	Poor spot.
"	"	"	25	5.2	--	--	--	--	--	--	--	--	??	WADC Oil	Poor spot from oil.
"	"	"	25	5.2	--	--	--	--	--	--	0.25(M)	0.16(M)	--	24Ph-26Ph	Good sepn.
"	"	"	25	5.2	0.20(M)	0.14(M)	--	--	--	--	--	--	--	PT-PANA	Good sepn.
"	"	"	22	2.5	--	--	--	--	--	--	0.28(M)	0.12(M)	0.21(M)	24Ph-26Ph-Qz	No sepn. 24Ph-Qz.
"	6:30:42	Circ.	25	1.0	0.39(M)	0.26(M)	--	--	--	--	--	--	0.30	PT-PANA	Fair sepn. PT-PANA.
"	"	Asc.	24	2.7	--	--	--	--	--	--	0.44(M)	--	0.25(M)	24Ph-Qz	Good sepn. 24Ph-Qz.
"	"	"	24	2.7	--	--	--	--	--	--	0.41(M)	0.26(M)	--	24Ph-26Ph	Good sepn. 24Ph-26Ph.
"	"	"	24	2.7	--	--	--	--	--	--	0.42(M)	0.25(M)	0.34(M)	24Ph-26Ph-Qz	Good sepn.-faint spots.
"	"	"	22	2.2	0.38	--	--	--	0.02	--	0.41(2M)	0.29(2M)	0.34(2M)	24Ph-26Ph-Qz	Poor sepn.
"	"	"	22	2.5	--	0.28	0.31	??	--	0.49	--	--	--	None	Poor diazotization.
"	"	"	25	2.5	0.36	0.26	--	--	0.01(M)	--	--	??	0.33(M)	DODPA-Qz Oil	Very faint spots.
"	"	Desc.	22	3.5	--	--	--	--	--	--	0.41(M)	0.30(M)	--	24Ph-26Ph	Good sepn.
"	"	"	22	3.3	--	--	--	--	--	--	0.42(M)	0.31(M)	0.33(M)	24Ph-26Ph-Qz	26Ph-Qz not sepd.
"	"	"	22	3.7	--	--	--	--	0.01(M)	--	--	--	0.33(M)	DODPA-Qz Oil	Faint spots.
"	"	"	22	3.7	--	--	--	0.32(M)	0.02(M)	--	--	--	--	DPA-DODPA	Very faint spots.
"	"	"	22	3.7	0.36(M)	0.28(M)	--	--	--	--	--	--	--	PT-PANA	Good sepn.
"	"	"	22	3.3	0.35(M)	--	0.26(M)	--	--	0.44(M)	--	--	--	PT-ANA-Bz	Very good sepn.
"	6:30:35	Asc.	23	3.0	--	--	--	--	--	--	0.49(2M)	0.36(2M)	0.40(M)	24Ph-26Ph-Qz	Poor sepns.
"	"	"	24	2.5	--	--	--	--	--	--	0.50(2M)	0.41(2M)	0.42(2M)	24Ph-26Ph-Qz	Poor sepns.
"	6:24:40	Circ.	25	1.0	0.28(M)	0.23(M)	--	--	--	--	--	0.13	0.29	PT-PANA	Poor sepn. PT-PANA.
"	6½:30:42	Asc.	23	2.5	--	--	--	--	--	--	0.43(M)	--	0.37(M)	24Ph-Qz	Faint spots.
"	"	"	23	2.5	--	--	--	--	--	--	0.42(M)	0.21(M)	--	24Ph-26Ph	Fair sepn. phenols.
"	"	"	23	2.5	--	--	--	--	--	--	0.39(M)	0.27(M)	0.35(M)	24Ph-26Ph-Qz	Poor sepn.
"	7:30:55½	"	23	3.0	--	--	--	--	--	--	0.23(M)	--	0.25(M)	24Ph-Qz	No sepn.
"	"	"	23	3.0	--	--	--	--	--	--	0.22(M)	0.09(M)	--	24Ph-26Ph	Good sepn.
"	"	"	23	3.0	--	--	--	--	--	--	0.17(M)	0.05(M)	0.23(M)	24Ph-26Ph-Qz	Poor sepn.
"	8:30:49½	"	23	3.0	--	--	--	--	--	--	0.27(M)	0.12(M)	--	24Ph-26Ph	Fair sepn.
"	"	"	23	3.0	--	--	--	--	--	--	0.24(M)	0.07(M)	0.28(M)	24Ph-26Ph-Qz	No sepn.

TABLE XVIII concluded on following page.

TABLE XVIII - Continued

SUMMARY OF RUNS WITH ANTIOXIDANTS ON ACETYLCELLULOSE PAPER

Solvent Combination*	Solvent Ratio (v/v)	Type Run	Temp. (°C)	Time (hrs)	R_f - VALUES** Amine-Type AOs* PT	PANA	ANA	DPA	DODPA	Bz	Phenol-Type AOs* 24Ph	26Ph	Qz	Components In Mixture	Comments
BuAcPyrWater	6:30:60***	Desc.	24	7.0	0.84	0.80	??	--	--	0.79	--	--	--	None	R_f-values too close.
"	"	Asc.	25	3.0	0.94	0.86	--	--	0.01	--	--	--	--	None	R_f-values too close.
"	"	"	25	3.0	0.91(M)	0.80(M)	--	--	0.01(M)	--	--	--	--	PT-PANA-DODPA	PT-PANA too close.
"	"	"	25	7.0	--	--	0.93	0.93	--	0.90	--	--	??	None	R_f-values too close.
"	"	"	25	7.0	--	--	??(M)	??(M)	--	??(M)	--	--	--	ANA-DPA-Bz	No sepn.
"	"	"	25	7.0	??(M)	0.74(M)	??(M)	--	--	--	--	--	--	PT-PANA-ANA	Only PANA separates.
"	"	"	25	7.0	0.84(M)	0.73(M)	--	--	--	--	--	--	??(M)	PT-PANA-Qz	Good sepn. PT-PANA.
"	"	"	25	7.0	??(M)	0.79(M)	??(M)	??(M)	--	??(M)	--	--	??(M)	Six AOs	Only PANA separates.
AmAcPyrWater	6:31:30	Asc.	5.6	5.5	--	--	--	--	--	--	??(M)	??(M)	??(M)	24Ph-26Ph-Qz	Two solvent fronts.
"	8:31:35	"	25	2.0	0.67(M)	0.45(M)	--	--	--	--	--	--	--	PT-PANA	Good sepn.-poor arcs.
"	"	"	24	2.7	--	--	--	--	--	--	0.56(M)	0.46(M)	0.44(M)	24Ph-26Ph-Qz	Fair sepn.
"	"	"	24	2.7	0.51(M)	0.42(M)	--	--	--	--	--	--	--	PT-PANA	Good sepn.
"	"	"	26	3.2	--	--	0.37(M)	--	--	0.56(M)	--	--	--	ANA-Bz	Good sepn.
"	"	"	26	3.0	0.48(M)	0.40(M)	--	--	--		--	--	--	PT-PANA	Fair sepn.
"	10:31:30	"	25	1.5	0.67(M)	0.57(M)	--	--	--	--	--	--	--	PT-PANA	No sepn.
"	"	"	24	3.0	--	--	--	--	--	--	0.62(M)	--	0.50(M)	24Ph-Qz	Good sepn.
"	"	"	24	4.0	--	--	--	--	--	--	0.64(M)	0.50(M)	--	24Ph-26Ph	Very large spots.
"	"	"	24	4.0	--	--	--	--	--	--	0.63(M)	0.49(M)	0.54(M)	24Ph-26Ph-Qz	Poor sepn.
"	"	Circ.	27	0.7	0.54(M)	??(M)	--	--	--	--	??(M)	0.21	0.43	PT-PANA-24Ph	No sepn.
"	"	"	18	1.7	--	--	--	--	0.00	--	0.24(M)	0.20(M)	0.33(M)	24Ph-26Ph-Qz	No sepn.
"	"	"	0	1.2	--	--	--	--	1.00	--	1.00(M)	1.00(M)	0.75(M)	24Ph-26Ph-Qz	All in solvent front.
EtAcTHFWater	6:35:47	Asc.	24	2.2	--	--	0.18(M)	--	--	0.38(M)	--	--	--	ANA-Bz	Good sepn.
"	"	"	24	2.2	0.28(M)	0.20(M)	--	--	??	--	--	--	--	PT-PANA	Two solvent fronts.
"	"	"	24	2.2	--	--	--	--	--	--	??(M)	??(M)	0.22(M)	24Ph-26Ph-Qz	Two solvent fronts.
"	"	"	26	2.5	0.26(M)	0.19(M)	--	--	--	--	--	--	--	PT-PANA	Fair sepn.
"	"	"	26	3.0	0.10	--	--	--	--	--	--	--	--	None	Faint spot.
"	"	"	26	2.7	--	--	--	--	0.03	--	--	--	--	None	Two solvent fronts.

* Abbreviations:
BuAc AmAc, EtAc = Butyl, Amyl, Ethyl Acetate
Pyr = Pyridine
THF = Tetrahydrofuran
PT = Phenothiazine
PANA = Phenyl-alpha-naphthylamine
ANA = Alpha-naphthylamine
DPA = Diphenylamine
DODPA = Di-octyl-diphenylamine
Bz = Benzidine
24Ph = 2, 4-Dimethyl-6-tertiarybutylphenol
26Ph = 2, 6-Ditertiarybutyl-4-methylphenol
Qz = Quinizarin

** Number in parentheses after the R_f-value is the number of runs used in averaging the R_f-value. Where no number appears, only one run was made. The letter M after the R_f-value indicates a mixture of AOs.; components of the mixture are given in a separate column. The presence of question marks (??) indicates an inconclusive run, in which the spots could not be positively detected or identified.

*** All runs with this solvent combination were performed on normal rather than acetylcellulose paper.

To increase the R_f-value of the different AOs and to achieve sharper separation, different ratios in the solvent system butyl acetate:pyridine: water have been investigated. Other similar systems in which butyl acetate was replaced by amyl acetate or ethyl acetate have also been investigated. In general an increase in the amount of ester or pyridine increases the R_f-value of the compound being chromatographed, but at the same time causes a decrease in sharpness of the separation. An increase in the water content decreases the R_f-value, and the separations and spots become more sharply defined. Hence with the correct solvent combination a separation can still be relatively sharp and yet the R_f-values sufficiently large to move the AOs away from the residual oil spot on the paper.

The following solvent combinations have been found feasible for qualitative separation and quantitative determination of amine-type AOs on acetylcellulose paper:

(1) Butyl Acetate:Pyridine:Water (6:30:60, v/v)

(2) Butyl Acetate:Pyridine:Water (6:30:42, v/v)

(3) Butyl Acetate:Pyridine:Water (6:30:50, v/v)

With this type of solvent combination good separations of PANA-PT-DODPA-Bz were achieved (see Figure 9, p. 89). The individual R_f-values are far enough apart to allow distinct separation of the different spots. Having values between 0.01 and 0.4, the range of R_f-values is not too high and thus the spots are not fuzzy; this in turn permits better quantitative determinations. With solvent combination (1) the following average R_f-values were obtained with different amine-type AOs:

Compound	R_f-values
p, p'-Dioctyldiphenylamine (DODPA)	0.01
N-Phenyl-alpha-naphthylamine (PANA)	0.14
Diphenylamine (DPA)	0.21
Phenothiazine (PT)	0.22
Benzidine (Bz)	0.37

Lowering the water content (thereby increasing the relative amount of lipophilic compounds) in the solvent combination increases the R_f-value somewhat. Thus with solvent combination (2) the following average R_f-values were found: DODPA, 0.02; PANA, 0.27; DPA, 0.32; PT, 0.37; and Bz, 0.47.

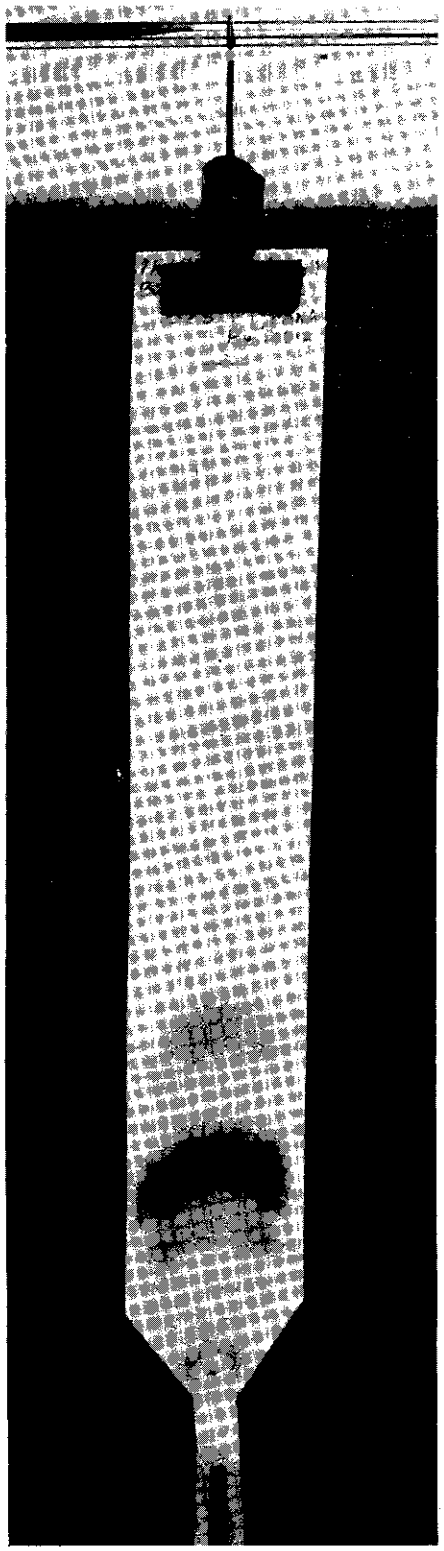


Figure 9. Ascending Qualitative Paper Chromatogram. Separation of Four Amine-Type Antioxidants.

Solvent combinations (1) and (2) are therefore both adequate for separation of the most commonly used amine-type AOs from the base-oils as well as from each other. It should be mentioned that there is a slight difference in the R_f-values of AOs according to whether they are chromatographed as pure compounds, e.g. in benzene solution, or dissolved in a lube-oil. The R_f-value of an AO chromatographed directly from a drop of lube-oil is on the average 0.03 R_f-units lower than the same AO chromatographed in the same concentration from a benzene solution. The reason for this effect is the fact that the base-oils (which are partially soluble in the lipophilic phase of the solvent combination) change to a certain extent the actual ratios in the solvent combination, and thus indirectly affect the R_f-values of the antioxidants. However, since this minor decrease occurs with all AOs present, the relative positions of the different AOs will remain the same.

Figure 9, p. 89, shows an example of a qualitative separation of four amine-type AOs by ascending paper chromatography. The paper strip is cut from acetylcellulose paper, prepared according to the procedure described in APPENDIX A, p.116. The paper strip is cut at an angle near its lower end and terminates in a tongue which is split into two tips, as shown in the figure. These tips are immersed to a depth of about 3 mm. in the developing solvent combination. In contrast to the rapid development when a full-width paper strip is used, the small tips cause the solvent to ascend the paper much more slowly, resulting in sharper separation of the compounds. The sample spots are placed on a starting point (which is located slightly above the junction of the tongue and the oblique cut of the strip) in such a way that the circumference of the spot does not quite touch the edge of the paper. In this way sharper and more distinctive arc-shaped spots can be obtained. After the solvent front has reached the upper part of the paper strip, requiring approximately 3-4 hours, depending on the temperature, the strip is removed from the chamber, the solvent front is marked, the strip is dried, and the spots are developed (see below). The R_f-values are then determined in the usual way.

Using the solvent combination butyl acetate:pyridine:water (6:30:60, v/v) a mixture of 50 gamma (0.05 mg.) each of p,p'-dioctyldiphenylamine, N-phenyl-alpha-naphthylamine, phenothiazine, and benzidine was separated with good results (Figure 9, p. 89). DODPA was barely moved from the starting point with an R_f-value of 0.01, whereas Bz was moved farthest, having an R_f-value of 0.37. PT and PANA are separated sufficiently that they can be identified without difficulty. The latter (PANA) can be identified not only by color reaction, but even more clearly by its fluorescence in UV-light. Similar separations can be achieved with solvent combinations (2) or (3), the latter having been used for a quantitative determination of PT and PANA in lube-oil (see Figure 11, p. 98).

Since the amines which were selected for these experiments are characteristic representatives of the aromatic amine-type AOs, it can be expected that other similar amine-type AOs can be separated by the same or similar solvent combinations and can be characterized by their R_f-values and color reactions.

2.2.2 Detection of the Spot on the Paper

After the chromatogram is dried, several different possibilities exist for detecting spots of the individual components:

(1) On normal paper the most effective color reagent for aryl-type amines is diazotized sulfanilic acid; the diazotization and coupling can be accomplished on the paper strip itself, and bright violet, red, or orange spots are formed. On acetylcellulose paper (which is hydrophobic), however, this reaction does not take place readily, and the diazo colors appear only after repeated spraying or dipping, but can nevertheless be produced. However, unless sufficient time is taken in treating the chromatogram, misinterpretation of the chromatogram can result. The diazotization reaction fails completely with DODPA, because the reactive para positions in this molecule are blocked by octyl groups which hinder the coupling reaction.

(2) A more efficient color reagent for amine-type AOs is phosphomolybdic acid. After dipping in alcoholic phosphomolybdic acid solution and heating for a few minutes to 50°C, most amine-type AOs like PT, PANA, Bz, and even DODPA form various shades of blue on the yellow background. Upon exposing the still damp strip to an NH_3 atmosphere, the yellow background color of unreacted phosphomolybdic acid disappears and the colored spots remain on a white background. PANA however tends to fade quickly by this procedure. A combination of this method preceded by method (1) is sometimes even more effective. In the case of certain AOs, e.g. PT, a combination of the two methods gives a dark purple spot which is much more intense than the colors from either individual method (Figure 11, p. 98).

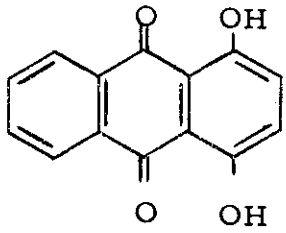
(3) Another color reagent for amine-type AOs is an alcoholic solution of glucose or fructose in mixture with phosphoric acid and water. Spraying with this reagent and heating the paper strip for 1/2 hour in a drying oven at 100°C develops characteristic red to brown spots for the different amine AOs. It was found, however, that the spots actually develop deeper colors when dried only 10-15 minutes at 110°C.,

removed from the oven, and kept in air for several days. DODPA gives only a slight coloration, and therefore this reaction as well as the diazotization reaction are not well suited for identification of this amine. The development of DODPA was achieved with another color reaction which is more effective for this specific compound than those reactions mentioned above.

(4) DODPA and other amine-type AOs like PT and PANA can be detected with active chlorine. The strip is sprayed or immersed in an alcoholic solution of HCl (1:1) and subsequently blotted and exposed to chlorine gas. The Cl_2 gas is developed in a small beaker from either calcium hypochlorite or perchlorate salts and HCl. The presence of DODPA is indicated by the development of reddish-brown spots. PT gives a bright yellow spot, PANA a yellow-orange spot, and diphenylamine a purple-blue spot. This color reaction is sufficiently characteristic to allow definite identification of the para substituted diphenylamine (DODPA) on the chromatogram.

3.0 PHENOL-TYPE ANTIOXIDANTS

In addition to the phenol-type AOs investigated in the first year's program, such as 2,4-dimethyl-6-tertiarybutylphenol (24Ph), and 2,6-ditertiarybutyl-4-methylphenol (26 Ph), a third phenolic type compound was investigated which is used at the present time in synthetic lube-oils: quinizarin, or 1,4-dihydroxyanthraquinone,



Since both amine- and phenol-type AOs can be present in the same lube-oil, it was desirable to have a solvent combination which would allow separation of the phenol-type AOs in approximately the same R_f-range as the amine-type AOs. In the course of the investigation it was found that solvent combinations (1) and (2), described in Paragraph 2.2.1 (page 85), were not only suitable for separation of amines, but also could be applied for chromatography of phenol-type AOs, giving R_f-values from 0.11 to 0.36.

3.1 QUALITATIVE IDENTIFICATION

Since quinizarin (Qz) is usually present in oils in very small quantities (0.02%), to be able to apply paper chromatographic techniques, it is necessary to apply a larger volume of oil than usual to the paper in order to detect the compound. This makes it desirable to detect Qz prior to setting up a chromatographic run; therefore color reaction was sought for detection of Qz in the original oil. Two such possibilities have been developed:

(1) The oil sample (1 ml.) is diluted in acetone (5 ml.) and then shaken vigorously with 5 ml. con. NH_4OH. After separation of the phases, Qz is identified by a deep royal purple color in the ammonia layer.

(2) A second reaction is based on the property of hydroxyanthraquinones to form colored lacquers (chelates) with certain metals like Mg, Ni, Fe, Al, and particularly with certain rare earth and related metal ions such as Ce, Zr, Th, etc. It was found that reaction with thorium ion gives a characteristic pink color which is feasible for detection of quinizarin in the original lube-oil. This reaction can also be used for detection of the chromatographed spot on the paper. For detection of Qz in the original oil, about three drops of the oil are dissolved in approximately 5 ml. of benzene; 5 ml. of a dilute (2%) alcoholic solution of thorium nitrate is added, and the test tube is shaken for a few seconds; after separation of the two layers (centrifuging is advisable if the separation is slow), the aqueous layer in the presence of Qz shows a strong pink coloration.

3.2 PAPER CHROMATOGRAPHIC SEPARATION OF SPECIFIC COMPOUNDS

In order to investigate the feasibility of paper partition chromatography for separation and determination of additional phenol-type AO in the presence of other phenol- or amine-type AOs, development of the chromatograms has been carried out with solvent combinations identical to those which were useful with amine-type AOs.

3.2.1 Solvent Combinations

For separation of phenol-type AOs, the same solvent combination may be used as that used for separation of amine-type AOs. A typical paper chromatographic separation of two phenol-type AOs is shown in the photograph

in Figure 10, p. 95, which illustrates separation of two hindered phenols, 24Ph and 26Ph, with solvent combination butyl acetate:pyridine:water (6:30:60, v/v). With this solvent mixture 24Ph has an R_f-value of 0.22 and 26Ph a value of 0.11. This allows good separation of the two components from mixtures, and the two spots or arcs are sufficiently separated to permit quantitative measurement. Although other solvent combinations could produce higher R_f-values, as for example the combination amyl acetate:pyridine: water (10:31:30, v/v)with R_f-values of 0.50 and 0.60 for the 24Ph and 26Ph phenols respectively (see also Table XVIII, p. 86, 87) the spots become blurred, spread out, and overlap. Thus quantitative determination by the spot area method as well as by the optical density method is practically impossible. Therefore the butyl acetate:pyridine:water combinations were finally selected for the separation.

With the same solvent combination or better with butyl acetate:pyridine: water (6:30:42, v/v) the separation of quinizarin from the two phenols or from amine-type AOs can be accomplished with good results. Such a separation is shown in Figure 10, p. 95, for Qz and DODPA, which are present in WADC synthetic lubricant MLO-8200. After development of the chromatogram Qz has an R_f-value of 0.36, whereas DODPA has moved only a slight distance from the starting point (the DODPA spot does not show up well in the photograph because it was detected at the time of the experiment with phosphomolybdic acid and had faded). The R_f-value of the Qz is high enough to permit its separation from other phenol-type AOs such as 24Ph or 26Ph, possibly present at the same time.

3.2.2 Detection of Compounds on the Paper

It has already been pointed out (141, p. 131) that detection of hindered phenols is complicated by the chemical structure of these compounds. The only color reagent for hindered phenols was found to be phosphomolybdic acid, which in an NH_3 atmosphere gives blue or bluish-green spots with 24Ph or 26Ph. Ammoniacal silver nitrate reacts slightly, but there is the side effect that the paper background turns brown, thus decreasing markedly the contrast between spot and background. Quinizarin on the other hand does not react with the phosphomolybdic reagent.

For the detection of Qz it is sufficient to expose the dried paper strip to an NH_3 atmosphere, the Qz appearing as a pink spot. This color, however, is not stable and fades quickly, but is adequate for the initial location of the Qz spot. In order to achieve a permanent color, the spot is sprayed or dipped

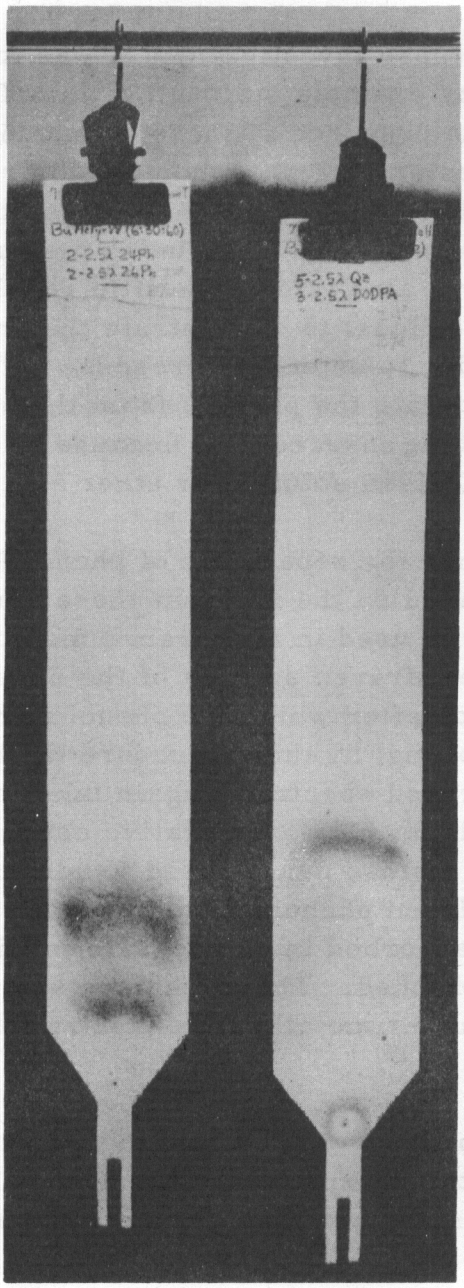


Figure 10. Ascending Qualitative Paper Chromatograms. Separation of Phenol-Type Antioxidants.

with a 2% solution of thorium nitrate, and dried. A bright pink spot appears which shows orange fluorescence in UV-light. When working with mixtures of phenols and Qz, the paper strip is treated with phosphomolybdic acid after the Qz spot is developed in order to detect other phenol-type AOs.

In the course of these investigations it was found that the presence of certain inhibitors, as for example sulfonates, interferes with detection of the hindered phenols. In the presence of these compounds as well as in the presence of certain dibasic acid esters the phosphomolybdic reaction with phenols does not occur. It appears that these compounds hinder the formation of the phosphomolybdate complex under the reducing media of NH_3. The silver nitrate color reaction was also tried with little result. In such cases it is necessary to isolate or at least to concentrate the phenol-type antioxidant from the base-oil in order to detect its presence before the actual chromatogram is run. Attempts to separate the phenols from the base-oils by solution in alkaline media proved to be unsuccessful because of the unexpected insolubility of hindered phenols in Claisen solution or other alkalies.

A practical method for separation of phenol AOs from base-oils prior to chromatography is based on the fact that these compounds are relatively volatile. This property is used in an infrared method of analysis for hindered phenols in lube-oils: the infrared spectra of the oil sample which contains the phenol is established, after which the phenol is removed from the base-oil by heating without boiling; by this procedure the hindered phenols volatilize quantitatively. The infrared spectra is again taken and this spectra is used as background for the qualitative and quantitative estimation of phenol in the oil. The same volatilization method can be used to advantage for any analytical scheme to separate hindered phenols from base-oils. In this case the volatilized phenols are absorbed in an adequate media, e.g. benzene, and subsequently chromatographed. This technique will eliminate interfering materials, and at the same time allows concentration of the AO from lube-oil.

Other phenol-type AOs which might eventually be present in an oil can be detected either with the phosphomolybdic reagent or, if the phenol is not hindered, by one of the more common reagents for phenols, such as $FeCl_3$, silver nitrate, etc.

4.0 QUANTITATIVE DETERMINATION OF ANTIOXIDANTS BY PAPER CHROMATOGRAPHY

The feasibility of paper chromatography for quantitative estimation of antioxidants in synthetic lube-oils was demonstrated in the first year's program (141, p. 135) with quantitative runs of hindered phenols per se and in mixtures with actual lube-oils. To corroborate these results for amine-type AOs, quantitative runs with WADC synthetic lubricants which contain phenothiazine and N-phenyl-alpha-naphthylamine have been carried out. Quantitative exploitation of these chromatograms is accomplished in two ways:

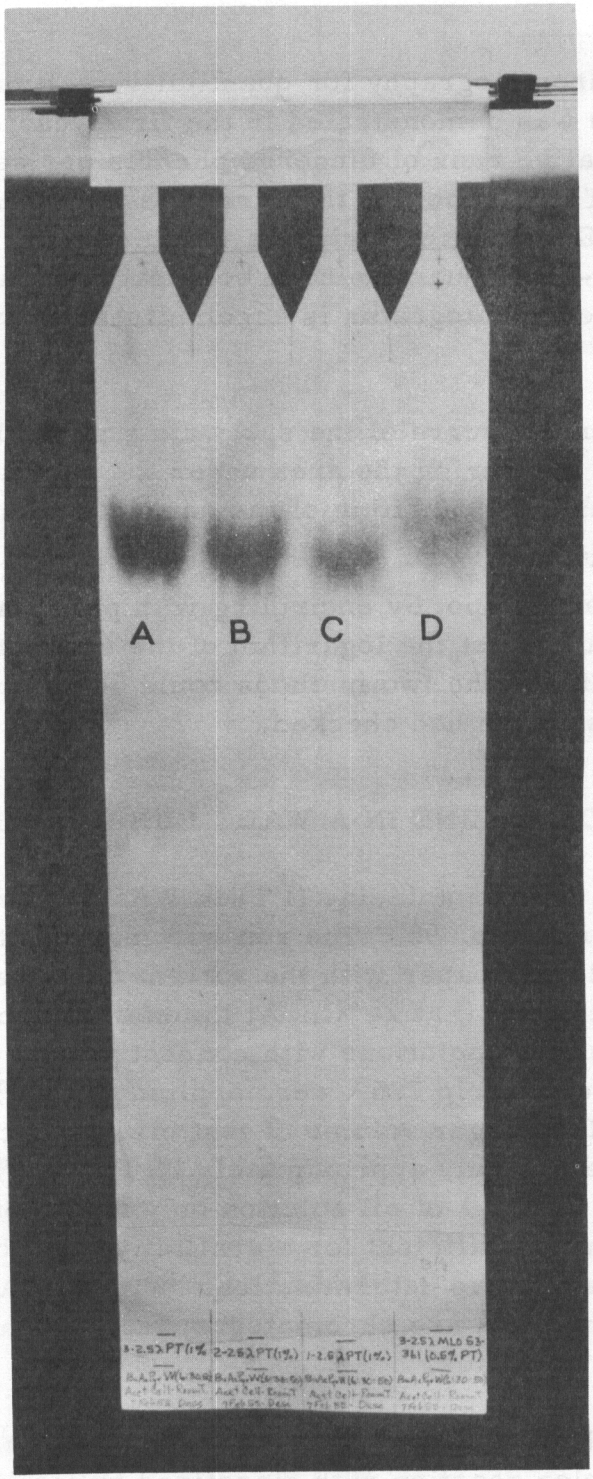
(a) Determining the optical density curve of the spot with a photoelectric densitometer, followed by measuring the area under the density curve, and plotting the area against the logarithm of the concentration of standard solutions (see 141, p. 136).

(b) Visually tracing the area of the spot by encircling with pencil and plotting the measured area against the logarithm of the concentration. In this manner the feasibility of the two methods could be compared and the deviation of the visual method checked.

4.1 DETERMINATION OF PHENOTHIAZINE IN A WADC LUBRICANT

Quantitative determination of phenothiazine (PT) in WADC Lubricant MLO-53-361 is illustrated in Figure 11, p. 98. The run was made by the descending technique on acetylcellulose paper with the solvent combination butyl acetate:pyridine:water (6:30:50, v/v) at 24°C. At the starting points were placed 2.5 λ spots of PT standard solutions with concentrations of 1, 2, and 3% (in benzene). On the fourth strip 7.5 λ were applied of a 50% benzene solution of the test oil. The larger volume of test oil was necessary because the original lube-oil contained only approximately 1% PT (0.5% PT in the 50% benzene solution). In 2.5 λ of oil solution only 12.5 δ of antioxidant was present; this amount is sufficient for a qualitative test but does not give good results in a quantitative determination. With 7.5 λ on the other hand around 37 δ of material are chromatographed, which is determined readily with sufficient accuracy.

After development of the chromatogram (in the course of about 4 hours) PT was detected first by color reaction with diazotized sulfanilic acid, followed by reaction with phosphomolybdic acid, and appeared on the



—Starting Points

Solvent Combination:

Butyl Acetate-Pyridine-Water
(6:30:50, v/v)

Temperature: 24°C.

A = 2.5λ Phenothiazine, 3.00%

B = 2.5λ Phenothiazine, 2.00%

C = 2.5λ Phenothiazine, 1.00%

D = 7.5λ WADC Oil MLO-53-361, 50% in Benzene, R_f = 0.25

Average R_f-Value of Phenothiazine = 0.28

—Solvent Front

(1/2 Actual Size)

Figure 11. Descending Quantitative Paper Chromatogram. Determination of Phenothiazine (PT) Content of WADC Oil By Comparison With Known Solutions.

chromatogram as dark blue-violet spots. After drying, the chromatogram was cut into strips and the optical density of each spot was measured with a photoelectric densitometer (Photovolt Densitometer, Model 525). The measured densities were plotted against the length of the spot, which resulted in the optical density curves shown in Figure 12, p. 100. The areas under the curves in Figure 12 were then measured with a planimeter (in the absence of a planimeter, the areas can be cut out and weighed). These values for the area (or weights) were plotted on a semi-logarithmic paper against the concentration, as shown in Figure 13, p. 100. The values for known PT concentrations are in a straight line, in accordance with theory.

From the area under the optical density curve of PT in the lube-oil, the concentration of PT in the 7.5 lambda sample is read directly from the plot. This area corresponds to 17.4 gamma PT. Conversion to the original oil gives a value of 1.15% PT in the lube-oil, calculated as percent by volume. This value is 0.15% higher than the value of approximately 1% given for the formulation for this oil. However, since several runs of the same oil corroborated this value it seems that the actual content of PT antioxidant in the oil is higher than 1%. This was later corroborated by infrared analysis which gave a value of 1.1% PT in the oil. The deviation from the value of the formulation is probably due to variations occurring in the compounding procedure during manufacture of the oil. Similar synthetic lube-oil mixtures compounded in this Institute have shown good agreement between the formulated and the experimentally determined values.

4.2 DETERMINATION OF N-PHENYL-ALPHA-NAPHTHYLAMINE IN A WADC LUBRICANT

Another quantitative paper chromatographic analysis was carried out with WADC Lubricant MLO-53-5277 which contains N-phenyl-alpha-naphthylamine (PANA). The analysis was carried out on a descending chromatogram with acetylcellulose paper and the solvent combination butyl acetate:pyridine:water (6:30:50, v/v). After 3 1/2 hour's development at 24°C the strips were dried and PANA was detected by repeated diazotization and subsequent treatment with phosphomolybdic acid. Although the spots developed relatively well at the beginning, they faded rapidly. Therefore quantitative evaluation of the chromatogram was carried out in two ways:

(a) Measurement of optical densities and plotting the density curve.

(b) Tracing the spot areas in UV-light, instead of tracing the visible color-detected spot.

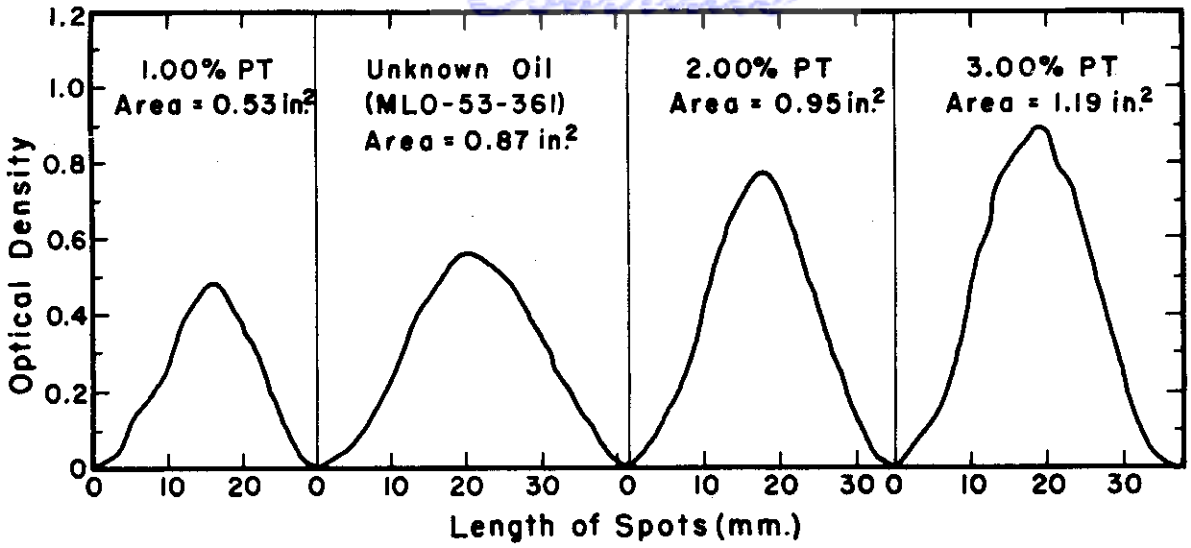


Figure 12. Optical Density Curves For Three Known Concentrations of Phenothiazine (PT) in Benzene and a WADC Oil Containing PT (Diluted 50% in Benzene).

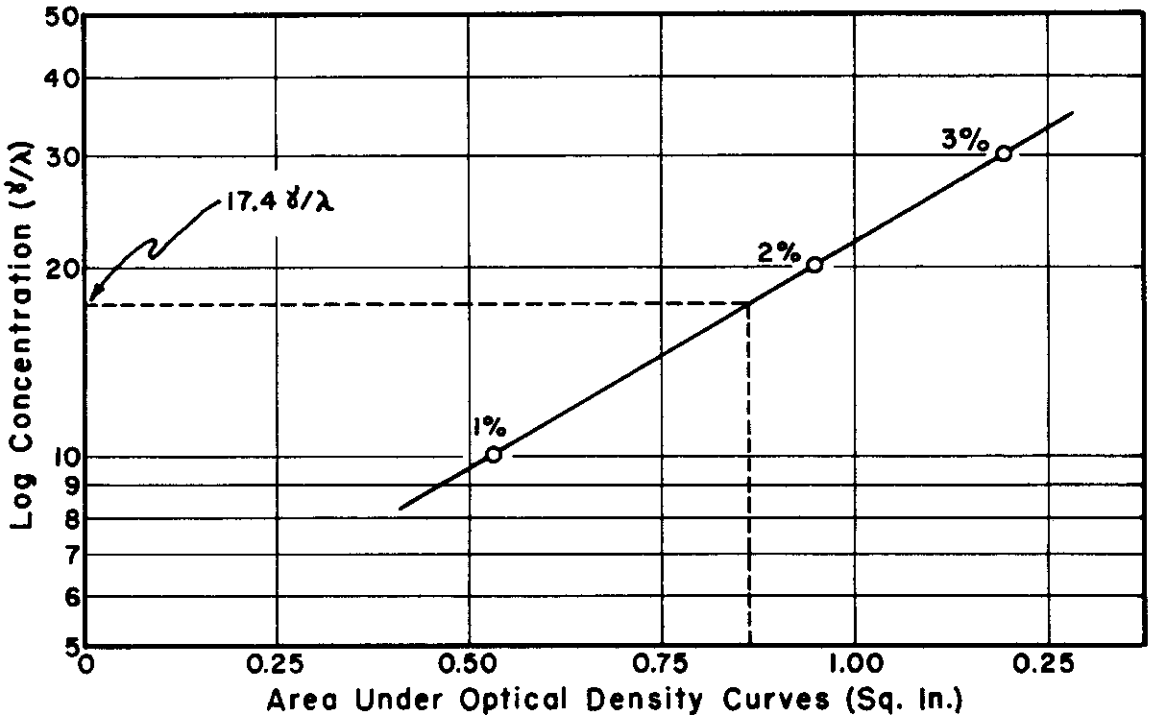


Figure 13. Plot of Three Known Phenothiazine Solutions and a WADC Oil, Showing Determination of Concentration of PT in the Oil.

The latter method can be used to advantage because PANA fluoresces brightly in UV-light, and even though the visible colored spots may fade, the fluorescence remains the same, regardless of the chemical treatment to obtain colored spots. The optical density curves were measured (Figure 14, p. 102), as were the areas under the optical density curves and the areas of the UV-traced spots; these areas were both plotted against the concentrations of the standard solutions. Because of fading of the spots in the visual region, the height of the optical density curves is relatively low, and the areas under the curves are also small.

The two curves, A for the optical density area and B for the visual area, are shown in Figure 15, p. 102. In curve A the points for standard solutions with known concentrations are situated in a straight line in agreement with theory. Since the spots have faded, i.e., their intensities are not the same at the time of measurement as they were shortly after producing the color, one might expect considerable error. As this experiment demonstrates, the degree of fading is apparently proportional to the concentration. This means that even those spots which are continuously fading and which in normal light could not be traced without considerable error can be evaluated with the photodensitometer.

Curve B, Figure 15, is the standard curve for the same substance and concentrations based on measurements of the spots traced in UV-light. In this case deviations of the spots from a straight line may be attributed to human error involved in tracing the spot in the fluorescent chamber. Nevertheless comparison of the concentration of PANA in the unknown oil as measured by the optical density and by the visual method reveals good agreement in the values read from Figure 15, which coincide at exactly 12 gamma/lambda. Conversion of this figure to the concentration of PANA in the original oil (MLO-53-5277) gives a value of 0.8% by volume. This value is 0.2% lower than the value of approximately 1% listed in the WADC formulation. The cause for this deviation may be of the same origin as that discussed in the preceding paragraph for the WADC oil containing PT, since in this case several parallel runs also gave results which were in good agreement with each other.

5.0 CONCLUSIONS

From the investigations it can be concluded that the general feasibility of methods developed in the first year's program was further corroborated by extending the experiments to include new types of AOs used in actual lube-

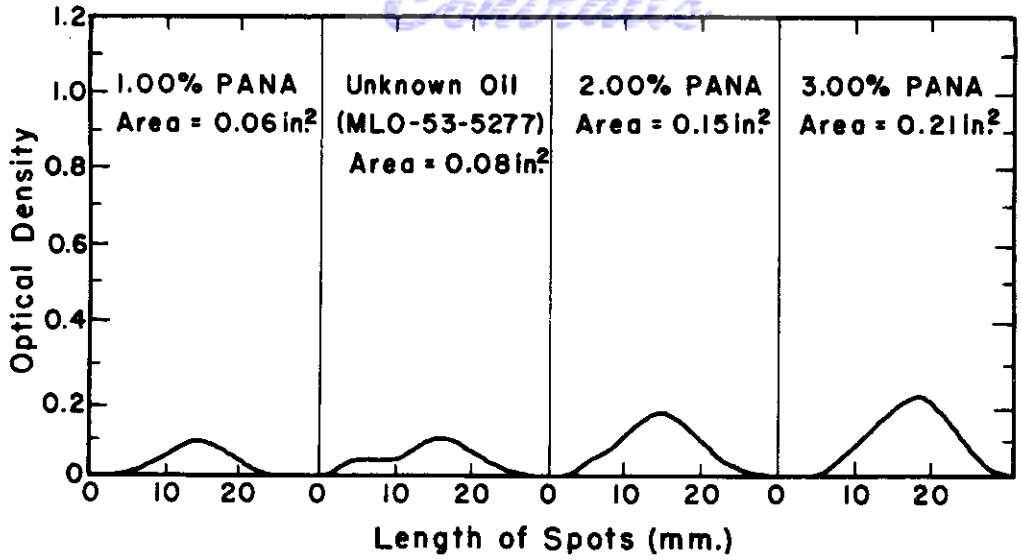


Figure 14. Optical Density Curves For Three Known Concentrations of Phenyl-Alpha-Naphthylamine (PANA) in Benzene, and a WADC Oil Containing PANA (Diluted 50% in n-Hexane).

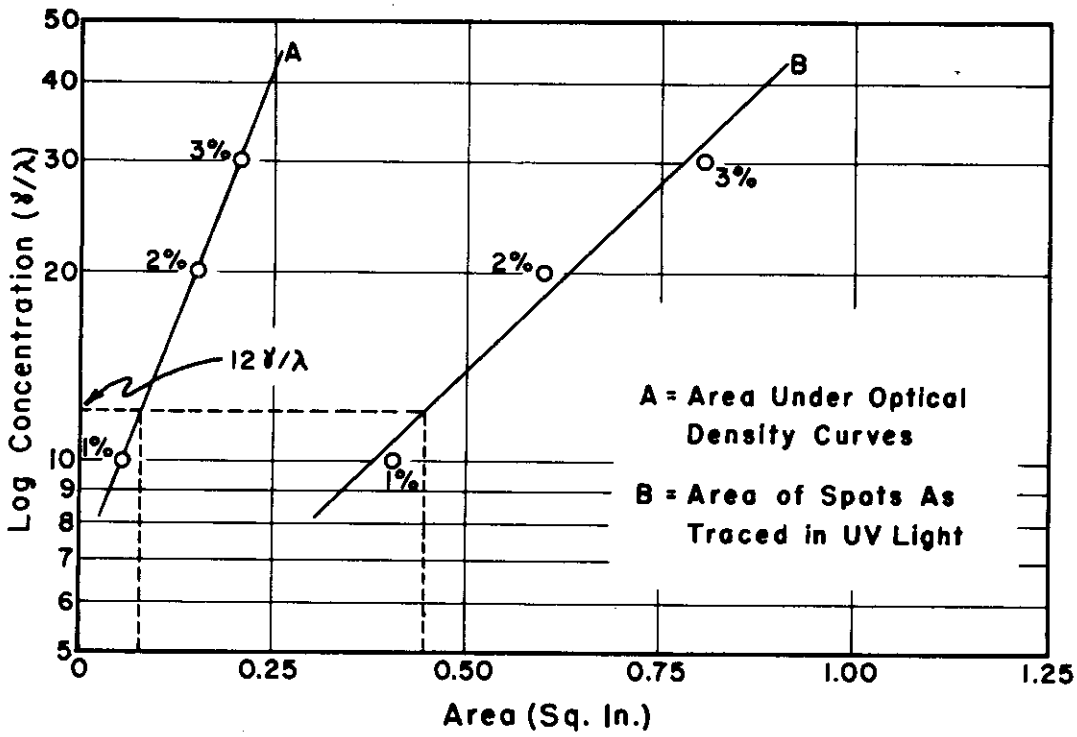


Figure 15. Plot of Three Known Phenyl-Alpha-Naphthylamine Solutions and a WADC Oil, Showing Determination of PANA in the Oil Either By Instrumental or Visual Methods.

oil. Quantitative determination of these AOs by the spot area method or by measurement of optical density has also been rechecked and the feasibility demonstrated.

It remains, however, to evaluate the possible optimal accuracy which can be achieved with these methods, particularly when using the original lube-oil directly in order to avoid extracting certain AOs from the oils prior to chromatographic runs. Irregularities can occur in certain cases which are summarized as follws:

(1) In a paper chromatogram for quantitative determination of AOs, the original oil is applied as a spot and development of the chromatogram is carried out in the usual way:

   (a) The R_f-value of the AO will be approximately 0.03 R_f-units lower than that of the pure substance in benzene or other solution. A possible reason for this deviation has been explained previously.

   (b) The spot will be more diffuse and the area relatively larger than that of spots with the same concentration of AO in benzene solution, although the area under the optical density curve remains the same. The reason for this phenomenon probably lies in the fact that the presence of base-oil components increases lateral diffusion of the AO spot during the chromatographic run. This interference could be compensated by using as solvent a composition similar to that of the base-oil instead of benzene.

(2) In the presence of certain inhibitors such as sulfonates the reaction for detection of hindered phenols with phosphomolybdic acid is suppressed, and will either have to be replaced with another color reaction, or the AOs will have to be separated from the base-oil prior to their chromatography. A possible means for achieving such a separation is based on the volatility of these phenols. The volatilization and subsequent absorption of phenols in a suitable media permits their identification and separation by the paper chromatographic method.

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APPENDIX A

I. PREPARATION OF ACETYLCELLULOSE PAPER FOR REVERSED PHASE CHROMATOGRAPHY

Acetylation of filter paper (strips or sheets) is carried out in a Pyrex glass resin pot of 5" diameter and 12" height with a 4-neck top with standard-taper joints, as illustrated in Figure 15. The top of the container is connected with a reflux condenser, a thermometer, and a dropping funnel. During acetylation, the lower section of the resin pot is immersed in a water thermostat at 70°C for six hours. Inside the resin pot is a removable glass rack on which the filter paper is mounted during acetylation.

The filter paper sheets (Whatman No. 1) are cut into strips of adequate length and width and wrapped around and through the glass rack in such a way as to provide a little space between the strips to obtain uniform acetylation. The rack is placed in the vessel, the cover pressed on tightly, and the lower part of the resin pot immersed in the thermostat. 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 resin pot in the thermostat, the acetylation mixture is added through the dropping funnel in one portion. After six hours' reaction the paper contains about 23% acetylcellulose. This degree of acetylation is sufficient to make the paper lipophilic and water-repellant. When the acetylation is complete, the thermostat is quickly drained and re-filled with cold water to cool the acetylation mixture. After cooling, the acetylation mixture is poured out and replaced with cold MeOH, and the entire unit with the filter paper is left overnight. In the morning the paper is removed from the glass rack, unrolled, washed in running tap water for three hours, and finally rinsed several times in distilled water. The paper is air dried while mounted between clips on a wire stretcher to prevent wrinkling, and is oven dried ten minutes at 110°C.

The paper now is water-repellant, does not show capillary action with water, is wettable with most organic solvents, and the acetyl content is fairly uniform for all parts of the surface. Acetone or any solvent combination which contains excessive amounts of ketones cannot, of course, be applied because of the solubility of acetylcellulose in these solvents. This must be kept in mind also for application of the sample oil, since samples dissolved in acetone fuse into the paper and are very difficult to run from the starting point.

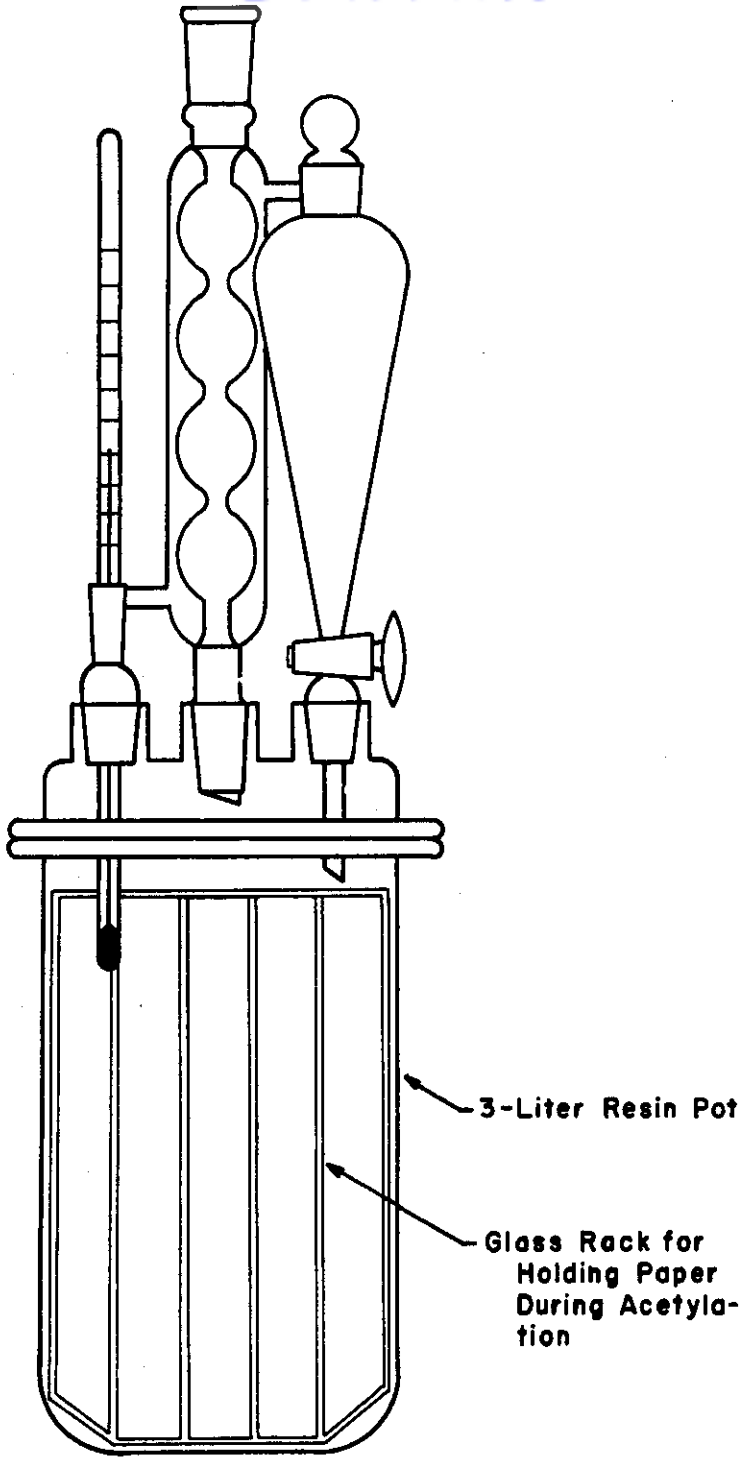

Figure 16. Acetylation Apparatus Used in Preparation of Lipophilic Chromatographic Paper.

The acetyl number of this paper can be determined according to the method of Koevennagel and Konig (124).

II. PREPARATION OF ACETYLCELLULOSE POWDER

Acetylcellulose powder is prepared in the same manner as acetylcellulose paper, with only minor modifications in the procedure. Stirring must be provided to prevent settling and caking of the powder on the bottom of the reaction vessel. Addition of several glass beads was found most useful for breaking up any cake which formed. The acetylation is performed in the 3-liter resin pot without the glass rack, using about 200 grams of Whatman Standard Grade Ashless Powder For Chromatography with at least two liters of the acetylation mixture. Washing is carried out by filtering off the liquid layer, transferring the wet powder to a large Erlenmeyer, and shaking with water. This procedure is repeated a half dozen times, finishing with two distilled water washings. Drying is done in a large diameter evaporating dish at a temperature of 70°C until dry, followed by 10 minutes at 110°C. The powder is then placed in a tightly stoppered bottle.

While not done initially in these laboratories, it is recommended that the dry powder be washed twice with ether before storing to eliminate this step in preparing the individual columns. Filtration and drying are necessary after these ether washes. The acetylation solution may be used to acetylate at least two more batches of powder.