

Armed Services Technical Information Agency

Because of our limited supply, you are requested to return this copy WHEN IT HAS SERVED YOUR PURPOSE so that it may be made available to other requesters. Your cooperation will be appreciated.

AD

42363

NOTICE: WHEN GOVERNMENT OR OTHER DRAWINGS, SPECIFICATIONS OR OTHER DATA ARE USED FOR ANY PURPOSE OTHER THAN IN CONNECTION WITH A DEFINITELY RELATED GOVERNMENT PROCUREMENT OPERATION, THE U. S. GOVERNMENT THEREBY INCURS NO RESPONSIBILITY, NOR ANY OBLIGATION WHATSOEVER; AND THE FACT THAT THE GOVERNMENT MAY HAVE FORMULATED, FURNISHED, OR IN ANY WAY SUPPLIED THE SAID DRAWINGS, SPECIFICATIONS, OR OTHER DATA IS NOT TO BE REGARDED BY INFORMATION OR OTHERWISE AS IN ANY MANNER LICENSING THE HOLDER OR ANY OTHER PERSON OR CORPORATION, OR CONVEYING ANY RIGHTS OR PERMISSION TO MANUFACTURE, USE, OR SELL ANY PATENTED INVENTION THAT MAY IN ANY WAY BE RELATED THERETO.

Reproduced by
DOCUMENT SERVICE CENTER
KNOTT BUILDING, DAYTON, 2, OHIO

UNCLASSIFIED

AD 042 363

T - 871

THE LIBRARY OF CONGRESS
ORDER FOR PHOTODUPLICATION

Address to:
Photoduplication Service
The Library of Congress
Washington 25, D. C.

Date 17 September 1954

Enclosed find \$ for which please duplicate the item listed below.

FOR OFFICE USE - DO NOT WRITE IN THIS SPACE

Signature

Rosena Weiss

Name Technical Information Division
ASTIA Reference Center

Address

☐ Photostat

☒ Microfilm

☐ Photograph

Negative
only

Positive
(Incl. negative)

Please make one NONPERATED microfilm of the following:
Naval Research Lab., Washington, D. C.
SYNTHETIC LUBRICANTS FROM BRANCHED CHAIN DIESTERS, by
Atkins, Baker, Kidder et al, July 45. Exp. @
(Rept. no. P-2576)

Exp. @

Exp. @

Exp. @

Exp. @

Exp. @

Special instructions:

Postal registry fee

Total cost or

Deposit

Balance due

Received by:

Date

Refund

*Declassified per ltr
8-348 file 1118-235/48
written by Sec. Control
officer.*

~~RESTRICTED~~

Navy Department - Office of Research and Inventions

NAVAL RESEARCH LABORATORY
Washington, D.C.

* * *

CHEMISTRY DIVISION - LUBRICATION SECTION

July 1945

SYNTHETIC LUBRICANTS
FROM BRANCHED CHAIN DIESTERS

By D. C. Atkins, H. R. Baker,
Helen Kidder, C. M. Murphy, Jr.,
H. Shull, Paula W. Taylor, and
W. A. Zisman

- Report P-2576 -

RESTRICTED

* * *

Approved by

W. A. Zisman - Head, Lubrication Section

Dr. P. Borgstrom Rear Adm. A. H. Van Keuren USN (ret)
Superintendent, Chem. Division Director, Naval Research Laboratory

Preliminary Pages...a-d
Numbered Pages.....55
Tables.....21
Plates.....7
Distribution List...e

NRL Problems: F-109
F-110

ABSTRACT

This report concerns a basic investigation and development of synthetic diester lubricating oils. A number of new lubricants have been prepared having optimum properties to make them especially suited for military uses. Among these are oils having unusually low evaporation rates and freezing points. These properties have been obtained without any sacrifice of oxidation stability or corrosion resistance.

A variety of synthetic diesters have been investigated and the aliphatic branched chain compounds have been shown to be especially suitable as base stocks for the development of instrument oils and certain special purpose lubricants. Oils of outstanding merit for use over the temperature range -100°F to 250°F have been developed. Addition agents have been found capable of imparting to these oils excellent resistance to rusting, improved viscosity indices and improved oxidation stabilities. The finished oils are adequately stable to hydrolysis, are practically insoluble in water, and have good demulsibility, low foaming tendencies and low freezing points. Data have been obtained on other properties of interest in lubrication such as specific gravity, thermal expansion, and water solubility.

Recommendations have been made for numerous applications of these oils to naval lubrication problems. Specification and availability problems have also been discussed.

RESTRICTED

TABLE OF CONTENTS

ABSTRACT

I. INTRODUCTION	
A. Authorization	1
B. Purpose of Investigation	1
C. Historical Background	2
II. PROPERTIES OF THE PURE DIESTERS AND DEVELOPMENT OF SUITABLE ADDITION AGENTS	
A. Theoretical Considerations	3
B. Preparation of Pure Diesters and some Properties Found During the Preparation	6
C. Viscosity-Temperature Characteristics	7
D. Volatility	13
E. Flammability Characteristics	17
F. Specific Gravity and Thermal Expansion	19
G. Oxidation Characteristics and Antioxidants	21
H. Oil Soluble Rust Inhibitors	26
I. Polymer Thickeners and V.I. Improvers	31
J. Foaming Properties	35
K. Water Solubility, Hydrolytic Stability, and Emulsifiability	37
III. DIESTER COMPOSITIONS FOR LOW TEMPERATURE INSTRUMENT OILS	
A. Non-Polymer-thickened Oils	40
B. Polymer-thickened Oils	47
IV. OTHER APPLICATIONS OF DIESTER COMPOSITIONS TO LUBRICATION	49
V. PRODUCTION AND SPECIFICATION OF DIESTER LUBRICANTS	52
VI. CONCLUSIONS AND RECOMMENDATIONS	53
VII. ACKNOWLEDGMENTS	55

APPENDICES

Comparison of Viscosities of Aliphatic Diesters and Normal Paraffins	<u>Table</u> I
Diesters Studied, their Molecular Weights, and Freezing Points	II
Viscosity-Temperature Characteristics of Diesters	III
Effect of Chain Length and Branching on Viscosity of Aliphatic Diesters	IV
Effect of Branching on Viscosity	V

- c -

RESTRICTED

TABLE OF CONTENTS (continued)

Effect of Position of Ester Groups on Viscosity and Freezing Point	<u>Table</u> VI
Comparison of Boiling Points of Diethyl Esters and those of the Normal Hydrocarbons of the Same Chain Length	VII
Evaporation Characteristics of Diesters at 150°F	VIII
Flammability Characteristics of Diesters	IX
Densities and Specific Gravities of the Diesters	X
Bomb Oxidation Tests of Typical Diesters at 212°F	XI
The Effect of Various Inhibitors on Oxidation Stability of di-(2-ethylhexyl) sebacate	XII
Modified Turbine Rust Test at 140°F	XIII
Results of Static Water Drop Tests	XIV
Spray Cabinet Test at 100°F with Distilled Water	XV
Viscosity-Temperature Characteristics of Some Polymer Thickened Diesters	XVI
Solubility of Water in Diesters at Room Temperatures	XVII
Some Diester Lubricating Oil Compositions	XVIII
Characteristics of some Diester Lubricating Oil Compositions	XIX
Diester Lubricating Oils - Bomb Oxidation Tests at 212°F	XX
Diester Lubricating Oils - Dynamic Oxidation Tests at 212°F	XXI
	<u>Plate</u>
Viscosity-Temperature Chart of Phthalic Acid Esters	1
Viscosity-Temperature Chart of Adipic Acid Esters	2
Viscosity-Temperature Chart of Azelaic Acid Esters	3
Viscosity-Temperature Chart of Sebacic Acid Esters	4
Thickening Effects of Acryloid HF 845 on di-(2-ethylhexyl) sebacate	5
Thickening Effects of Acryloid HF 880 on di-(2-ethylhexyl) sebacate	6
Thickening Effects of Acryloid F 10 on di-(2-ethylhexyl) sebacate	7

INTRODUCTION

A. Authorization

1. This report concerns two investigations carried on concurrently by this Laboratory. This is considered advisable, for although the properties of the desired end products differed, the same chemical approach was employed and the same basic lubricating problems were involved. It is hoped that the resulting combined report will be of increased value. In Project Order No. 40227 of June 22, 1944 the Bureau of Ordnance authorized this Laboratory to conduct research on the development of synthetic oils and greases for ordnance applications. In Project Order No. 101/45 of July 19, 1944 the Bureau of Aeronautics authorized the investigation and development of improved aircraft instrument lubricants and damping fluids.

B. Purpose of Investigation

2. In numerous types of equipment in present day naval use extreme operating conditions are often involved. This led to an increasing demand during the war for lubricants having unusual properties. Designers, manufacturers, and users of fire control equipment, depth bomb mechanisms, fuse mechanisms, aeronautical compasses, gyroscopes, clocks, gun sights, bomb sights, recorders, and aerial photographic equipment have been concerned with various lubrication problems. The most common difficulty has been that of obtaining sufficiently effective and chemically stable lubricants having pour points ranging from -40°F for ordnance equipment to -80°F for aeronautical equipment. The problem has been made more difficult by the need for non-volatile fluids having viscosities at 100°F of not over 10 to 15 centistokes and having the smallest possible temperature coefficient of viscosity. The best obtainable rust inhibition, and hydrolytic and oxidation stabilities are required to care for service use and for eventual long time storage conditions. Because of the high cost of the equipment involved and the relatively small volume of lubricant needed per unit, the cost of the lubricant is clearly a relatively minor matter. However, early commercial availability and manufacturing control such that different production batches would have the same performance characteristics are essential. Other properties desired are non-toxicity, resistance to mold growth, and compatibility with petroleum lubricants to care for accidental contamination so likely to occur under wartime service conditions.

3. The required combination of properties: low viscosity at -40°F , low freezing point, and low rate of evaporation made it very difficult to produce the required lubricants from petroleum

oil fractions. Although suitable hydrocarbons could be synthesized and might conceivably be prepared from petroleum by the adoption of unusual fractionation procedures, either the synthesis or the careful selection and control of base stocks and the special equipment and specially trained personnel involved would make the product as expensive as non-hydrocarbon synthetics. Furthermore, it would be a time-consuming and unwelcome task for any petroleum manufacturer to produce such fluids since the volume required, although large as compared with pre-war standards of instrument oil production, would still appear small or insignificant to the producers possessing the necessary trained personnel and special equipment. It was therefore considered advisable to develop a homologous group of synthetic organic chemicals for the naval lubricating applications involved.

C. Historical Background

4. Esters of dicarboxylic acids have been widely used in industry in the past twenty years for plasticizers and vacuum pump oils. The use of diesters as plasticizers is the earliest large scale application known to this Laboratory. The dimethyl, diethyl, dibutyl, dioctyl, diphenyl, and dibenzyl phthalates and sebacates have been among the commonly used plasticizers. Dibutyl phthalate was investigated and recommended for use as a vacuum pump oil by Hickman and Sanford (1,2). Later a variety of other diesters of phthalic acid were studied and applied by Hickman (3). In present high vacuum distillation practice, use is made of the dibutyl, diamyl, and dioctyl esters of either phthalic or sebacic acid, the dioctyl esters presumably being the 2-ethylhexyl esters.

5. Although monoesters have been used for a long time as lubricants or for lubricant additives, the use of diesters for such purposes is relatively new. In connection with developmental work on polymer thickened hydraulic oils, the Petroleum Refining Laboratory of the Pennsylvania State College tested a number of undisclosed esters and diesters and reported finding that a commercial grade of di-(2-ethylhexyl) sebacate was an effective antitack additive for use in the low flash point petroleum hydraulic oils being studied (4). That laboratory also reported that the same diester was a useful base fluid for preparing viscous polymer thickened, damping fluids of high viscosity indices. A group of commercially available esters were described with respect to their viscosity temperature and melting point characteristics, but no further information was given as to the chemical nature or purity of the compounds used.

6. Although the diesters of Paragraph 4 were commercially available, due to the uncertainty as to their purity and the

necessity for reliable data on their physical and chemical characteristics; it was decided to synthesize and purify all of the diesters studied in this investigation. Such a program would permit a study of the relation of structure to the properties of interest in lubrication and would permit developing the best possible low temperature lubricants. It was planned that later in the research program, after performance standards were set up by the development of lubricants made from the pure compounds, lubricant compositions could be prepared safely from less carefully purified diesters.

II. PROPERTIES OF THE PURE DIESTERS AND DEVELOPMENT OF SUITABLE ADDITION AGENTS

A. Theoretical Considerations

7. An important advantage of diesters as compared to monoesters is that compounds of relatively high molecular weight can be prepared without resorting to the use of either alcohols or acids of high molecular weight. In addition, more variety in the possible molecular configurations is possible due to the availability in such compounds of two reactive linkages. By the full use of a variety of commercially available branched chain aliphatic alcohols, a diverse group of diesters can be prepared. As in the development of vacuum pump oils the desired low vapor pressure can be assured by preparing compounds of sufficiently high molecular weight, this factor being limited by the molecular weights of the available alcohols and dicarboxylic acids. Thus dioctyl phthalate or dioctyl sebacate would have lower vapor pressures than diethyl phthalate or diethyl sebacate. Likewise, esters of sebacic or azelaic acids, which have ten and nine carbon atoms respectively, are preferable to esters of an acid such as succinic which has only four carbon atoms per molecule.

8. For application to lubrication, consideration must be given to obtaining the proper viscosity and freezing point characteristics. To keep the viscosities of the fluids low at -40°F , it is essential that the branched chains be as short as possible consistent with the need for obtaining low freezing points. This can be done readily by using branched aliphatic alcohols reacted with straight chain dicarboxylic acids, by using branched chain monocarboxylic acids and straight chain dihydric alcohols such as decamethylene glycol, or by using branched aliphatic dicarboxylic acids reacted with straight chain alcohols. At present the relatively lower cost and availability of the diesters made from dicarboxylic acids reacted with branched chain alcohols makes their use preferable. Presumably this has been the decision of others in developing vacuum pump oils and plasticizers. The required low freezing points can be obtained by two methods. The first method is to cause branching of the molecule to give hindrance to the regular

alignment and closest packing of the major molecular chains. The second method is to apply the well known rule of alternation of the melting points of organic compounds of a homologous series and of the lower melting points of straight chain compounds having an odd number of carbon atoms per molecule. Thus, much lower melting point esters of dicarboxylic acids should be made from azelaic acid which has nine carbon atoms than from either sebacic acid or suberic acid having ten and eight carbon atoms per molecule respectively. Of course, the presence of the ester group itself is advantageous in causing the diester compound to have a lower freezing point than the analogous hydrocarbon compound.

9. The hydrolytic stability of a diester should be capable of being increased by the addition of one or more minor hydrocarbon chains branching from the major ester chain in such a way that each branch is close enough to an ester group to create hindrance or blocking to the close approach of water or acid molecules. Hence, the branching of the major chain of the diester should occur on the beta carbon atom of the alcohol or of the acid. If the blocking effect is increased too much, however, there will be an added difficulty in obtaining good yields in the esterification reaction. Hence, long hydrocarbon chains branching from the beta or nearby carbon atoms are undesirable.

10. The viscosity-temperature characteristics of the pure diesters can be related to the characteristics of analogous hydrocarbon compounds. Also differences in the viscosity-temperature characteristics of the various diesters can be related to differences in their molecular structure. The esters of dibasic straight-chain acids would be expected to have viscosity-temperature characteristics similar to those of the analogous paraffin hydrocarbons. It has been shown that the normal paraffin hydrocarbons have the most favorable viscosity-temperature characteristics of the hydrocarbons. Various generalizations on the effect of chain length, branching, cyclic groups, unsaturation, and functional substituents for hydrocarbons have been made by several investigators (5,6,7,8,9).

11. A very limited amount of information is available in the literature on the viscosity-temperature characteristics of the higher molecular weight paraffin hydrocarbons. Much of the published information is of limited value as the purity of the compounds studied is unknown. Likewise, only the lower molecular weight esters of the dibasic aliphatic acids have been investigated as regards their viscosity-temperature characteristics. A comparison of the kinematic viscosities of the diethyl esters of aliphatic dibasic acids and of the normal paraffin hydrocarbons of the same chain length is presented in Table I. The chain

lengths of the diesters were considered to be the number of atoms in the longest chain; thus, one oxygen atom from each ester group is included in the calculated chain length.

12. The kinematic viscosities of the diesters were calculated from the absolute viscosity and density data of Dunstan, Hilditch, and Thole (10). The viscosities of the normal hydrocarbons except tridecane and pentadecane were obtained by interpolating the viscosities given by Evans (11) from their curves on an ASTM viscosity-temperature chart. The viscosities of tri- and pentadecane were calculated from values of absolute viscosity and density given by Doss (12). The viscosity of pentadecane is inconsistent with the other data.

13. Table I reveals that these diesters are more viscous than the analogous paraffins of the same chain length but tend to approach them in viscosity at higher chain lengths. The diesters being more viscous than paraffins of the same chain length will not require as long a molecule to give the desired viscosity. This is advantageous from the synthetic point of view as the difficulties of synthesis increase with the size of the molecule. Also the smaller diester molecule will have a lower freezing point than the analogous paraffin due to both its shorter chain length and the effect of the two ester groups.

14. Thorpe and Rodger (13) in their studies on viscosity pointed out that "It seems futile to expect that any definite stoichiometric relations should become evident by comparing observations taken at the same temperature". Many other investigators have reached this same conclusion. Better correlations have been found when comparing properties at the melting and boiling points and all other equivalent points. These results are of considerable theoretical significance, but it is difficult to translate them into useful data. It is simpler to determine the viscosities over the temperature working range. However, certain generalizations have been worked out which are useful in predicting the viscosity and the viscosity-temperature characteristics of liquids from their structural configurations.

(a) Increasing the chain length increases the viscosity and improves the viscosity-temperature characteristics as evidenced by high value of V.I. and low value of the slope.

(b) The addition of side chains increases the viscosity and impairs the viscosity-temperature characteristics. The amount is dependent upon the number and extent of the branches.

(c) The position of the branched chain exerts a variable influence on the viscosity.

(d) The addition of cyclic groups causes larger increases in viscosity and greater increase of viscosity-temperature coefficient than aliphatic chains.

(e) Increasing the ratio of the cross section of the molecule to its length increases the viscosity-temperature coefficient.

15. These generalizations were used to outline a program for the synthesis of a group of diesters to be prepared by other members of the Lubrication Section from available dibasic acids and branched chain alcohols. In order to obtain the smallest viscosity-temperature slope (or the maximum V.I.) an entirely aliphatic diester was preferred. In order to obtain fluids which were of as low viscosity as possible consistent with the need for low evaporation rates at room temperature, branched chain diesters were preferred having branches with no more than several carbon atoms.

B. The Preparation of Pure Diesters and Some Properties Found During the Preparation

16. The above conclusions coupled with considerations of the availability of starting materials and of the need for a group of fluids having a range of viscosities resulted in a definite program for the synthesis and development of a number of diester lubricants. The group studied and reported here includes esters of sebacic, azelaic, and adipic acids. Some esters of phthalic acid were included for comparison. The alcohols used were confined to the branched-chain saturated aliphatic alcohols at present commercially available in volume i.e., 1-ethylpropyl, 2-ethylbutyl, isoamyl, undecyl, tetradecyl, and heptadecyl alcohols, the last three being the branched-chain aliphatic alcohols manufactured by the Carbide and Carbon Chemicals Corp. A discussion of the synthesis, purification, and chemical identification of the resulting diesters will be found in another report of this Laboratory (14).

17. The physical and chemical properties of each pure diester were subsequently examined and special emphasis was placed on properties of interest in lubrication. Chemical additive agents were developed for use as antioxidants, rust inhibitors, and V.I. improvers. The data obtained, the lubricants developed, and the conclusions pertaining to them are presented in this report.

18. In Table II are listed the diesters synthesized and purified by this Laboratory for this and related investigations. The theoretical molecular weights and the observed freezing points

were obtained from NRL Report P-2573 (14) and are listed here for convenience of reference. The compounds are grouped by the acids used and usually within each such group by increasing molecular weight. It was found that the freezing points were depressed by the presence of impurities especially of traces of the alcohols used in the synthesis. Also, due to the branched structure of these organic compounds, the liquids readily supercooled to give much lower apparent freezing points than the true values. It was therefore necessary to chill each liquid until solid and then slowly warm it in order to measure the melting point correctly. The pour points as defined in the specifications for petroleum oils were considered too unreliable to be of any value in discussing diesters.

19. Focussing attention first on the pure diesters those having freezing points below -75°F are: the 1-ethylpropyl diesters of adipic, azelaic and sebacic acids, the 2-ethylhexyl diesters of adipic and azelaic acids, and the 2-ethylbutoxy diester of adipic acid. Those having freezing points below -40°F but not below -75°F are the 2-ethylhexyl diesters of phthalic and sebacic acids, the 3-methylbutyl diester of adipic acid, the 2-ethylbutyl diester of azelaic acid, and the branched undecyl, tetradecyl and heptadecyl diesters of adipic, azelaic, and sebacic acids. If mixtures of these pure diesters are used, many extremely low freezing point mixtures can be made, while any of the above mixed with the ethyl or butyl diesters of phthalic acid, the 2-ethylbutyl diesters of adipic acid, or the 2-methylbutyl diester of azelaic acid may also be useful for numerous moderately low temperature uses. Two component mixtures of particular interest in connection with the development of instrument oils suitable for extremely low temperatures are those of the 2-ethylhexyl diesters of adipic, azelaic and sebacic acids. In NRL Report P-2543 (14) it was reported that mixtures of the azelate and sebacate containing over 20 per cent by weight azelate and mixtures of the adipate and sebacate containing over 35 per cent by weight adipate had freezing points below -75°F . Of course, all mixtures of the adipate with the azelate would have freezing points below -90°F .

C. Viscosity-Temperature Characteristics

20. The kinematic viscosity-temperature characteristics of the diesters were determined over the temperature range of interest. The viscosities were determined in calibrated Cannon-Fenske modified Ostwald type viscometers according to the ASTM Method D445-42T. ASTM kinematic viscosity thermometers calibrated by the National Bureau of Standards were used to measure the temperatures at 77° , 100° , 130° and 210°F . The baths were thermostatically controlled to $\pm 0.03^{\circ}\text{F}$.

21. For the low temperature determinations a well-insulated constant temperature bath with double windows was used. Temperature control was maintained by balancing a low wattage immersion heater against the cooling effect resulting from the sublimation of the dry ice contained in a compartment surrounding the liquid bath. "Methyl cellosolve" was used as the bath liquid. The temperature was measured by the E.M.F. from a 6-junction copper-cupron thermopile (calibrated at the freezing points of water and mercury and the sublimation point of solid carbon dioxide) in conjunction with a type B Rubicon potentiometer and a sensitive external galvanometer. The E.M.F. from the thermopile was 120 to 140 microvolts per degree F.

22. The Cannon-Fenske modified Ostwald viscometers were calibrated at 100°F. At all other temperatures the usual correction factor was applied to compensate for changes in the dimensions of the viscometer and in the volume of the liquid. These factors have been determined over the range 60° to 210°F, and the values for the lower temperatures were obtained by extrapolating the curve through the known points to the desired temperature. The variations of the viscosity with temperature of each diester are given in Table III, and the data plotted on extended ASTM viscosity temperature charts D341-43 are shown on Plates 1 to 4 inclusive.

23. Of the several methods of rating lubricants according to their viscosity-temperature characteristics the most common are the viscosity-temperature slope or the "ASTM Slope" and the "Viscosity Index", usually abbreviated to V.I. The ASTM slope is the tangent of the angle made by the viscosity-temperature curve on the ASTM chart and is measured linearly. This method is advantageous in that the slope may be determined for any portion of the liquidus range of the fluid desired. The lower the value of the slope the less is the change in viscosity with temperature. The slope value is quite useful in comparing fluids having approximately the same viscosity at a given reference point.

24. The kinematic viscosity index or V.I. was determined by ASTM method D567-41. The V.I. is the figure calculated from the kinematic viscosities at 100° according to the following equation:

$$V.I. = \frac{L-U}{L-H} \times 100$$

"U" is the viscosity of the oil in question at 100°F. "L" and "H" are the 100°F viscosities of hypothetical oils having the same viscosity at 210°F as the oil under consideration. Hypothetical oil "L" has a V.I. of 0 and oil "H" a V.I. of 100. For oils having viscosities below 4.20 centistokes at 210°F the values of "H" and "L" may be calculated by the following equations:

$$H = 1.4825x + 0.91375x^2$$

$$L = 1.655x + 1.2625x^2$$

where x is the kinematic viscosity at 210°F. Tables of the "H" and "L" values are included in the ASTM procedure. The "H" and "L" values were originally based on the viscosity-temperature characteristics of contrasting types of petroleum lubricating oils. A V.I. of 100 is considered good for petroleum oils not containing polymer thickeners and is about as high a rating as can be obtained by present industrial refining methods. As the reference temperatures are 100° and 210°F this method gives no information as to the low temperature characteristics of the oil in question.

25. A third equation very commonly used to predict the viscosity-temperature characteristics is that of Andrade (15):

$$\text{Equation (A)} \quad \eta = Ae^{B/T}$$

where η = viscosity in absolute units (poises), T = absolute temperature, and A and B are constants. This equation holds with a fair degree of accuracy for a large variety of liquids. Many variations of this equation have been proposed in hopes of improving the linear relationship, frequently by the inclusion of a third constant in the equation which makes it more difficult to use. If the constant B is multiplied by R or K, the gas or Boltzman constant respectively, the dimensions of the product are that of energy. Thus, $B = I/R$ where I = increment of energy of activation of viscosity; therefore:

$$\text{Equation (B)} \quad \eta = Ae^{I/RT}$$

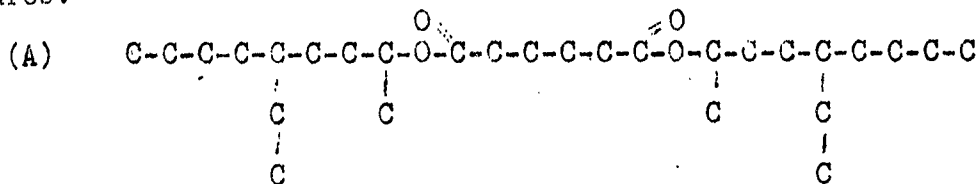
26. Evans (16) found equation (A) to fit the data on the simpler hydrocarbons with a fair degree of accuracy but this equation gave curves instead of straight lines for the higher hydrocarbons. He concluded that the ASTM equation fitted the hydrocarbons with a greater degree of accuracy than any of the nine equations investigated. Nissan, Clark and Nash (17) investigated the viscosity-temperature characteristics of a number of liquids including normal paraffins, isoparaffins, olefins, alkyl halides, alcohols, aldehydes, ethers, esters, acids and others and found that I in equation (B) was not a constant even when temperatures of equivalent states were used instead of the absolute temperature of the determinations. Thus I or the constant B in Andrade's equation is not constant but varies with the temperature. The degree of association of the liquid probably influences the variation of B more than any other factor, but B varies even for unassociated liquids, notably the paraffins.

27. In Table III the data are arranged in families of diesters according to the dibasic acid involved. The graphs of the viscosity vs. temperature on the ASTM chart of Plates 1 to 4 are nearly all straight lines. As previously mentioned the ASTM equation is an empirical one, and there is no known theoretical reason why the viscosity-temperature curves of the diesters should be straight lines on this chart. It is known that polar compounds whose degree of association varies with temperature give curved graphs on the ASTM chart. This suggests that the association of these diesters does not vary much with temperature. Whatever the theoretical basis, the ASTM slope is an excellent means of characterizing the entire viscosity-temperature curve of diesters. The slope and, for comparison, the V.I. of each compound are given in Table III.

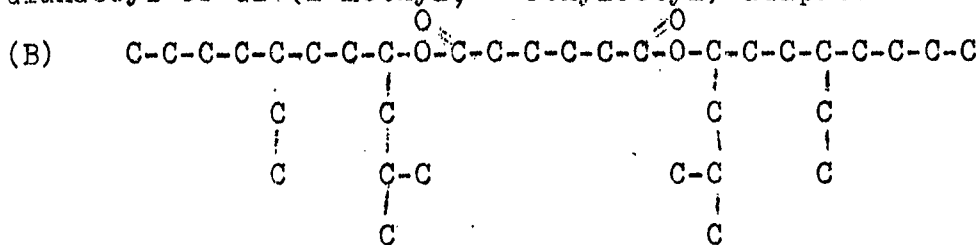
28. Using 100°F as a reference temperature an examination of the data in Table III shows that the diesters of orthophthalic acid, U-shaped molecules with the cyclic group as the base of the U, are more viscous than the diesters of the aliphatic dibasic acids. Also the viscosity-temperature relationships of the phthalate esters are less favorable as evidenced by V.I.'s and slopes, than those of the aliphatic dibasic acid esters of comparable molecular weight. The phthalate esters have much higher cross section length ratios than do the corresponding aliphatic dibasic acid esters. Methyl phthalyl ethyl glycolate is more viscous than the corresponding ethyl ester which is unexpected. As these esters are commercial preparations their purity is doubtful.

29. The effect of increasing chain length of the acid on the viscosity is made more apparent by rearranging some of the data of Table III to form Table IV. In these examples the increase in chain length is attained by increasing the chain length of the straight chain dibasic acid; thus the branching and ester groups occur at identical positions from the ends of the chain for each example cited. Therefore, Table IV shows that the viscosity is increased by increasing the chain length. Increasing the chain length also improves the viscosity-temperature slope if the amount and extent of the branching remains constant. A comparison of the data on the di-(3-methylbutyl) and di-(1,3-dimethylbutyl) adipates and sebacates shows that increasing the number of branch chains increases the viscosity but impairs the viscosity-temperature characteristics. These results are in full agreement with the theoretical conclusions of Section A relative to the relation of diester structure to viscosity and viscosity-temperature slope.

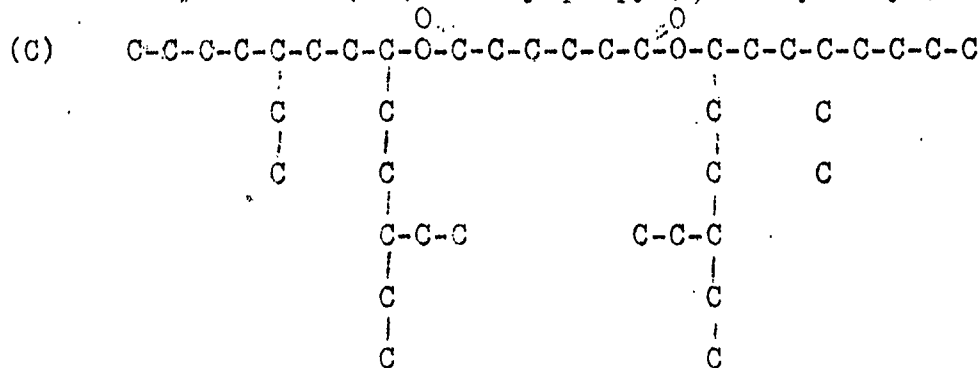
30. The un-, tetra-, and heptadecyl diesters of adipic acid exemplify the effect of increasing the extent of branching on viscosity. Graphically these esters have the following structures:



diundecyl or di-(1-methyl, 4-ethyloctyl) adipate



ditetradecyl or di-(1-(2-methylpropyl),4-ethyloctyl) adipate

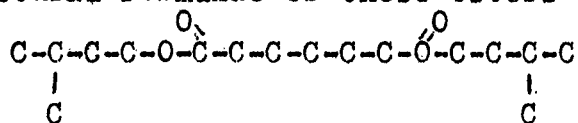


diheptadecyl or di-(1-(3-ethylamyl),4-ethyloctyl) adipate.

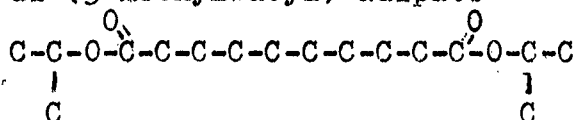
From the above description of the molecular structures involved, it is seen that these diesters all contain an ethyl group in the 4 position and that the difference in branching is due to the increases in length and branching of the side chain at the 1 position.

31. The viscosities, slopes and V.I.'s are compared in Table V. The increases in viscosity due to increasing the size of the branched chain are apparent. The di-heptadecyl adipate does not conform to the theory that the viscosity-temperature characteristics are impaired by increasing the branching. These esters were synthesized at this Laboratory (14) from commercial alcohols of unknown purity and being so viscous were difficult to purify by distillation and adsorption.

32. A comparison of the viscosities of diesters of two different dibasic acids, whose over-all structural configurations are identical except for the differences in the positions of the ester groups, leads to some interesting conclusions. The structural formulae of these esters are:



di-(3-methylbutyl) adipate



di-(1-methylethyl) sebacate.

Both diesters have a major chain having a length of 16 atoms and have a methyl side chain at the 2 position. The results are arranged in Table VI for comparison. From Table VI it is seen that the position of the ester may be varied without causing appreciable changes in viscosity or viscosity-temperature characteristics if the structural skeleton remains the same. The freezing point is, however, greatly influenced by the relative positions of the groups being much lower for the di-3-methylbutyl adipate. It is unfortunate that this is the only example available for comparison.

33. An examination of the viscosity vs. temperature graphs of the diesters; Plates I to IV inclusive, reveals that in general a straight line is obtained on the ASTM Chart. However the graphs of diesters of alcohols containing an ether-oxygen linkage curved upward in the low temperature region. It was also noticed that the graphs of other diesters curved upward when their viscosities were determined below their freezing points, i.e. when they were supercooled liquids and in a metastable state. The observed curvature in this region may be attributed to increased association. Several of the commercial diesters of phthalic acid also have curved graphs. It is believed that the curvature is in many cases due to the presence of impurities. In the course of this investigation it was found that as the purity of a diester was improved the viscosity vs. temperature graph tended to approach a straight line. It is concluded that the viscometric properties of aliphatic diester series approach, at high molecular weights, those of the analogous hydrocarbons. The most desirable diesters for maximum V.I. and low freezing points are those having a long principal chain with two or more short side chains such as methyl or ethyl (and possibly propyl) groups.

D. Volatility

34. The evaporation of low viscosity instrument oils and polymer thickened hydraulic oils has been the source of considerable trouble to the Navy. The evaporation of the volatile, less viscous fraction of petroleum oils used in such lubricants has in many instances left residual oils with considerably increased viscosities and pour points. Increasing the viscosity increases the torque and thus reduces the sensitivity of many instruments for low temperature operation. In extreme cases of evaporation so little lubricant remained that the mechanism was not adequately lubricated. In other applications the evaporation and recondensation of the lubricant on optical parts of the instrument was sufficiently great to obscure the vision, thus rendering the instrument useless.

35. As many naval instruments and indicator and control systems contain delicate complicated mechanisms and often many inaccessible parts, their relubrication is a major overhaul operation requiring the services of an expert. Therefore, it is essential that the time intervals between relubrication periods be increased as much as possible. One of the requisites of a suitable lubricant is a low evaporation rate.

36. Petroleum oils are fractions or cuts containing a variety of hydrocarbons of different volatilities and viscosities. The evaporation of the more volatile constituents changes the physical properties of the lubricant. Thus it was reasoned that a lubricant made from a base fluid consisting of one or two pure organic compounds each having a sufficiently low volatility would ideally satisfy this requirement.

37. The boiling points of the diethyl esters of the dicarboxylic acids (18) (oxalic through sebacic, with the exception of azelaic) as compared to those of the analogous hydrocarbons, (12) i.e., normal paraffin hydrocarbons of the same chain length, are given in Table VII.

38. From Table VII it is evident that the lower members of the homologous series of the diethyl esters of aliphatic dicarboxylic acids have considerably higher boiling points, and therefore lower evaporation rates, than the same chain length unbranched hydrocarbons. On going up this homologous series the hydrocarbon portion of the molecule increases while the diester portion remains constant. Therefore, the influence of the latter on the boiling point will be less noticeable as the molecular weight increases.

39. It is well known that the physical properties of the normal alkyl hydrocarbons differ from those of their branched chain isomers. General rules have been given on the effect of branching on the boiling point. Briefly they are as follows:

(a) The boiling point of the branched chain hydrocarbon will be lower than that of the normal hydrocarbon isomer.

(b) The addition of a side chain to a normal paraffin hydrocarbon will increase the boiling point.

(c) The increase in boiling point by the addition of side chains will vary according to the amount and extent of the branching and to a lesser extent, it will be influenced by the position of the side chain.

40. From the above considerations it is evident that the diesters of the normal alcohols will be less volatile than those of their branched chain isomers. However, there are other properties desired in an instrument lubricant; in particular, the freezing or pour-point of the oil must be considered, as temperatures of -80°F are reported to be encountered in certain aeronautical applications. As the diesters of the normal alcohols not only have higher boiling points than their branched chain isomers, but also higher freezing points, some compromise must be made to obtain a fluid with sufficiently low freezing point and a satisfactory degree of non-volatility.

41. The rate and the amount of evaporation of the diesters were determined by the following empirical test procedure. The change in weight with time of a standard sample in a standard container under controlled conditions of heating and circulation of air was determined. Crystallizing dishes 45 mm. inside diameter and 35 mm. deep containing a 10g. sample of the diester were maintained at a temperature of $150^{\circ}\text{F} \pm 0.5^{\circ}\text{F}$ in a convection type drying oven. The liquid surface exposed was 16 sq. cm. The samples were cooled and weighed at intervals of 24 hours until 168 hours of exposure elapsed. At the end of the evaporation test the viscosity of the non-volatile fraction was determined and the change in viscosity calculated. The neutralization number was also determined on the sample before and after the test using the procedure described in Federal Specification VV-L-791b Method 510.31 (B). None of these diesters changed in neutralization number.

42. The results of the evaporation tests on the diesters are shown in Table VIII. The diesters are arranged in families (according to the dibasic acid) in the ascending order of chain length. Branch chain diesters having the same chain length

are arranged in order of increasing molecular weight. Di-substituted diesters precede monosubstituted ones of the same molecular weight. The phthalic acid diesters are arranged in the order of increasing molecular weight, and no attempt was made to estimate the chain length of the molecules as they are "U-shaped" and have a ring as the base of the "U". These are also commercial products whose purification has been described (14).

43. Of this group only diethyl phthalate lost more than one per cent by weight during the evaporation test. Increasing the ester groups from ethyl to butyl reduced the evaporation loss from 7.3 to 0.6 weight per cent. The di-(2-ethylhexyl) phthalate showed no loss in weight during the evaporation test. The evaporation-time curves for these phthalate diesters are approximately straight lines indicating the evaporation of a one component system rather than one containing a small amount of a volatile impurity. The negligible change in viscosity after evaporation, which is within experimental error, is further confirmation of this fact.

44. The phthalyl glycolates, which are triesters, also showed decreasing evaporation rates with increasing molecular weights. They are less volatile than diesters of o-phthalic acid which would be expected because of the addition of the third ester group. The considerable increase in viscosity after the evaporation test is greater than would be expected from the evaporation loss. The evaporation-time curves show a high initial rate which flattens out after the first 24 hours, indicating a volatile component. It was impossible to determine the neutralization number of these samples as the end point faded badly. This is evidence of hydrolysis.

45. The diesters of adipic acid investigated ranged in chain length from 12 to 28 atoms and included fluids having a boiling point of 124°C at 10mm. pressure to those requiring "molecular distillation" under high vacuum. The (1-methylethyl) diester with a chain length of 12 lost 46 weight per cent during the evaporation test, while the (1-ethylpropyl) diester lost only 2.1 per cent, and the viscosity change was within experimental error. All other adipic acid diesters except (1, 3-dimethylbutyl) and diundecyl or (1-methyl- 4-ethyloctyl) had evaporation weight losses of less than 1/2 per cent. The former sample decreased in neutralization number during the evaporation test. This could be explained as due to the evaporation of the monoester. However, there was a negligible change in viscosity. The undecyl diester had a high initial change in viscosity. The undecyl diester had a high initial evaporation loss indicating a volatile contaminant. The per cent viscosity change and neutralization number increase were

4.2 and 0.05 respectively which confirms presence of a volatile component.

46. The di(2-ethylbutoxy)ethyl adipate, though having a low evaporation loss, showed increases in neutralization number and viscosity indicative of oxidation instability. The molecularly distilled diesters had high neutralization numbers, indicating that they contained some acidic impurities. There was insufficient material available for evaporation tests on the ditetradecyl and di-(2-(2-butoxyethoxy)ethyl) adipates.

47. The diesters of azelaic acid investigated ranged in chain length from 17 to 25 atoms and in boiling points from 192°C at 5 to 6 mm. to 235°C at 2.5 mm. All had evaporation losses of 1/2 per cent by weight or less except the (2-butoxyethyl) diester. This sample had a high neutralization number which increased during the evaporation test. The viscosity increase was 2.9 per cent at 100°F. The other diesters had negligible increases in neutralization numbers and viscosities except the (2-methylbutyl) diester which increased 1.3 per cent in viscosity, indicating the presence of a volatile impurity or some reaction during the test.

48. The diesters of sebacic acid investigated ranged in chain length from 16 to 28 atoms and included fluids having a boiling point of 175°C at 13 mm. pressure to one that had to be molecularly distilled under a high vacuum. Only the (1-methylethyl) diester (chain length 16 atoms) had an evaporation loss greater than 1/2 per cent. These diesters all had low neutralization numbers except the di(2-ethylbutoxy)ethyl sebacate whose neutralization number of 0.30 decreased to 0.20 after the evaporation test. This sample also increased 1.7 per cent in viscosity (100°F) due to evaporation.

49. It is evident that numerous diesters of the aliphatic dicarboxylic acids can be prepared having low evaporation losses. The evaporation rate can be reduced by increasing the chain length and/or molecular weight. Due to the pour points or freezing points required, the diesters must contain branched chains for the applications under consideration. Because of the difficulties encountered in preparing all the diesters in sufficiently high degree of purity, it is not yet possible to predict accurately the minimum chain length required to get a predetermined evaporation loss. However, from the results given here it is estimated that diesters having a chain length of 18 atoms or more will have evaporation losses under the test conditions of approximately 0.3 per cent by weight or less depending upon the amount and extent of branching. The evaporation losses of these diesters are much less than those of petroleum oils of the same viscosity. Numerous comparative data on this and related points are presented in another report of this Laboratory (ref. 19).

E. Flammability Characteristics

50. Information relative to the flammabilities of the diester oils is necessary to determine to what extent precautions should be taken for their storage and use. No one test has been found that is capable of characterizing the flammability of an oil under all the conditions to which it may be exposed. Therefore, several tests have been used to evaluate this property.

51. The flash point is frequently used as a measure of the tendency of an oil to ignite when exposed to an open flame or spark. However, for high flash point oils this test is more nearly a measure of their volatility or vapor pressure, as the temperatures required for ignition are not attained without an external source of heat. The Cleveland Open Cup flash and fire points (ASTM Method D92-33) of several typical diesters are given in Table IX. The results show that the least viscous diester di-(1-ethylpropyl) azelate with a viscosity of 6.66 cs at 100°F, had a flash point of 370°F, and a fire point of 395°F. The most viscous diester tested, di-(2-ethylhexyl) sebacate with a viscosity of 12.6 cs at 100°F, had a flash point of 450°F, and a fire point of 500°F. The diesters of intermediate viscosities had flash and fire points between these extremes. The flash and fire points of pure diesters, stripped of volatile impurities, are related to their boiling points or vapor pressures as a comparison with Table VIII indicates.

52. The additives used to inhibit oxidation and prevent rusting had only a slight effect on the flash and fire points of the diesters. The addition of 0.1 per cent of the antioxidant 4-tert-butyl-2-phenylphenol and of 0.25 per cent of the rust inhibitor zinc di(phenylstearate) to the oil di-(2-ethylhexyl) adipate increased the flash and fire points from 380 to 400°F, and from 430 to 440°F, respectively. As the flash point is very sensitive to the presence of small amounts of volatile flammable impurities the heating procedure used to hasten the solution of the additives may account in part for the increase in the flash point observed. The fire point is not so sensitive to the presence of such impurities. The spread observed in the values reported is within experimental error. The addition of the rust inhibitor calcium di(phenylstearate) in concentrations up to 3 per cent by weight to di-(2-ethylhexyl) sebacate containing 0.2 per cent 4-tert-butyl-2-phenylphenol had no effect on the flash and fire points beyond that which may be attributed to experimental error.

53. The spontaneous ignition temperature is the temperature to which the oil must be heated before it will ignite spontaneously. To obtain reproducible results in the laboratory the test procedure must be rigidly controlled as the ignition temperature is affected by numerous variables. The apparatus used was that of Sortman, Beatty and Heron (20) and the procedure has been described in detail in previous reports of this Laboratory (21, 22). The ignition cup was of stainless steel and electrically heated. A 10 milligram drop was used with an air flow of 125 cc./min.

54. The spontaneous ignition temperatures of some diesters, all of which had ethyl side chains, are reported in Table IX. The results show that the di-(1-ethylpropyl) azelate had the highest ignition temperature, 842°F., and di-(2-ethylhexyl) adipate the lowest, 743°F. The (2-ethylhexyl) diesters of azelaic and sebacic acids were somewhat higher being 756°F. & 765°F. respectively. Data included in reference (22) indicate that the spontaneous ignition temperatures of esters decrease as the chain length increases. Also, it is known that the spontaneous ignition temperatures of the normal paraffins decrease as the chain length increases. The deviations from this generalization observed in the ignition temperatures of the 2-ethylhexyl esters is believed to be due to impurities and to some extent, experimental errors.

55. The addition of up to 3 per cent of calcium di-(phenylstearate) to di-(2-ethylhexyl) sebacate containing 0.2 per cent of 4-tert-butyl-2-phenylphenol had little effect on the spontaneous ignition temperature. The addition of the acryloid polymer thickener HF-880 to di-(1-ethylpropyl) sebacate reduced the spontaneous ignition temperature slightly. Since this polymer was received as a toluene solution it is possible that a small amount of toluene could have remained after the stripping operation employed. But, any remaining toluene which has an ignition temperature of 1165°F. would not be expected to lower the ignition temperature. Therefore the lowering of the ignition temperature is attributed to the acryloid polymer. This effect is not unexpected as it has been previously observed that the ignition temperatures decrease with increasing chain lengths.

56. The "spray inflammability" or the ability of a spray or mist of oil to propagate a flame was determined in the apparatus developed at this Laboratory and described in earlier reports (21, 22). The oil was sprayed from an artist's air brush in a mixture of oxygen and nitrogen gases at the rate of 10 ml. of oil to 10 liters of gas per minute. The per cent of oxygen by volume required to propagate the flame at a speed exceeding 350 cm/min. in such a spray was used as the criterion of flammability.

57. The results of the spray inflammability tests (Table IX) reveal that 16 to 23 per cent of oxygen is required to propagate the flame in a spray of the diester oils. This is a higher concentration of oxygen than the 12 per cent required by light mineral oils such as used in the preparation of petroleum base hydraulic oils. However, as air contains approximately 21 per cent oxygen by volume such a spray would propagate a flame in air. Hence a spray in air of any of these diester oils would present a serious fire hazard.

58. An incendiary firing test was made on di-(2-ethylhexyl) sebacate (22) and that fluid was found to be as flammable as petroleum oils of the same viscosity grade. This is in agreement with the prediction made from the result of the spray inflammability test.

59. The diesters though flammable were much less susceptible to ignition from a spark or open flame than were petroleum oils of similar viscosities as evidenced by their higher flash and fire points. The additives used to stabilize oxidation and prevent rusting had at most only a slight effect on the flash and fire points of the diesters. The spontaneous ignition temperatures were all above 700°F. The ignition temperature decreased as the chain lengths of the diesters increased, this also being typical of hydrocarbons. Though data are limited, the ignition temperatures of the diesters were somewhat higher than those of hydrocarbons of similar structures. It is possible that lower or higher ignition temperatures could have been obtained if another type apparatus or different test conditions had been used. The catalytic effect of different surfaces may also affect the temperature of ignition greatly. The "spray inflammability" test revealed that 16 to 23 per cent of oxygen was required to propagate a flame in a mist or spray of the diesters. As air contains 21 per cent of oxygen by volume such a spray of the diesters would be flammable. Incendiary firing experiments revealed that di-(2-ethylhexyl) sebacate, the only diester tested, was flammable under such conditions. Additional flammability data on the other diesters prepared for this report will be obtained when sufficient quantities of the pure diesters are available.

F. Specific Gravity and Thermal Expansion

60. The densities of the diesters were determined at 25°C. (77°F.), as referred to water at 4°C., in a 5 ml. pycnometer. The pycnometer was calibrated with water at this temperature using the corrections in Standard Density and Volumetric Tables, Circular of the Bureau of Standards, No. 19. The results are given in Table X.

61. As would be expected the diesters of phthalic acid were the heaviest of those investigated since they contain an aromatic ring as well as two ester groups. Increasing the aliphatic portion of the molecule reduces the density, as evidenced by the densities of 1.114, 1.043, and 0.981 respectively for the diethyl, dibutyl and di-(2-ethylhexyl) esters of phthalic acid. The phthalyl glycolates with three ester groups have a greater density than the alkyl phthalates.

62. The esters of the dibasic aliphatic acids are less dense than those of phthalic acid. These compounds also decrease in density as the hydrocarbon portion of the molecule is increased. Branching of the hydrocarbon chain will cause a variation of density. As the hydrocarbon chain is increased the diesters would be expected to approach the densities of the analogous hydrocarbons. Some of the density results reported are inconsistent with the above reasoning, e.g. the di-(2-ethylbutyl) adipate has a greater density than any of the other adipic acid esters except di-(1-methylethyl) ester. These few inconsistencies probably are due to impurities not yet removed by the method of purification employed.

63. The diesters of the aliphatic dibasic acids are more dense than petroleum oils of the same viscosities. Unlike petroleum oils the densities of the diesters investigated decrease with increasing chain length or viscosity. The reason for this has been discussed above.

64. The specific gravities of four of the esters, di-(1-ethylpropyl) azelate and the di-(2-ethylhexyl) esters of adipic, azelaic and sebacic acids were determined over the temperature range - 40° to 210°F. A Westphal balance was used and the observed apparent specific gravities at temperatures other than 60°F. were corrected for changes in the volume of the glass plummet. The specific gravity - temperature curves were straight lines over this temperature range, but their slopes differed slightly. The changes in specific gravity per degree F. were 422, 413, 397 and 394 $\times 10^{-6}$ respectively for di-(1-ethylpropyl) azelate and the di-(2-ethylhexyl) esters of adipic, azelaic and sebacic acids. Therefore, the smaller the hydrocarbon portion of the diester molecule the greater the change in specific gravity with temperature.

65. The specific volume, or volume per unit mass, of each of the above four diesters was calculated from the specific gravity and the specific volume-temperature curves were plotted. These curves were practically linear over the range - 40° to 100°F. The deviations from linearity became more pronounced above 100°F. From these the coefficients of thermal expansions

obtained (- 40° to 100°F.) were 486, 471, 464 and 464 X 10⁻⁶ and from 100° to 210°F. were 518, 509, 491 and 491 X 10⁻⁶ respectively for di-1-(ethylpropyl) azelate and the di-(2-ethylhexyl) esters of adipic, azelaic and sebacic acids. The coefficients of thermal expansions of these esters are somewhat higher than those of petroleum oils of the same specific gravity grade, for, according to the Abridged Volume Correction Table for Petroleum Oils, Supplement to National Bureau of Standards Circular C410, Group I Petroleum Oils (specific gravities of 0.850 to 0.996) have coefficients of expansion of 400 X 10⁻⁶ per °F.

66. The specific gravities (60/60°F.) of the diesters were calculated from the densities at 25/40°C. by converting to specific gravities at 77/60°F. and using 0.0004 as change in specific gravity per °F. This was the value determined on the four esters mentioned above. The specific gravities of the diesters are also given in Table X.

G. Oxidation Characteristics and Antioxidants

67. Information as to the oxidation stability of a new additive compound or lubricating fluid is generally necessary before its range of usefulness can be appraised. Under service conditions the fluid should not oxidize to form quantities of precipitates, sludges, or gums capable of clogging oil lines or interfering with the lubrication process or other functions of the oil. Also it should not separate into non-miscible liquids. It is obviously important that the acidic oxidation products be held to a minimum and that these products should not be corrosive to the metals in the system. Also it is desirable that the viscosity and the viscosity-temperature characteristics of the oil after oxidation should not differ greatly from that of the original fluid.

68. There is a dearth of information in the literature as to the oxidation characteristics of esters, particularly under conditions approximating service applications for instrument oils. From bond energy determinations (23) it would be predicted that the ester linkages are more thermally stable than the C-C bond. Therefore, the oxidation stability test should not be confused by the oxidation of cracked products due to the pyrolytic instability of the ester groups. Spontaneous ignition temperature measurements (see Section E) reveal that the esters and diesters ignite at higher temperatures than aliphatic hydrocarbons of the same chain length. Thus in an uncatalyzed reaction the esters would be expected to be somewhat more stable than the analogous hydrocarbons and to follow the same general rules governing the oxidation of the alkanes.

69. G. Egloff (24) has enumerated the generalizations relating molecular structure to the thermal oxidation of alkanes. These are summarized below:

(a) As the length of the normal hydrocarbon chain increases, the oxidation stability decreases.

(b) Branching and condensation of the molecule increases the oxidation stability.

(c) An increase in temperature usually results in a shorter induction period and a more rapid rate of oxidation.

(d) An increase in pressure may influence the oxidation in several ways: (i) It increases frequency of molecular collisions with subsequent increase in reaction rate. (ii) It deactivates chain carriers. (iii) It alters the electrostatic field giving rise to induced or increased polarity. (iv) The direction of the reaction is that leading to a decrease in volume of the system. (v) Foreign gases, solids, or intermediate reaction products may inhibit, accelerate or have no effect on the oxidation reaction. (vi) An excess of oxygen may cause a decrease in the amount of oxidation.

70. If the oxidation characteristics of the aliphatic diesters follow the generalizations worked out for the alkanes, then the shorter diester molecules would be expected to be more oxidation stable than the longer chain ones. Branching, particularly if it tended to form more condensed molecules, should increase the stability. The effect of varying the position of the ester groups on the oxidation stability of diester molecules having the same structural configurations is not known. It seems reasonable to assume that the stability would decrease if the length of any hydrocarbon chain in the molecule greatly exceeded the others.

71. A static type test using Norma Hoffman bombs was used to evaluate the oxidation characteristics of the diesters. The oil sample (25 grams) was contained in a cylindrical glass vessel or liner that fit snugly into the bomb. Metal specimens of electrolytic copper, 24ST duralumin, and SAE 1020 cold-rolled steel 1-1/2" x 1/2" x 1/16" were used as oxidation catalysts in certain of the tests. The surface area of each was 1.75 sq.in. (11.12 sq.cm.). The specimens were polished and degreased as described in Section (H). The specimens were arranged in the form of an equilateral triangle with the 1/2" edges in contact with the other specimens. The bomb assemblies were flushed with oxygen to remove the air before filling to 100 psi of oxygen at room temperature. The bombs were maintained at $212^{\circ}\text{F} \pm 0.5^{\circ}\text{F}$, at which temperature the initial pressure was 125 psi. The change in pressure with time was observed during the test period of

168 hours. At the conclusion of the test period the samples were allowed to cool to room temperature and then were examined for changes in viscosity, neutralization number, odor and color, the formation of precipitates or sludges and separation of immiscible liquids. When the metal specimens were used, they were examined for evidences of corrosion and rusting.

72. Several typical diesters were selected for non-catalyzed bomb oxidation tests. These were the di-(2-ethylhexyl) esters of adipic and sebacic acids and the di-(1-ethylpropyl) esters of adipic, azelaic and sebacic acids and the di-(1,3-dimethylbutyl) ester of sebacic acid. They were chosen in order to obtain some indication of the relative stabilities of esters of different acids and of different alcohols. The results of these tests, Table XI, indicate that the di-(1-ethylpropyl) esters of adipic, azelaic, and sebacic acids are more resistant to oxidation than the di-(2-ethylhexyl) esters. No differences in the oxidation stabilities of the same esters of the different acids could be detected by this test. The di-(1,3-dimethylbutyl) sebacate was the least stable of the diesters examined. Since the purity of the diester samples varied, it is difficult to draw rigorous conclusions from the oxidation tests as small amount of impurities may influence the course and rate of the oxidation reaction. However, it appears that the shorter chain and more condensed diesters are the more stable to the oxidation conditions used in the tests, and they therefore appear to follow the quoted generalizations of paragraph 69 relating molecular structure to oxidation stability of alkanes.

73. The results of the oxidation tests indicate that the pure diesters have approximately the same oxidation stabilities as the corresponding alkanes of the same molecular configurations. But the increase in neutralization number and the formation of precipitates during oxidation reveal that these oils as such are not sufficiently oxidation stable to be considered as satisfactory lubricants for all of the naval applications of interest.

74. The oxidation stabilities of many compounds and fluids can be improved by the addition of small amounts of oxidation inhibitors. The effect of various inhibitors on the stability of gasolines, petroleum oil fractions, fatty oils, rubbers and many other products has been widely investigated and reported in the scientific, technical and patent literature. A review of the results of many investigators on the effect of antioxidants in gasoline and petroleum oil fractions, as well as an extensive bibliography on the subject, may be found in two books by Ellis (25,26). The results show that some substances effective as inhibitors of the oxidation of a given type of compound may be ineffective or even act as oxidation accelerators for another type compound. The effectiveness of different antioxidants was found to vary even among the various hydrocarbons, such as alkanes, alkenes, aromatics, and naphthenes. In addition, the effectiveness of many inhibitors varied with the temperature of oxidation, some being more effective at high temperatures than at low temperatures, and vice versa.

75. Most of the accepted theories on the oxidation of hydrocarbons, and of many other types of organic compounds, postulate an autocatalytic reaction. The antioxidant retards or prevents the oxidation by breaking the chain of the reaction. Such theories include:

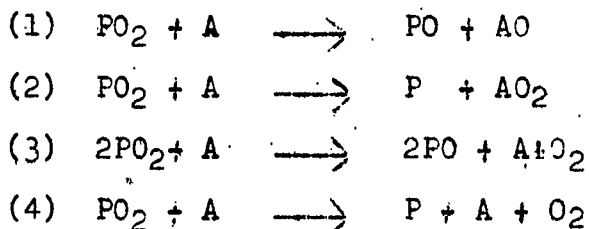
(a) The hydroxylation theory of Bone (27) which postulates the formation of an alcohol as the primary step.

(b) The peroxide theory of von Elbe and Lewis (28) which postulates the formation of a per-acid as the primary product.

(c) The dehydrogenation theory of Lewis (29) which postulates the formation of an unsaturated hydrocarbon and its oxidation to an unstable peroxide.

(d) The aldehyde degradation theory of Pope, Dykstra and Edgar (30) which postulates the formation of an aldehyde which is further oxidized with the loss of a carbon atom.

76. The peroxide theories of von Elbe and Lewis (28) and Lewis (29) are the most generally accepted. Four possible mechanisms have been considered by which the antioxidant A could react with the auto-oxidizable peroxide PO_2 to break the chain.



Method (4) is the most desirable as it inhibits the oxidation and does not consume the antioxidant, but rarely is this attained. Method (1) is believed to occur most frequently in practice. This method retards the oxidation reaction to a lesser extent than Method (4). Also, the inhibitor will be consumed in time; then the reaction will revert to an autocatalytic one. Regardless of whether the auto-oxidizable substance is a peroxide, if the inhibitor reacts with it to break the reaction chain, the oxidation reaction rate will be retarded or inhibited. As monomolecular and bimolecular reactions frequently require a greater activation energy than autocatalytic reactions, addition of an inhibitor will usually increase the induction period thus prolonging service life.

77. Of the many compounds investigated (25) (26) as oxidation inhibitors those containing an easily oxidizable group were in general found to be the most effective, the aromatic hydroxy and amine compounds being the best petroleum and hydrocarbon inhibitors. Lowry (31) and Egloff, Morrell, Lowry and Dryer (32) found that alkyl, aryl, or tertiary amino groups ortho or para to the amino or hydroxyl group gave increased inhibition. The presence of nitro, carbonyl or carboxyl radicals had the opposite effect.

78. Because the results of the oxidation tests and spontaneous ignition temperatures indicated that the diesters were not oxidized at the ester linkages, it seemed reasonable to assume that the inhibitors generally effective in retarding the oxidation of hydrocarbons and petroleum fractions would also be effective in the diesters. The di-(2-ethylhexyl) ester of sebacic acid was chosen as the solvent diester for this phase of the investigation, as it was available in the greatest quantity and highest purity. The oxidation test used was the bomb test previously described. Metal catalysts were also used because an oil is seldom used in an all glass system.

79. The effectiveness of some aromatic hydroxy and amino compounds, all soluble at - 60°F., in inhibiting the oxidation of di-(2-ethylhexyl) sebacate under the conditions described are shown in Table XII. Of the compounds investigated only 2, 4-dichlorobenzophenone, which is not readily oxidized, had no inhibiting effect on the oxidation reaction. All of the aromatic hydroxy and amine compounds investigated had a marked inhibiting effect on the oxidation reaction as reflected by the much smaller changes in oxygen pressure, neutralization number and viscosity as compared to those of the uninhibited di-(2-ethylhexyl) sebacate.

80. The tests made on the inhibiting action of diphenylamine, p-cyclohexylphenol and p-hydroxydiphenyl were with a less pure sample of the base stock diester as reflected by its higher initial neutralization number. The catalytic effect of the acidic impurities present may account for the greater neutralization number increase observed. The green coloration of the oil after oxidation is attributed to a reaction on the copper catalyst forming soluble copper salts. None of the tests with other compounds except that with 4-tert-butyl catechol, was accompanied by green coloration of the oil which is indicative of copper corrosion.

81. A number of the compounds investigated even in small weight concentrations of 0.1 to 0.2 per cent inhibited the oxidation of the di-(2-ethylhexyl) sebacate so effectively that the oxygen

consumption was less than one pound per sq. in. in 168 hours, the neutralization number increase was 0.20 or less and the viscosity change was negligible. Neither was there evidence of any attack or corrosion of the metal catalyst or formation of precipitates or sludges. The compounds having such effective inhibitory properties were p-tert-butyl o-cresol, 4-tert-butyl 2-phenylphenol, p-tert-amyl phenol, o-cyclohexyl phenol and thymol. The oxidation stability imparted to the di-(2-ethylhexyl) sebacate by these inhibitors was equal or superior to that of many petroleum instrument oils (19).

82. It has been shown by Dornte et al. (33) (34) (35) that the oxidation reaction may be unaffected, accelerated or retarded by volatile reaction products. The influence of high pressures and excess oxygen concentration on the oxidation reaction has been referred to already (24). Therefore, to characterize more fully the oxidation stabilities of the diesters, oxidation tests at atmospheric pressure without an excess of oxygen and with the removal of the volatile products should be made. Such tests have been made on finished diester oil compositions and are discussed in Part III of this report.

83. The pure diesters as such did not have the oxidation stability required for lubricant applications as evidenced by their oxygen consumption, increase in neutralization number and the formation of precipitates. However, a number of compounds were found to be capable of inhibiting the oxidation of the diesters even in the presence of the common metal catalysts, so that the oxygen consumption for a 168 hours test period at 212°F. was negligible. The neutralization number increase was 0.2 or less and no precipitates or sludges were formed. Nor was there evidence of any attack on the metal catalysts. The inhibition to oxidation obtained was equal or superior to that of most petroleum oils of comparable viscosity grades. The effective inhibitors were of the same types as those used for hydrocarbon and petroleum oils.

H. Oil Soluble Rust Inhibitors

84. Highly refined petroleum oils and many other types of base stocks have little or no rust inhibiting action in the presence of water. One of the most common and effective methods of imparting rust inhibiting properties to these fluids is by the addition of a small amount of a suitable oil-soluble polar organic compound. An explanation of the mechanism or mode of action of such compounds in preventing rusting has been given in a report of this Laboratory (36). This report also discussed test methods and the efficiency of many compounds and additives as rust inhibitors in Navy Symbol 2135 petroleum oil. As the

mode of action of rust inhibitors will be the same in the diester oils as in petroleum oils, the good rust inhibitors found then should also be effective in the diester oils if soluble. However, differences in the solubilities of the compounds in the two base stocks may affect their relative ratings as rust inhibitors.

85. Laboratory tests discussed in (36), which were designed to simulate increasingly strenuous service conditions, were used in this study to evaluate the compounds considered promising as rust inhibitors against the rusting action of both distilled water and synthetic sea water. The inhibitors discussed here do not include all examined, but are only those showing the most promise for the applications under consideration.

86. A modification of the ASTM Rust Prevention Test (D665-44T) was used to evaluate the effectiveness of the inhibitors against drops of water dispersed in the oil. This test was designed to simulate the rusting action of drops of water dispersed in the oil and was developed to test rust inhibition properties of turbine oils. The drops of water that adhere to the test specimen are continuously being washed away by the oil stream. Therefore, the water drops must penetrate the protective film within a short time if rusting is to take place. The average time of adhesion of the water drop is dependent upon the size of the drop (degree of dispersion) and method and speed of stirring. This is one of the least rigorous of the rust protection tests and simulates the protection against rusting afforded by the oil when the system is in operation and the water is dispersed in the oil.

87. As the quantities of available diesters of high purity were limited, a modification of the A.S.T.M. Test (D665-44T) was used to conserve the diester oils. The modification consisted essentially of a reduction in the size of the oil sample and test specimen. The test specimen was a cold rolled steel (SAE1020) strip - 4 1/4" X 1/4" X 1/32". The oil sample was 75 ml. and 10 per cent of this volume of water was used. A glass paddle rotating at 1080 rpm was used to disperse the water in the oil. The procedure was the same as that described in the ASTM Method except for the preparation of the test specimen. The test temperature was 140°F. and the duration of the test 24 hours. This test has been found to be somewhat more rigorous than the A.S.T.M. test as some samples that pass the former test allow a slight amount of rusting with the modified procedure.

88. Each specimen was polished and degreased as follows: After the use of new No. 150 and No. 320 emery papers, every possible precaution being taken to avoid handling the specimen with the fingers, it was placed in a clean glass container of

commercial C.P. benzene and boiled for three or four minutes. The specimen was transferred directly from the benzene by means of clean metal tweezers to another vessel containing either high grade petroleum ether or C.P. ethyl ether and boiled for approximately one minute. The specimen was then transferred from the solvent directly into a beaker of the oil to be tested. It was necessary to make this last transfer rapidly, due to the fact that any delay with such a degreased steel specimen resulted in the rapid appearance of a layer of rust due to exposure to the atmosphere. The warm ether evaporated rapidly allowing the transfer to be made with adequate speed.

89. The effectiveness of the degreasing procedure was tested by the water drop method. A drop of grease - free distilled water was allowed to fall upon the surface to be tested. If the test specimen was completely degreased, the drop of water spread to cover uniformly the entire surface, did not draw up to form drops, and evaporated showing interference colors during the last stage of evaporation.

90. As the properties of the diester oils suggested their most promising applications to be for low temperature lubricants, only those rust inhibitors soluble at low temperatures are discussed in this investigation. All of the inhibitors investigated showed no evidence of precipitates after 96 hours at -65°F . except the sorbitan monooleate and the amine salts of aliphatic acids and these were completely soluble at -40°F . In seeking rust inhibitors use was made of di(2-ethylhexyl) sebacate as the solvent or base stock since at the time it was the only pure diester available in sufficient quantity. The effectiveness of these compounds as rust inhibitors in the other aliphatic diesters would be expected to be only slightly different. Any differences found would be attributed to the relative solubilities of the inhibitors in the various diester oils.

91. The results of the modified Turbine Oil Rusting Tests with di-(2-ethylhexyl) sebacate as the base stock are given in Table XIII. The compositions were rated numerically as to the amount of rust formed on the test specimen. If the whole surface of the test specimen was rusted a rating of 10 was given the oil. No rust is denoted by a rating of zero, and numbers between 0 to 10 denote the fraction of surface rusted. Fractional ratings of $1/4$ or less denote the number and size of small rust spots, $1/64$ denoting one small rust spot.

92. All of the divalent metal soaps of the aryl stearic acids investigated when present in a weight concentration of 0.35 per cent prevented the test specimens from rusting in the presence of distilled water. When synthetic sea water was

used only the magnesium di-(xylyl)stearate) completely prevented the rusting of the test specimen. The calcium and barium soaps though having a marked inhibiting action allowed a slight amount of rusting as denoted by their ratings in Table XIII. As indicated in the table the emulsions formed during the test period were relatively unstable, breaking completely in less than an hour. The pH of the separated water was determined after the tests and the higher results obtained when magnesium di-(xylyl)stearate) was used indicate a greater degree of hydrolysis than in case of the calcium or the barium soaps.

93. For many applications a greater degree of rust inhibition is desired than can be evaluated by the Modified Turbine Oil Rusting Test. Therefore a more rigorous test, the static water drop test, was used. This test simulates the rusting action of a drop or pocket of water in a system where the oil is quiescent, i.e. dead ends or a system not in operation. The test specimens were cold rolled steel (SAE1020) plates approximately 1 inch square and 1/16" thick. In the center of one face a shallow conical depression approximately 1/32" deep was made with a 7/16" diameter center drill whose tip was ground to form an included angle of 148°. Immediately following the degreasing procedure, previously described, the test specimen was immersed, drilled-face upward, in a 1/4" layer of the oil to be tested contained in a small beaker (100 ml.) or petri dish. After the metal test specimen had been in contact with the oil for one hour at the test temperature to allow a reasonable approximation of adsorption equilibrium to be reached, a drop of water was placed in the oil so that it rested in and just filled the conical depression. The specimens were observed at 24 hour intervals and rated as to the amount of rust formed. The usual duration of the test was 168 hours.

94. The results of static water drop test when distilled water at 140°F. was used are given in Table XIV. The metal salts of the aryl stearic acids, completely prevented the rusting of the test specimens during the test period (168 hours) when present in 0.25 weight per cent concentration. No differences could be detected in the rust inhibitory action of these compounds in the various diesters. The zinc salts of the substituted shorter chain aliphatic acids employed also prevented the rusting of the test specimen when present in a concentration of 0.50 weight per cent. The sorbitan monooleate and the amine salts of the substituted aliphatic acids though active in inhibiting the rusting of the specimen did not completely prevent its rusting, as shown by the ratings in Table XIV.

95. In general, the effectiveness of rust inhibitors has been found to decrease with increasing temperature (36). One

of the more promising rust inhibitors, calcium di-(phenylstearate), was examined in concentrations from 3.0 per cent to 0.35 per cent by weight using the static water drop method with distilled water at 160°F. The results revealed that only 0.35 weight per cent of inhibitor prevented the formation of rust at 160°F. for the duration of the test (168 hours).

96. The effectiveness of the inhibitors in preventing rusting in the presence of sea water was determined by the static water drop at 100°F. The di-(2-ethylhexyl) sebacate offered little or no protection from the rusting action of the synthetic sea water as shown by a corrosion rating of 10 obtained in less than 24 hours of exposure Table XIV. All of the compounds investigated exerted an inhibiting effect, but none completely prevented rusting for the test period (168 hours). The most effective inhibitors of those tried were the divalent metal soaps of substituted aliphatic acids and these allowed only a slight amount of rusting during the 168 hour test period as evidenced by the small fractional value assigned the rust rating. Increasing the concentration of the rust inhibitor calcium di-(phenylstearate) from 0.35 to 3.0 weight per cent caused only a slight improvement in the rust protection and this was evident only after several days.

97. The effectiveness of the inhibited diester oils in preventing the rusting action of water on iron or steel parts covered by only a thin film of the diester was determined by a spray cabinet test. The test specimens for this test were rectangular, cold rolled steel (SAE 1020) strips, 3" long, 1-1/2" wide and 1/8" thick. They were cleaned and degreased as previously described after which they were dipped in the test oils for one minute and then allowed to drain at room temperature for two hours before being placed in the spray cabinet. The specimens were supported perpendicularly from the bottom. The spray cabinet was the Type B, Size 2, rubber lined cabinet of the Industrial Filter and Pump Manufacturing Company. The test temperature was 100°F. and distilled water was atomized with a glass nozzle having a 1 mm. tip and operated by clean air under a pressure of 25 psi. The spray was deposited at the rate of 0.1 ml./sq.cm./ 8 hrs.

98. In this test there is no opportunity for the oil film to be replaced or repaired once it is broken. Also the continuous leeching action of the water will gradually remove the rust inhibitor. Therefore, the test is probably more of a leeching test and simulates a condition where water is continually being deposited and allowed to drain off the parts or mechanism.

99. The results of various concentrations of calcium di-phenyl-

stearate) and magnesium di-(xylylstearate) in di-(2-ethylhexyl) sebacate in preventing the rusting action of a continuous spray of distilled water are given in Table XV. The rust ratings indicate that the calcium and magnesium aryl stearates had approximately the same inhibiting power when used in same weight concentrations. Increasing the concentration of these compounds improved the amount of inhibition obtained both as regards the extent of rusting and the time required for rust to appear.

100. These experiments show that the diester oils have little or no rust inhibition properties and if used as lubricants where there is the likelihood of water accumulating in the system, a rust inhibiting additive should be incorporated in the oil. Laboratory tests simulating increasingly severe service conditions were used to evaluate the compounds investigated. The most satisfactory rust inhibitors found were divalent metal soaps of substituted aliphatic acids and were capable of preventing the rusting of iron or steel parts for 16 hours by a static drop of distilled water when tested at 140°F. These inhibitors were effective in concentrations as low as 0.25 to 0.35 weight per cent and were soluble in the diesters at temperatures as low as - 65°F. The divalent metal soaps of substituted aliphatic acids, though unable to completely prevent the rusting of the test specimen in the presence of a static drop of synthetic sea water at 100°F., greatly inhibited its rusting action. Further increases in the concentration of the inhibitor had only a slight effect on the rust inhibition obtained. Low concentrations of these soaps retarded the rusting of iron and steel when subjected to a continuous spray of distilled water but did not prevent rusting. High concentrations of approximately 2 per cent of these soaps were found necessary to prevent the rusting of specimens when subjected to such conditions. Specifications should not require a greater degree of rust inhibition than that necessary to give satisfactory service operation because increasing amounts of rust inhibitors frequently affect some other desirable property of the lubricant adversely.

(1) Polymer Thickeners and V.I. Improvers

101. The changes in viscosity with temperature of the best petroleum oils are so great that they do not fulfill the requirements of many Naval applications. Synthetic fluids have been investigated in the hope of finding an oil with the desired viscosity - temperature characteristics. Although some fluids with unusually low temperature coefficients of viscosity have been developed, often their use has been restricted by other physical or chemical properties as well as by excessive costs and limited availability. Petroleum fractions can be thickened with polymer additives to form fluids with viscosity - temperature characteristics superior to those of conventional petroleum oils; however, other considerations limit the improvement ob-

tainable. Experience has shown that if two oils of the same type, one being less viscous than the other, are thickened to the same viscosity at a given reference point with the same polymer, the less viscous base stock oil will have the better viscosity-temperature characteristics. Therefore, further improvement in the viscosity temperature-characteristics will require the use of less viscous base stocks. But as the viscosity of petroleum fractions decreases, the volatility increases. Since in many applications non-volatility is an important requirement, it is obvious that the volatility requirement will limit the useful improvement in V.I. obtainable by dissolving polymers in petroleum oils. Numerous lubricants with improved viscosity-temperature characteristics have been obtained by the addition of linear polymers to petroleum fractions, the most common being the so-called "flat viscosity" hydraulic oils, e.g. AN-VV-O-366b, OS-2943 and OS-1113. Since the addition of the polymer increases the viscosity of the fluid, lighter (less viscous) and hence more inflammable petroleum fractions must be used as base stocks in blending polymer additive oils.

102. Staudinger (37) developed an empirical equation relating the molecular weight of homologous polymers to the specific viscosities of the diluted solutions.

$$\eta_{sp}/c = K_m M$$

where $\eta_{sp} = \frac{\eta_{\text{solution}}}{\eta_{\text{solvent}}} - 1$ = specific viscosity

and M = molecular weight of polymer

K_m = constant

c = concentration of polymer

η = viscosity (poises)

There has been much discussion and criticism as to the accuracy of this equation and it has been found η_{sp}/c is not a constant even at high dilutions for high molecular weight polymers. But regardless of its accuracy it is known that the increase in the ratio $\frac{\eta_{\text{solution}}}{\eta_{\text{solvent}}}$ is some direct function of the molecular weight

and molecular weight distribution of homologous polymers for equivalent concentrations. Therefore, the higher molecular weight polymers of homologous series have the greater thickening effect. Considerations of economy make preferable the use of the higher molecular weight polymers. However, it has been observed, that under certain operating conditions the viscosity of polymer additive oils decreases, and that the viscosity decrease is greater

for oils containing very high molecular weight polymers. An earlier report of this Laboratory (38) discussed this effect and attributed it to three causes, shearing stresses being by far the most important. An equation was also presented for calculating the highest molecular weight polymer that could be safely used for a given application. The rates of shear encountered in hydraulic systems, in which the above mentioned oils are used, are much greater than those likely to be encountered in other applications. The viscosity breakdown to be expected of diester oils thickened with these polymers would be expected to be smaller in instrument lubricants.

103. The diesters investigated were much less volatile than petroleum oils of the same viscosity grades and had viscosity-temperature characteristics equal or superior to comparable petroleum oils. Therefore, it was considered possible to prepare polymer thickened diester oils with viscosity - temperature characteristics superior to polymer thickened petroleum oils of the same volatilities. In an effort to find polymers for this purpose, the approximate solubilities of a number of linear polymers in di-(2-ethylhexyl) sebacate were measured.

104. The polymeric materials investigated included cellulose esters and ethers, polyvinyl alcohol, polyvinyl acetate and polyvinyl acetal, cumarone - indene resins, polystyrene, polybutene, and polyacrylic esters. The cellulose and polyvinyl-type polymers were relatively insoluble in the diester. Only low molecular weight polystyrenes and polybutenes were soluble and the solubility decreased rapidly with decreasing temperature. The cumarone-indene resins, though quite soluble, had molecular weights too low to have an appreciable thickening effect unless high concentrations were used. The polyacrylic esters (Rohm and Haas Company F-10, HF-845 and HF-880) were quite soluble in this diester. The HF-345 and HF-880 "Acryloids" have been much used during the war as thickening agents and V.I. improvers for hydraulic and recoil oils, e.g. specifications AN-VV-O-366b, O.S.-2943 and AXS-808.

105. As the di-(2-ethylhexyl) ester of sebacic acid was at the time the only diester of the aliphatic acid series available in large quantity, it was used as the solvent or base stock for determining the thickening and V.I. improving effects of the "Acryloid" polymers. This was not a limitation since the thickening action of the "Acryloids" on this diester should be of the same order of magnitude as on the other aliphatic diesters reported here for they are confined to a rather narrow group of homologues. However, it is known that the thickening effect will be greater on the more fluid diesters and less on the diesters

more viscous than di-(2-ethylhexyl) sebacate. Also, differences in the solubilities of the acryloid polymers in the various diesters may also exert an influence on the relative thickening effects and V.I. improvement.

106. The effect of the addition of 1.0, 3.0, 5.0, 10.0 and 20.0 per cent by weight of the "Acryloids" "HF-845", "HF-880" and "F-10" on the viscosity and viscosity-temperature characteristics of di-(2-ethylhexyl) sebacate are given in Table XVI. and shown graphically on Plates 5 to 6. It can be seen from the table that of the three "Acryloids" investigated, "Acryloid HF-880" had the greatest thickening action and "HF-845" the least. "Acryloid HF-880" also gave the greatest improvement in viscosity-temperature characteristics as evidenced by the increased viscosity indices and the decreased ASTM Slopes. Table XVI shows that the addition of 1.0 per cent of the "Acryloids" resulted in a solution with a higher V.I. and a smaller slope than the base stock. Increasing amounts of the acryloids steadily decreased the V.I. of the solution. Upon the addition of 20.0 per cent, the resulting solution had a lower V.I. than the base stock or solvent. This apparent anomaly is due to the peculiarity of the V.I. scale and deserves a brief discussion here.

107. A tabulation of the V.I.'s of some hypothetical ideal oils, i.e. oils showing no change in viscosity with temperature, may help understand this apparent anomaly.

<u>Viscosity Centistokes</u>	<u>V.I.</u>
2.00	365.5
5.00	299.8
7.50	229.1
10.00	208.0
25.00	168.0
50.00	148.5
75.00	140.8

The above table shows that the V.I. scale is no more suitable for comparing oils of different viscosities than is the ASTM Slope method.

108. At the higher concentrations of the "Acryloids" several of the resulting solutions exhibited non-Newtonian behavior. This has been observed in the polymer thickened petroleum base hydraulic fluids and may be due to the orientation of the linear polymeric molecules with the direction of flow, resulting in a decrease in viscosity with increased rates of shear. The decrease in viscosity is some function of the number and length

of the polymeric molecules present and the rate of shear. It is probable that the non-Newtonian behavior would have been observed in the fluids of lower polymer concentrations and at the higher temperatures if the rates of shear had been sufficiently high. The graphs of Plates 5, 6 and 7 reveal that the addition of the polymers to the base stock, di-(2-ethylhexyl) sebacate resulted in solutions whose graphs deviated from linearity. The curvature is more apparent at the high temperatures and increases with increasing polymer concentrations. The linearity of the graphs of the diesters on the ASTM chart has been discussed in Part I, Section C of this report.

109. The thickening effects of the "Acryloids" in the di-(1-ethylpropyl) esters of azelaic and sebacic acid are also given in Table XVI. The addition of 3.3 weight per cent of "Acryloid HF-845" increased the viscosity of di-(1-ethylpropyl) azelate from 6.66 cs. to 13.3 cs. at 100°F. This is greater than the viscosity of di-(2-ethylhexyl) sebacate (12.6 cs) at 100°F, yet at - 40°F. the former fluid had a viscosity of 826 cs as compared to 1410 cs. for the latter. The thickening effects caused by the addition of 1.0, 2.0, 2.23 and 3.0 weight per cent of "Acryloid HF-880" to di-(1-ethylpropyl) sebacate are presented. These data demonstrate that the viscosity - temperature characteristics are improved by increasing the concentration of polymer and also that the fluids made by thickening the less viscous diester, di-(1-ethylpropyl) sebacate, had better viscosity-temperature characteristics than polymer thickened fluids made by thickening di-(2-ethylhexyl) sebacate. This is in conformity with the predicted results.

110. Though fluids with better viscosity - temperature characteristics may be obtained by the addition of polymers to the less viscous diesters, they are obtained at the price of increased volatility. The volatilities as determined by weight losses with time of polymer thickened diesters were found to be approximately the same as the base stocks or solvents. As the diesters are much less volatile than petroleum oils of the same viscosities the polymer thickened diesters offer a means of preparing oils of superior viscosity - temperature characteristics and materially reduced volatilities.

(J) Foaming Properties

111. This is a brief explanatory study of the foaming tendencies of representative members of the group of aliphatic diesters. This is of interest because of the difficulties that have been met in practice with other oils in hydraulic equipment of many types of design.

112. The test apparatus used was in no way novel, consisting of a fritted glass filter of medium porosity to which was sealed a length of glass tubing to make a long column. The oil to

be tested was placed in the column to a depth of 1 inch and clean air was passed upward through the filter and into the oil at a rate of 166 ml/minute as measured by a calibrated flowmeter. The air-flow at this rate was continued for five minutes, after which it was cut off. The height of foam and the height of clear liquid at the end of the five-minute period and every ten seconds thereafter until the free liquid surface appeared was recorded. This enabled one to compare not only the amount of foam produced in a given length of time under standard conditions, but also the rate at which the foam broke when once formed.

113. No irrefutable evidence has as yet been reported in the literature in which a pure liquid has been found to foam. This has been confirmed in the cases of the pure diesters examined. The above foaming test was applied to the di-(2-ethylhexyl) esters of adipic, azelaic, and sebacic acids. In each case the bubbles of air formed at the filter rose quickly through the liquid without coalescing and burst immediately upon reaching the surface. No bubbles were found to be stable for a period as long as a second.

114. In addition, tests were run on some of the diester base lubricants containing various additives in order to determine the effects of these additives upon the foaming properties. E-25c, E-25d, E-17b, E-33a (see Part III - Section A) were each tried in the above manner and were found to behave exactly like the pure esters. In no case was a stable foam formed. A sample of di-(1-ethylpropyl) sebacate was tested with 2.23 per cent of an acryloid ester polymer thickener to determine if this type of polymer might not cause foaming. This also was found to form no stable foam whatsoever.

115. Certain diester compositions have shown indications of being an improvement on N-28 Aircraft Instrument Oil. For comparison, a foaming test on the N-28 oil Sample L-6-44 prepared by the Mellon Institute was made. In the same tube in which the diesters produced no foam, this light oil produced almost five inches of foam requiring nearly a minute to break completely. This is probably to be expected from the diversity of materials used in making this oil and from the presence of the high molecular - weight polystyrene used as a V.I. improver.

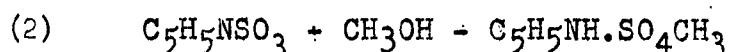
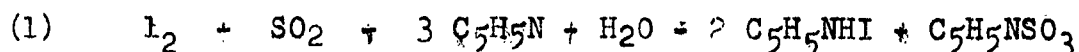
116. Hence, the diesters examined, both pure and compounded, showed freedom from foaming tendencies superior to those of other oils of equivalent viscosities. All these diesters and the lubricating compositions made from them which have been tested thus far have produced no stable foam. This is in agreement with other work on other pure fluids. Other oils, for which they may be found to be useful substitutes, are known to form considerable

foam under various test conditions.

K. Water Solubility, Hydrolytic Stability, and Emulsifiability

117. Some idea of the solubility of water in the diester oils is necessary to determine their range of applications. If an oil has a high water solubility it is possible that the dissolved water may react with, dissolve, or precipitate the additives that may have been incorporated in the oil composition. Also it has been observed at this Laboratory that it is much more difficult to inhibit the rusting of steel with additive oils having an appreciable water solubility.

118. The volumetric chemical method of Karl Fischer (39) for the determination of water was selected because of its simplicity and wide range of application. This method consists of titrating the unknown with a methanol solution of iodine, sulfur dioxide and pyridine to the appearance of the brown color of free iodine. Smith, Bryant and Mitchell (40) studied this reaction and showed that the fundamental reaction occurred in two distinct steps.



Only the first equation involves water absorption. The deterioration of the reagent with time was attributed to side reactions, but these did not cause any decrease in the quantitative accuracy of the results obtained when the reagent was standardized daily against a known water solution.

119. Fischer pointed out that the colorimetric end point could not be detected in the presence of dark colored substances and suggested that an electrometric method might be developed. Several electrometric methods (41, 42, 43, 44) have been reported in the literature and their developers state that these methods give sharper and more reproducible end points than the colorimetric method.

120. Diesters saturated with water at room temperature, approximately 30°C, were prepared by shaking 50 ml. of diester with 25 ml. of distilled water. The ester-water mixtures were centrifuged to separate any occluded or emulsified water and then allowed to stand at room temperature for a day to approach equilibrium. Duplicate samples of 10 to 15 grams of the clear supernatant diester were taken and stored in clean, dry, glass-stoppered flasks for titration.

121. The Fischer reagent was purchased from Eimer and Amend and standardized against a methanol solution containing 1 mg. of water per ml. of solution. As the diesters are not completely soluble in the reagent and separate into two phases during titration they were dissolved in methanol. Dry methanol was prepared

by refluxing with magnesium and distilling according to the method of Gilman and Blatt (45). This methanol was found to contain a slight amount of water. To eliminate the necessity of a blank determination the methanol was titrated with the Fischer reagent to the appearance of the free iodine end point. Approximately 25 ml. of this methanol was added to each sample of the diester and immediately titrated with the Fischer reagent.

122. The results of the duplicate determinations on several of the typical diesters and diester oil compositions are given in Table XVII. Duplicate determinations agreed within ± 0.1 percent, by wt. Two duplicate determinations were made on different samples of di-(1-ethylpropyl) azelate on different days. The spread in the water content obtained did not exceed ± 0.1 per cent. The discrepancies observed in the duplicate determinations are attributed to two main causes.

1. Reagent reacting with the moisture in the air and adsorbed on surface of titration flask.

2. The difficulty of obtaining a saturated solution and excluding occluded water from the samples.

Very little difficulty was observed in obtaining the end point since the diesters and solvent were colorless. More exact determinations could be obtained by the use of the titration flask and assembly described in the literature (44).

123. The results show that the solubility of water in the diesters decreases with increasing chain length, varying from 0.19 weight per cent for di-(1-ethylpropyl) adipate to 0.06 for the di-(2-ethylhexyl) azelate and sebacate. This was expected, as the water solubilizing effect of diester groups would decrease as the hydrocarbon portion of the molecule increased. No differences in the water solubilities of the diester oil compositions as compared to the pure base diesters could be detected. The water solubilities of the diesters, though exceeding that of analogous hydrocarbons, is quite low, approximately 0.1 per cent or less for most of the diesters.

124. The hydrolytic stabilities of the diesters are of interest since this property governs or limits their suitability as lubricants in applications where there is a possibility of contamination by water. The hydrolysis of carboxylic esters is probably one of the most widely studied of all chemical reactions. It is a slow, reversible reaction whose equilibrium conversion is readily measured. Remick (46) has discussed and summarized the conditions governing reactions of this kind and the mechanisms by which they proceed. Hydrolytic reactions

are catalyzed by both hydrogen and hydroxyl ions, the alkaline hydrolysis of esters being generally a second order reaction whereas the acid hydrolysis is a ternary reaction between ester, water, and catalyzing acid.

125. As the water solubilities of the diesters investigated were 0.1 per cent or less, they would be expected to hydrolyze very slowly since the concentration of water available for reaction is very small. The apparent hydrolysis rate would be accelerated slightly by increasing the interfacial area where the two reactants of the heterogeneous systems come in contact. If a solubilizing agent or mutual solvent for the water and diester could be found, it is quite possible that it would influence the rate of hydrolysis. With the above difficulties in mind it was considered undesirable to try to determine the absolute rate of hydrolysis of the diesters. An empirical test was used to determine the amount of hydrolysis taking place under the test conditions.

126. A 50 g. sample of diester and a 50 g. sample of water were placed in a 250 ml. flask and mixed to saturate the diester with water. After the emulsion separated, the flask was connected to a water cooled condenser and the flask placed in a bath maintained at 212°F. Alkaline (pH 10), acid (pH 4) and freshly boiled distilled water were used to hydrolyze each diester. The esters investigated were di-(2-ethylhexyl) sebacate, the diester of a primary alcohol, and di-(1-ethylpropyl) azelate, the diester of a secondary alcohol. A 5 g. sample of the oil phase and a 5 g. sample of the aqueous phase were removed in each experiment and titrated with 0.1 N KOH solution just before placing the test solution in the thermostat, and also after 24, 72, and 168 hours exposure to the test temperature.

127. The amount of potassium hydroxide consumed in the titration, as determined by the differences between the titrations at the start and at the various test intervals, was within experimental error for all samples and times involved. The greatest difference observed was equivalent to a consumption of 0.05 mg. of potassium hydroxide per gram of diester. As the theoretical saponification numbers are 262.9 and 341.6 respectively for the di-(2-ethylhexyl) sebacate and di-(1-ethylpropyl) azelate, it is apparent that if either of the diesters hydrolyzed the amount of hydrolysis was insignificant. No differences in the amount of hydrolysis could be detected when boiled distilled, alkaline, or acid water was used. It is concluded that these diesters are extremely stable hydrolytically and that no difficulties due to hydrolysis are likely to be observed when these diesters are used as lubricants in ordinary lubricating systems even if small amounts of water are present.

128. No extensive series of emulsion tests were made on the diester oils. However, it was found in the course of the investigation that the pure diesters would not form stable emulsions with water. The rates of emulsion separation were approximately in the inverse order of their densities. The incorporation of 0.2 per cent by weight of the antioxidant, 4-tert-butyl, 2-phenylphenol, had no noticeable stabilizing action on the emulsions formed.

129. When rust inhibited diesters were tested by the modified turbine oil rust test (Section H), it was observed that the diester-in-water emulsions formed were stabilized by the rust inhibitors to a degree depending on the inhibitor used. Thus the emulsions with divalent salts of aryl stearic acids were less stable than with petroleum sulfonates. When distilled water was used, it required about 30 minutes for the emulsions to break when the di-(2-ethylhexyl) sebacate contained aryl stearate inhibitors. For comparison the emulsion of the non-rust-inhibited oil broke in less than ten minutes. When synthetic sea water was used approximately 60 minutes were required for the inhibited oils as compared with ten minutes for the non-inhibited oil.

130. Several of the commercial lubricating oil compositions received at this Laboratory were formulated using di-(2-ethylhexyl) sebacate as the base stock. Those containing alkaline earth petroleum sulfonate rust inhibitors were observed to form much more stable emulsions with water. Some of these emulsions showed only slight separation even after standing several days. Therefore in applications where the rate of breaking of emulsions is important it is recommended that such a requirement be included in specifications for diester oil compositions.

III. DIESTER COMPOSITIONS FOR LOW TEMPERATURE INSTRUMENT OILS

131. It has been shown in Part II of this report that the diesters have many properties desired in lubricants and some not obtainable in any available oils. Other desirable properties were imparted to the diester oils by the incorporation of small concentrations of suitable chemical additives. The preparation and properties of low temperature instrument lubricating fluids compounded of diesters and chemical additive agents and a description of some compositions of immediate naval interest are discussed below.

A. Non-Polymer-Thickened-Oils

132. A low temperature instrument oil capable of giving satisfactory lubrication over a wide range of temperatures has been desired for naval uses. Such an oil should have a viscosity of approximately 10 cs. to 15 cs. at 100°F. Several of the pure diesters discussed (Part II) were in this viscosity range, while a larger number could be prepared from suitable mixtures of these compounds. Some instrument oil compositions prepared with these diesters as base stocks are listed in Table XVIII. For convenience and brevity these diester oil compositions will be referred to hereafter by the code designations listed in the first column

of that Table.

133. The requirements and characteristics desired of a lubricant for naval fire control equipment have been outlined in another report of this Laboratory (19). The service requirements of a lubricant for such instruments are exceptionally rigorous. In addition some aeronautical instrument oils have required freezing or pour points varying from -65° to -80°F .

134. Viscosity - temperature data on the diester oil compositions are given in Table XIX. It will be seen from a comparison of this table and Table III that the addition of the antioxidant and up to 0.35 weight per cent of the rust inhibitor had only a negligible effect upon the viscosity. Increasing the concentration of the rust inhibitor thickened the oil. This is particularly apparent for the E-25d series oils containing calcium di-(phenylstearate) as the rust inhibitor. The viscosity of the oil was increased from 12.6 to 16.3 cs. by the addition of 3 per cent of rust inhibitor. Also this inhibitor decreased the V.I. (or increased the viscosity slope). At -40°F the E-25d series of oils containing 1 per cent or more of calcium di-(phenylstearate) all exhibited non-Newtonian behavior and the E-25d₃ oil had anomalous viscosity properties at 0°F . It is probable that the other oils of this series will exhibit similar anomalous viscosity characteristics when investigated over a greater range of shear rates. The substitution of the magnesium for the calcium aryl stearates as rust inhibitors (E-25h and E-25k series of fluids) caused much smaller increases in the viscosities and only small changes in the V.I. or slopes.

135. It was observed that the magnesium and zinc soaps were more readily soluble in the diester fluids than were the calcium soaps. It is probable that the greater viscosity changes caused by the calcium soaps were due to the formation of colloidal solutions and that the use of magnesium and zinc soaps resulted in more nearly true solutions, therefore causing smaller viscosity changes.

136. The majority of the oil compositions investigated to date had di-(2-ethylhexyl) sebacate as the base fluid. This was done because that diester was readily made available in pure form by a suitable purification procedure (14) applied to a commercial grade of the diester sold for use as a plasticizer. Slightly less viscous oils may be prepared from the di-(2-ethylhexyl) esters of azelaic and adipic acids as exemplified by compositions E-33a and E-17b. The base fluid for compositions E-17a and E-17c was a blend of the di-(2-ethylhexyl) esters of adipic and sebacic acids. Though the sebacic ester is the minor constituent of the blend, the resulting composition had viscosity-temperature characteristics much superior to that of the di-(2-ethylhexyl)

adipate, the major constituent, and approached that of the sebacate.

137. Low temperature storage tests of at least 96 hours duration were made on all of the compositions. The E-25 compositions remained fluid with no evidence of crystals or precipitates after storage at -65°F . There was some evidence that the higher concentrations of the rust inhibitors used tended to depress the freezing points of the pure diesters so that such oil compositions had even lower freezing points. The azelaic and adipate base oils E-33a and E-17b had lower freezing points than the sebacates. These compositions were fluid and no crystals or precipitates were observed after storage for over 96 hours at -75°F , the lowest temperature investigated. It is believed that these oils could be subjected to even lower temperatures without deleterious results since the base diesters have freezing points below -100°F and -90°F respectively. Oils E-17a and E-17c which are sebacate adipate blends also withstood storage at -75°F . Very low pour or freezing point oils can be obtained by proper blending of the diesters of Table III. The freezing points of blends of the di-(2-ethylhexyl) esters of sebacic, azelaic, and adipic acids have been previously given (Part II, Section B). The evaporation losses of the diester oil compositions described in Table A were practically identical with those of the pure diester base stocks and will not be discussed further.

138. The neutralization numbers of the base oils if properly purified, (determined by Federal Specification Board Test 510.31 Method B) were very low, not exceeding 0.03. The addition of the antioxidant had a negligible effect on the neutralization number. However, some of the rust inhibitors caused a considerable increase. The zinc and magnesium soaps used as rust inhibitors caused a considerable increase. The zinc and magnesium soaps used as rust inhibitors caused much greater increases in the neutralization numbers than did the calcium soaps. This is attributed to differences in the ease of hydrolysis and/or replacement of the metal of the soap by the potassium of the KOH used in the titration. It was very difficult for even the same operator to get consistent results on the neutralization number of oils having high concentration of hydrolyzable soaps. The neutralization numbers of the oils containing zinc and magnesium soaps were calculated assuming that the metal would be replaced by potassium from the potassium hydroxide solution used in the titration. Within the limits of experimental error and purity of the soaps the observed and calculated values agreed in the case of oils containing zinc soaps. For oils containing magnesium soaps the observed neutralization number was approximately 80 to 85 per cent of the calculated value. Only from

10 to 30 per cent hydrolysis or replacement by potassium was observed in the oils having calcium soaps. Hence the neutralization numbers of E-33a, E-25h and E-25d oils containing zinc, magnesium, or calcium soaps of di-phenylstearic acid in practically equimolal concentrations (4.6×10^{-4} molal or 0.35 wt per cent) were respectively 0.53, 0.46, and 0.06, while the base fluids had neutralization numbers of 0.05, 0.03 and 0.02.

139. As some of the oil compositions containing 1 per cent or more rust inhibitor had rather high neutralization numbers, it was considered advisable to determine their corrosive action if any. The Federal Specification Board copper strip corrosion test at 212°F, Method 530.31, was used. At the end of the three hour test period the copper test strips had a very slight brown discoloration as compared to a freshly polished copper strip. The specimens were replaced in the oil and the test continued for a total of 24 hours. Upon examination it was observed that the brown discoloration had increased slightly but there was no evidence of any black or green discoloration which is considered indicative of corrosion. No differences could be detected in the amount of discoloration caused by the various soaps used. There was some indication that the amount of discoloration decreased with increasing soap content.

140. The rust inhibiting properties of the diester oil compositions described in Table XVIII were found to be the same as those of the pure diesters to which had been added the same concentration of the respective rust inhibitors. It was concluded that the small amounts of antioxidants used in the oil compositions did not affect the efficiency of the rust inhibitors. Because of the full discussion of rust inhibition tests in Part II, Section H, the results of the rust inhibition tests on the lubricant compositions of Table XVIII will not be repeated here.

141. The diester oil compositions of Table XVIII differ from some of the oxidation stabilized diesters investigated in Part II, Section G only by the addition of soap rust inhibitors. It is known that metals, and particularly some of the soluble metallic salts or "soaps", exert an enormous influence on the rate and possibly the course of the oxidation reactions of petroleum and vegetable oils. Thus it was necessary to determine if the metal soaps used as rust inhibitors caused any significant acceleration of the oxidation of the diester oil compositions of Table XVIII.

142. The bomb oxidation test described in Part II, Section G was used first. The results of oxidation in the presence of metals under such conditions (168 hours using an initial oxygen pressure of 125 psi at 212°F) of some E-25 oils containing zinc, magnesium and calcium soaps are shown in Table XX. None of the

oils tested developed precipitates, or showed an appreciable change in viscosity. The change in the neutralization number was less than 0.5 in all cases. However, as described in paragraph 133, Part III, it was difficult to get consistent results with the test due to the hydrolysis of the soap or the replacement of the metal by potassium. The drop in oxygen pressure was zero for the oils containing zinc and magnesium soaps and never exceeded 4 psi for E-25d series oils. Only Oil E-25c, containing the zinc soap, developed a slight green cast which was considered indicative of copper corrosion. No evidence of chemical attack or corrosion by these oils of any of the metal specimens was observed. Of the other fluids examined the E-25d series oils darkened in color somewhat while the E-25h series oils darkened even less. Increasing the calcium or magnesium soap content of the oil had little if any effect on the oxidation stability of the diester as determined by this test.

143. Hence the bomb oxidation tests indicated the magnesium soap rust inhibitors caused no significant changes other than a neutralization number rise of less than 0.5 in di-(2-ethylhexyl) sebacate stabilized by 0.2 per cent 4-tert-butyl 2-phenylphenol. The calcium soaps showed a smaller neutralization number rise and only a slight amount of oxidation. The zinc soaps, though causing negligible oxidation of the oil and no discernible corrosion of the iron and aluminum metal specimens, caused enough copper corrosion to develop a light green tinge in the oil.

144. A dynamic type of oxidation test also lasting 168 hours was applied to these oils. In this test clean dry air was used to oxidize the oil. The oxidation cell was a cylindrical glass vessel 250 mm long and 18 mm I.D. with ground glass joint. An air inlet tube was sealed into the cell near the top and ran down the side terminating in an upturned tip 0.5 mm in diameter at the bottom center of the cell. The same metal catalysts were used as in the bomb test. These were arranged in the form of a triangle with the long edges touching. A 25 gram sample of oil was charged into the oxidation cell which was then connected to a water-cooled reflux condenser. The assembly fitted snugly into a hole in an electrically heated and thermostatically controlled duralumin block, capable of maintaining the oil temperature at $212 \pm 0.5^\circ\text{F}$. The air flow rate was 20 ml/min. The effluent gases from the oxidation cell and condenser assembly were allowed to bubble into a known volume of standard alkali which was back titrated at intervals to determine the amount of volatile acids produced.

145. The evaluation of the oxidation characteristics of the diester oils by such a test was considered necessary as Dornte

et al (33, 34, 35) have shown that the volatile reaction products may influence the course and rate of the oxidation reaction. The volatile-acid neutralization number or the number of mg. of potassium hydroxide required to neutralize the volatile acids produced by one gram of oil during the oxidation test was also calculated. The formation of considerable amounts of volatile acids is, besides being a criterion of the extent of oxidation, indicative of the corrosion and rusting likely to be observed if such lubricants were to be in closed or poorly ventilated systems. The volatile or short chain organic acids are the stronger acids and would be more corrosive to metals.

146. The results obtained by this test procedure are listed in Table XXI. Oils E-25c and E-33a, each of which contained a zinc soap, turned green during the oxidation test indicating that the oxidized oil was corrosive to copper. The copper specimen in oil E-33a was slightly corroded but there was no visible evidence of corrosion on the other metal specimens. The changes in neutralization number, viscosity, and the amounts of volatile, acidic products formed are not considered excessive. The oils containing calcium and magnesium soaps gave no evidence of corrosive action on any of the metals, nor was there any green color in the oil after oxidation. The E-25d series oils (containing calcium soaps) darkened slightly during oxidation. The E-25H series oils (containing magnesium soaps) showed little if any change in color during the oxidation test. The viscosity changes were not significant. The decreases in neutralization numbers observed after oxidation of E-25d₂ and E-25d₃ oils are attributed to the difficulties of obtaining reproducible titration results with soap type additives. The amount of volatile acids produced was significantly decreased by raising the concentration of soap in the oil. The oils containing the magnesium soaps produced smaller amounts of volatile acids than those containing calcium soaps.

147. The results of the dynamic oxidation tests are in agreement with those of the static tests. Therefore, the volatile oxidation products do not radically affect the oxidation reaction. The changes in properties observed on oxidation indicate that the magnesium soaps had, at most, only a slight accelerative effect on the oxidative breakdown of the inhibited diester oils, while the calcium soaps had a somewhat more pronounced action. Oils containing zinc soaps formed products corrosive to copper during oxidation. In fact, a comparison of the oxidative stabilities of the diester lubricating oils listed in Tables XX and XXI, and probably those listed in Table XVIII, reveals them to be equal or superior to the petroleum instrument oils whose properties have been examined and discussed by this Laboratory elsewhere. (19).

148. These diester instrument oils were found markedly superior to the conventional petroleum instrument oils as regards non-volatility and viscosity-temperature characteristics. The incorporation of the antioxidant and small amounts (approximately 0.35 per cent) of soap type rust inhibitors had a negligible

effect upon the viscosity and viscosity-temperature characteristics of the lubricants. Increasing the concentration of rust inhibitors thickened the oils, the calcium soap having a much greater effect than the magnesium soaps. The low temperature storage stability was satisfactory as low as -65°F . for di-(2-ethylhexyl) sebacate, and -75°F or lower for corresponding adipate and azelate compositions, and for the di-(2-ethylhexyl) adipate-sebacate blend. Good rust inhibition properties were imparted to diester oils by the addition of suitable soap type additives. The use of zinc or magnesium soap rust inhibitors caused a large increase in the neutralization number. This was attributed to hydrolysis and formation of the potassium soap. The calcium soap rust inhibitors caused a much smaller increase in neutralization number. Though some of the diester oil compositions had an apparent high acidity as indicated by their neutralization numbers, none were found to be corrosive to copper as evidenced by the absence of black or green colorations after immersion of a copper specimen in the oil for 24 hours at 212°F . The stabilities of the diesters were adversely affected by the zinc soap rust inhibitors and the oils developed a slight green discoloration indicative of copper corrosion after oxidation in contact with copper metal. The magnesium soap rust inhibitors when present in concentrations up to 3 per cent caused no corrosion of metals and no noticeable increase in the oxidation rate. The calcium soaps only slightly increased the amount of oxidation. The oxidation stabilities of the diester oil compositions were equal to, or superior to, those of all the petroleum instrument oils investigated.

149. For the formulation of non-polymer-thickened, non-volatile, instrument oils having freezing points below -75°F , the compositions recommended consist of a base fluid of: (a) 20 per cent of di-(2-ethylhexyl) azelate mixed with 80 per cent of di-(2-ethylhexyl) sebacate, or (b) 40 per cent di-(2-ethylhexyl) adipate mixed with 60 per cent di-(2-ethylhexyl) sebacate, or (c) pure di-(2-ethylhexyl) azelate. If the freezing point need not be below -60°F , the di-(2-ethylhexyl) sebacate alone is a satisfactory base fluid. To any one of the above fluids 0.2 per cent by weight of an antioxidant such as 4-tert-butyl 2-phenylphenol, o-cyclohexylphenol, p-tert-amylphenol should be added. For rust prevention, concentrations of 0.25 to 2 per cent by weight of the calcium salt of an arylstearic acid are recommended, the concentration required being higher the more extreme the conditions of exposure. Satisfactory arylstearic acids are phenylstearic, xylylstearic, xenylstearic and dodecylphenyl-stearic acids.

B. Polymer-Thickened Oils

150. Many naval applications require lubricants with the lowest obtainable viscosity-temperature coefficients. This is particularly true of aeronautical applications where the operating temperature range is wide and lubricants having pour or freezing points as low as -80°F are required. The freezing points of many of the diesters investigated meeting or exceeding this requirement are given in Table II and paragraph 19. In Section I, Part II of this report the properties of some "Acryloid" thickened diesters are summarized and generalizations made as to the properties of other thickened diesters.

151. The compositions of two experimental polymer-thickened oils E-21b and E-22a using di-(1-ethylpropyl) azelate and di-(1-ethylpropyl) sebacate respectively are given in Table XVIII. Their viscosity vs. temperature characteristics over the temperature range of 210°F to -60°F are tabulated in Table XIX. The Bureau of Aeronautics is using for a low temperature instrument oil a synthetic lubricant developed at the Mellon Institute and denoted by them as N-28 oil. The viscosity requirements for this oil are listed below:

<u>Temperature</u>	<u>Kinematic visc., cs.</u>
100 $^{\circ}\text{F}$	13.5 minimum
32	50.0 maximum
-40	900 "
-60	2800 "

152. A comparison with the viscosity-temperature characteristics of oil E-21b reveal that the diester fluid meets or is below the specification viscosity requirements at all temperatures except 32°F where it is slightly more viscous. A comparison of the viscosity-temperature graphs on the ASTM chart reveals that the N-28 oil curves upward more rapidly at sub-zero temperatures than E-21b oil. The E-21b oil has a slightly less favorable viscosity coefficient than the N-28 oil in temperature range 130 to 0°F but is considerably better at the sub-zero temperatures.

153. Oil E-22a is somewhat more viscous than the N-28 specification oil at all temperatures. However, a somewhat less concentrated polymer thickened solution of di-(1-ethylpropyl) sebacate has been described in Table XVI. A comparison of this diester base fluid with oil E-21b reveals that the latter has the better viscosity-temperature characteristics. This is in agreement with the generalization of Section I, Part II that the thickening of oils, to some reference viscosity, results in better

viscosity-temperature coefficients, the less viscous the base fluids. Therefore, the polymer thickened di-(1-ethylpropyl) adipate would be expected to have a lower ASTM viscosity slope (or a higher VI) than the corresponding azelate or sebacate base oils. The use of less viscous diesters as base fluids would result in oils with even lower slopes.

154. The price exacted for decreasing the viscosity slope by the use of less viscous base stocks is increased volatility. The evaporation loss after 168 hours at 150°F by the test described in Section F, Part II was approximately 0.7 weight per cent for E-21b and E-22a. This is greater than the evaporation losses of the pure diesters which were 0.4 and 0.2 weight per cent respectively for the azelate and sebacate. This increased volatility of the two diester compositions is attributed to the incomplete removal of the toluene solvent in which solution the polymer was prepared. The increase in viscosity after evaporation was 1.5 per cent when determined at 100°F. These oils are much superior to polymer thickened petroleum oils of comparable viscosity and V.I. as regards evaporation and constancy of viscosity.

155. Both oil compositions E-21b and E-22a were clear, free from cloud or precipitates, and poured after 96 hours storage at -80°F.

156. The rust inhibition properties of these oils were determined by the static water drop test. Both oils completely inhibited the rusting action of distilled water at 140°F for the test period of 168 hours. When tested with synthetic sea water at 100°F the oils had rust ratings of 1 and 1½ after 24 hours and 3 and 4 after 168 hours. This is not quite so good as the results obtained with the same concentration of rust inhibitor dissolved in the pure diester. Therefore the "Acryloid" polymer used interfered slightly with the action of the soap rust inhibitor. Similar behavior of "Acryloid" thickened oils has been noted by this Laboratory in other diester fluids as well as in petroleum base oils.

157. The oxidation stability of oil E-22a was investigated using the dynamic test described in part III, Section A. The results of this test summarized in Table XXI reveal that the neutralization number increased from 0.06 to 0.68. No corrosion of the metals and no formation of corrosive products was observed. The only change in the appearance of the oil after oxidation was a slight deepening of the pale yellow color. No change in viscosity as a result of the oxidation test was observed. It is concluded that the "Acryloid" polymer has little or no deleterious effect on the oxidation stability of this diester oil. The oxidation stability of this oil was found markedly superior to that of the N-28

oil and compares very favorably with the stability of the best petroleum base oils (19). Although no oxidation tests have yet been made on oil E-21b, from its similar composition it would be expected to be as stable as the E-22a oil.

158. Two polymer-thickened, high V.I., low pour point oils have been developed using diester base fluids and addition agents discussed in Part II. One of them has been shown to be superior to the N-28 instrument oil developed by the Mellon Institute in viscosity-temperature characteristics, non-volatility, rust inhibition, oxidation stability, and freedom from corrosiveness. It has equally satisfactory low cloud and pour points.

IV. OTHER APPLICATIONS OF DIESTER OIL COMPOSITIONS TO LUBRICATION

159. The non-volatility, excellent oxidation stability, low freezing points and good V.I. characteristics of the diester instrument oil compositions discussed in Part III, Sections A and B, suggest the use of diester base lubricants for other naval applications. Applications need not be restricted to the viscosity grades investigated here. Diesters of other viscosity grades could be prepared by blending or synthesis if the need is indicated. The properties of such blends, and of new synthetic diesters, could be predicted with a fair degree of accuracy from the constants of the pure diesters discussed in Part I.

160. It should be pointed out here that the viscosity grade of petroleum base oils recommended for many instrument applications is not necessarily based on the viscosity requirements of the instrument. Frequently an oil of higher viscosity is recommended because of volatility and oxidation stability considerations. Not only do the volatilities of petroleum fractions decrease with increasing viscosity but also the oxidation stabilities are improved because of the transition to more stable hydrocarbon types or configurations and the presence of naturally occurring antioxidants. Therefore, the diesters investigated here having viscosities below 10 centistokes at 100°F should be given consideration as lubricants for sensitive mechanisms where small changes in torque have serious effects on the sensitivity of the instrument.

161. For heavier duty applications where oils are desired having viscosities at 100°F of from 20 to 50 cs. the diesters of the branched chain undecyl, tetradecyl and heptadecyl alcohols are available. Intermediate viscosity grades may be prepared by blending these with less viscous diesters. The more viscous diesters could be used advantageously as base stocks for lubricants suitable for use in oil-lubricated gear trains, particularly for low temperature applications. It is also quite possible that

many extreme pressure additives can be successfully incorporated in the diester base stocks.

162. An obvious application of the branched-chain diesters is to the lubrication of refrigeration machinery. It is possible that some refrigerants such as ammonia and sulfur dioxide may react with the diesters causing this application to be restricted to refrigeration machinery operating with the more stable "Freons" and carbon dioxide.

163. As the diesters have higher flash points and spontaneous ignition temperatures and require higher concentrations of oxygen for the formation of explosive mixtures than petroleum products of similar viscosity grades, their use as lubricants for air compressors is suggested. The danger of explosions in this type of equipment should therefore be materially reduced. The more viscous diesters would be required for such applications.

164. The so-called "spindle oils" of the textile industry are low viscosity (approximately 12 cs. at 100°F) practically water-white oils. The pure diesters are water white and have the advantage over petroleum oils in that they are relatively non-volatile.

165. There is also much promise in the use of diester fluids as crankcase oils for internal combustion engines in Arctic climates and at high altitudes. Polymer thickened diester oils would be especially valuable because of their low viscosity at sub-zero starting temperatures and non-volatility and stability at the higher operating temperatures. The diesters of tetradecyl and heptadecyl alcohols fall in the SAE 10 viscosity classification and their viscosities only slightly exceed the requirements of an SAE 10W oil. The di-undecyl adipate is less viscous than an SAE 10 oil. It is estimated that 3 per cent of "Acryloid HF-880" would thicken this diester to an SAE 10 oil having a viscosity of approximately 20 cs. (106 S.U.S.) at 130°F and 1000 cs. (4600 S.U.S.) at 0°F. Such an oil has a better viscosity at 0°F than an SAE 10W oil. Even smaller percentages of this polymer (approximately 1 per cent) would be required to thicken the tetradecyl and heptadecyl diesters to SAE 20 oils whose 0°F viscosities are within the requirements of SAE 20W oils. In short, the higher diesters are comparable to winter grade petroleum oils but are superior in that they have higher flash points, lower evaporation rates and lower pour points. Furthermore, the use of polymer thickened diesters of undecyl alcohols results in fluids superior to petroleum winter grade oils, having higher flash points, lower volatilities, lower pour points, higher V.I.'S and possibly better oxidation stabilities.

166. Excellent hydraulic and recoil oils having very good V.I.'s and low pour points could be prepared from diester base fluids. Hydraulic oils with very high V.I.'s could be prepared meeting the viscosity requirements of the specification AN-VV-O-366b and O.S. 2943 by the addition of polymer thickeners. Approximately 5 per cent of "Acryloid HF-280" would be required to thicken the di-(3-methylbutyl) adipate to the viscosity requirements of the specification AN-VV-O-366b. Approximately 10 per cent of this polymer would be required to thicken di-(3-methylbutyl) adipate to O.S. 2943 viscosity requirements. More viscous diesters could be used as base stocks for the preparation of O.S. 1113 oils. Approximately 5 per cent of "Acryloid HF-280" would be required to thicken di-(2-ethylhexyl) sebacate to the viscosity requirements of O.S. 1113. The polymer-thickened, diester base, hydraulic fluids would be much less volatile than the corresponding petroleum base oils, and hence the present tackiness problem would be materially alleviated. It is important to note that the diester base hydraulic oils would necessitate a change from the present packings and gasket materials because they cause swelling of many of the type rubbers now in use.

167. It was realized that diesters were of promise in the development of low volatility, stable, low temperature greases. Numerous synthetic, diester base greases have been developed by this Laboratory and will be described in a report to be submitted this fall.

168. Non-lubricating applications of the diester oil compositions include their use as damping fluids. Their low volatilities, even at high temperatures, makes them ideally suited for this use. An example is the use of di-(2-ethylhexyl) sebacate as a base for high viscosity polymer additive damping oils which has been fully discussed by Fenske et al (4).

169. Hick an et al (1, 2, 3) have discussed and patented several of the diesters included in this investigation as vacuum and diffusion pump oils. Many of the other diesters described here deserve consideration for such uses. The incorporation in such vacuum pump oils of small amounts of any one or combinations of the antioxidants described in Part II, Section G might improve their efficiency and increase the service life.

170. The above discussion of possible naval uses of the diester base oils was made without reference to considerations of availability or cost. It is quite possible that the advantages to be gained by the use of diester lubricants will be outweighed by the greater availability and lower cost of corresponding petroleum products. However, for certain military applications these considerations may be of secondary importance, while for others

the performance gain with the diester lubricants may be such as to eliminate the consideration of relative availability and cost.

V. PRODUCTION AND SPECIFICATION OF DIESTER LUBRICANTS

171. One limitation to large scale applications of diester lubricating oils is their cost. Potentially available in the United States is a supply roughly estimated to be between 250,000 and 1,000,000 gallons of diester oil per year. This amount should not seriously limit other commercial uses of the requested acids and alcohols provided the demand is not built up too rapidly

172. Diester oils could be made cheaper by omitting unnecessary purification of the alcohols and acids employed in the synthesis. Thus mixed dibasic acids could be used instead of a pure acid. Also mixtures of isomeric alcohols or narrow distillation cuts could be used for many applications. For some uses the addition of selected petroleum fractions may have advantages with respect to lower cost and improvement in compatibility with certain commercially available addition agents. In some applications small initial concentrations of volatiles such as unreacted alcohols will not be detrimental. However, in making or using cheapened diesters certain precautions will be advisable. The presence of volatile impurities such as the unreacted alcohols will cause only a temporary lowering of the freezing point and pour point, and addition agents initially in true solution may eventually form a cloud or even precipitate as the volatiles disappear.

173. Specifications requiring or permitting the use of diester lubricants should include a freezing point rather than a pour point test, a copper strip corrosion test on the base stock or preferably on the finished lubricant, and a hydrolysis test for adulteration with less stable esters such as monoesters. A maximum evaporation requirement and test is recommended as a check on the manufacture of a quality diester lubricant. For some uses a minimum saponification number requirement is desirable for identification purposes or prevention of adulteration with petroleum or other non-saponifiable materials. If necessary, diester base stocks can be obtained essentially water-white while finished inhibited oils having a color no darker than No. 1 ASTM can be prepared. It has been shown here that pure diesters do not form stable emulsions with water. Some addition agents, particularly certain common rust inhibitors, cause greatly increased emulsion stability. However, good demulsifiability characteristics can be required of inhibited diester oils, and such a requirement will exclude only some but not all satisfactory addition agents. Any of the common oxidation tests can be used in specifying the oxidation stability of diester oils.

VI. CONCLUSIONS AND RECOMMENDATIONS

174. A wide variety of branched-chain aliphatic diesters have been studied and have been shown to be admirably suited to serve as base stocks for the development of numerous synthetic lubricating oils. The relation of organic structure to physical properties such as freezing point, volatility, viscosity, and V.I. have been studied and some rules of value have been obtained. Diesters have been found which have high V.I.'s and very low freezing points and evaporation rates. Especially recommended for instrument oil bases are the diesters made by reacting adipic, azelaic, or sebacic acids with branched-chain alcohols such as 2-ethylhexyl and 1-ethylpropyl alcohols. For uses requiring oils of higher viscosities the diesters made from the same acids and the branched-chain undecyl, tetradecyl and heptadecyl alcohols are recommended. A number of single diesters and mixtures of diesters suitable for instrument oil bases have been found having freezing points below -75°F and exceedingly low evaporation rates.

175. Efficient anti-oxidants, rust preventive additives, polymer thickeners and V.I. improvers have been found for use in the development and improvement of diester lubricating oils for a wide range of applications. A number of physical and chemical properties of diesters of importance in lubrication have been studied in the absence and in the presence of addition agents. These include hydrolytic stability, solubility for water, emulsifiability, specific gravity, thermal expansion, foaming, volatility and inflammability. A number of instrument oils have been developed of medium or high viscosity index, of remarkably low volatility, and having freezing points ranging from -60 to below -100°F . Good oxidation stabilities, low foaming tendencies, satisfactory demulsibility and good rust inhibition properties have been obtained. These oils are recommended for use in instruments in storage or in service.

176. Possible uses of these or related diester oils have been discussed and it has been concluded that certain ones are especially suited for general instrument use. Laboratory preparations of these oils have already been tested by naval or cooperating industrial activities in clocks, meters, controller mechanisms, gyroscopes, cameras, gun and bomb sights, synchronous motors, and fuse mechanisms. Others are now recommended for future tests in oil gear trains, particularly for low temperature applications, and refrigerator machinery and as air compressor lubricants, spindle oils and winter grade lubricating oils in internal combustion engines. They also are recommended for use as hydraulic and recoil oils (in systems provided with suitable packings)

Although less flammable than present petroleum hydraulic oils the diester fluids like petroleum are not sufficiently resistant to incendiary fire (22). Diester fluids are also recommended for use in the formulation of non-volatile low temperature low torque greases for damping fluids, and for vacuum and diffusion pump oils. It is believed the applications tests recommended will result in improvements in naval lubrication practice in such equipment.

177. Considerations have been advanced relative to the available supply of diester oils and methods of decreasing their cost. Specification problems have been discussed and recommendations have been made.

VII. ACKNOWLEDGMENTS

178. The authors wish to express their appreciation to Eleanor M. Bried Sp(X) 2/c and Harriet A. Foltman AMMI 2/c for their valuable assistance in gathering data on viscometric properties and volatility.

BIBLIOGRAPHY

- (1) K. C. Hickman and C.R. Sanford, Rev. Sci. Instr. 1,140; 1930
- (2) K. C. Hickman, J. Frank. Inst. 221, 215; 1936
- (3) K. C. Hickman Ibid. 221, 383; 1936
- (4) M. R. Fenske and coworkers, O.S.R.D. Report No. 1894 of Oct. 6, 1943.
- (5) L. A. Mikeska, Ind. Eng. Chem. 28, 970; 1936
- (6) J. N. Cosby and L. H. Sutherland, Proc. A.P.I. 22, III, 13; 1943
- (7) R. W. Schiessler, J. N. Cosby, D. G. Clarke, C. S. Rowland, W.S. Sloatman, and C. H. Herr, Proc. A.P.I. 23, III, 15; 1942
- (8) R. W. Schiessler, D. G. Clark, C. S. Rowland, W. S. Sloatman, and C. H. Herr, Proc. A.P.I. 24, III, 49; 1943
- (9) A. H. Nissan, L. V. W. Clark, and A. W. Nash, J. Inst. Pet. 26, 155; 1940
- (10) A. E. Dunstan, T. P. Hilditch, and F. B. Thole, J. Chem. Soc. 103, 133; 1913
- (11) E. B. Evans, J. Inst. Pet. 24, 38; 1938
- (12) N. P. Doss, "Physical Constants of the Principal Hydrocarbons" 4th Ed. 1943 The Texas Co., N. Y. C.
- (13) T. E. Thorpe and J. W. Rodger, Phil Trans. A(185) 397; 1894
- (14) N. R. L. Report P-2573 of June 1945, "The Synthesis of Esters of Dibasic Acids for Use in the Development of Lubricants."
- (15) N. Andrade, Nature (125) 309, 580; 1930
- (16) E. B. Evans "IIme Congres Mondial du Petrole" sect. II p. 993, Paris 1937
- (17) A. H. Nissan, L. V. W. Clark, and A. W. Nash, J. Inst. Pet. 26 155; 1940
- (18) Beilstein "Hand. Organ. Chem." 4th Ed., Springer, Berlin
- (19) N. R. L. Report P-2541 of May 1945 "A Laboratory Evaluation of Lubricating Oils for Naval Fire Control Equipment".
- (20) Sortman, Beatty and Heron, Symposium on Petroleum Chemistry. Petroleum Division A. C. S. Detroit Meeting. Sept. 1940
- (21) N. R. L. Report P-2165 "The Laboratory Evaluation of Hydraulic Oils. I - Methods for Inflammability Test"
- (22) N. R. L. Report P-2308. "The Laboratory Evaluation of Hydraulic Oils II-New Fluids Having Improved Inflammability Characteristics"
- (23) L. Pauling "The Nature of the Chemical Bond". (1940) Cornell University Press Ithica, N. Y.
- (24) G. Egloff "The Reactions of Aliphatic Hydrocarbons" in Gilman's "Organic Chemistry" vol. I, p55. 2nd Ed., John Wiley & Sons; N. Y. C.
- (25) C. Ellis "The Chemistry of Petroleum Derivatives" vol I, 1934, The Chem. Catalogue Co., N. Y. C.
- (26) C. Ellis "The Chemistry of Petroleum Deviations" vol II, 1937, The Reinhold Publ. Com., N. Y.
- (27) J. Bone, J. Chem. Soc. 1599; 1933
- (28) G. von Elbe and E. Lewis, J. Am. Chem. Soc. 59, 976; 1937

RESTRICTED

- (29) J. S. Lewis, J. Chem. Soc. 759; 1929
- (30) J. C. Pope, F. J. Dykstra, and G. Edgar, J. Am. Chem. Soc. 51, 1875; 1929
- (31) C. D. Lowry, Trans. Electrochem. Soc. 69, 279; 1936
- (32) G. Egloff, J. C. Morrell, C. D. Lowry, and C. G. Dryer, Proc. World Pet. Cong. 2, 50; 1933
- (33) R. W. Dornte, Ind. Eng. Chem. 28, 26; 1936
- (34) R. W. Dornte and C. V. Ferguson, Ind. Eng. Chem. 28, 863; 1936
- (35) R. W. Dornte, C. V. Ferguson, and C. P. Haskins, Ind. Eng. Chem. 28, 1342; 1936
- (36) N. R. L. Report P-2474 of February 1945 "Anti-rust Additives for Lubricating, Power Transmission, and Protective Oils."
- (37) H. Standinger and H. Heuer, Ber. 63, 222; 1930
- (38) N. R. L. Report P-2075 of May 1943 "Viscosity Breakdown of Oil."
- (39) K. Fisher, Angew. Chem. 48, 394; 1935
- (40) D. M. Smith, W. M. D. Bryant and J. Mitchell, J. Am. Chem. Soc. 61, 2407; 1939
- (41) E. G. Almy, W. C. Griffin and C. S. Wilcox, Ind. Eng. Chem. Anal. Ed. 12, 392; 1940
- (42) G. Vermont and F. J. Hopkinson, Ind. Eng. Chem. Anal. Ed. 15, 272; 1943
- (43) C. M. Johnson, Ind. Eng. Chem. Anal. Ed. 17, 312; 1945
- (44) O. T. Appli and W. S. McCarter, Ind. Eng. Chem. Anal. Ed. 17, 316; 1945
- (45) Gilman and Blatt "Organic Synthesis" Collective Volume I 2nd. Ed. 1941, John Wiley & Sons, Inc, N. Y.
- (46) A. E. Remick "Electronic Interpretations of Organic Chemistry" 1943, John Wiley & Sons, Inc. N. Y.

TABLE I

Comparison of Viscosities of Aliphatic Diesters and Normal Paraffins

Diester	Visc. cs.	Chain length	Visc. cs.	
	at 77°F. for	at 77°F. for	at 77°F. for	
Diester	Diester	Number of	Hydro-	Hydrocarbon
		atoms	Carbon	
Diethyl oxalate	1.63	8	0.72	n-octane
Diethyl malonate	1.79	9	0.92	n-nonane
Diethyl succinate	2.32	10	1.15	n-decane
Diethyl glutarate	2.49	11	1.44	n-undecane
Diethyl adipate	2.74	12	1.77	n-dodecane
Diethyl pimelate	3.30	13	1.89	n-tridecane
Diethyl suberate	4.06	14	2.55	n-tetradecane
Diethyl azelate	--	15	1.86?	n-pentadecane
Diethyl sebacate	5.28	16	3.98	n-hexadecane (cetane)

TABLE II

Diesters Studied, Their Molecular Weights
and Freezing Points

Diester	Molecular weight	Freezing point*	
		°C	°F
<u>Phthalates</u>			
Diethyl phthalate	222.23	below -3#	-27
Methyl phthalyl ethyl glycolate	266.29	" -35	below -31
Ethyl phthalyl ethyl glycolate	281.27	+ 20	+ 68
Dibutyl phthalate	278.34	-35#	-31
Butyl phthalyl butyl glycolate	336.37	below -35	below -31
Di-(2-ethylhexyl) phthalate	390.54	" -55	" -67
<u>Adipates</u>			
Di-(1-methylethyl)	230.30	2	36
Di-(1-ethylpropyl)	286.40	below -78	below -108
Di-(3-methylbutyl)	286.40	-46	-51
Di-(1,3-dimethylbutyl)	314.45	4	39
Di-(2-ethylbutyl)	314.45	-26	-15
Di-(2-ethylhexyl)	370.56	-68	-90
Di-(2-(2-ethylbutoxy) ethyl)	402.56	-62	-80
Di-(undecyl)(1)	454.70	glass at -60	below -76
Di-(tetradecyl)(2)	538.86	glass at -60	below -76
Di-(heptadecyl) (3)	623.02	glass at -60	below -76
Di-(2-(2-butoxyethoxy) ethyl)	434.54	-17	+ 1
<u>Azelates</u>			
Di-(1-ethylpropyl)	328.48	below -78	below -108
Di-(3-methylbutyl)	328.48	-37	-35
Di-(2-ethylbutyl)	356.52	-45	-49
Di-(2-ethylhexyl)	432.64	below -78	below -108
Di(2-butoxyethyl)	388.73	-17	+ 1
<u>Sebacates</u>			
Di-(1-methylethyl)	286.40	+ 3	+ 37
Di-(1-ethylpropyl)	342.50	below -78	below -108
Di-(butyl)	314.45	+ 14	57
Di-(3-methylbutyl)	342.50	-10	+14
Di-(1,3-dimethylbutyl)	370.56	-25	-13
Di-(2-ethylbutyl)	370.56	-22	-8
Di-(2-ethylhexyl)	426.66	-55	-67
Di-(2-(2-ethylbutoxy) ethyl)	458.66	-15	+ 5 0
Di-(tetradecyl) (2)	594.94	glass at -60	below -76

TABLE II (continued)

Legend: (1) undecyl or (1-methyl - 4-ethyloctyl)
(2) tetradecyl or (1-(2-methylpropyl) - 4-ethyloctyl)
(3) heptadecyl or (1-(3-ethylamyl) - 4-ethyloctyl)
* extracted from NRL Report 2573 (14)
manufacturers data

RESTRICTED

TABLE III

Viscosity-Temperature Characteristics of Diesters

Identification	Chain length	Visc. in cs. at °F:					Kinematic V.I.	ASTM Slope	
		210	130	100	77	32			
<u>Phthalates</u>									
Diethyl phthalate	--	1.73	3.99	6.26	9.73	31.4	26.6	0.94 d	
Methylphthalyl ethyl glycolate	--	3.63	14.2	34.1	85.8	1500	-218	1.07 b	
Ethylphthalyl ethyl glycolate	--	3.51	12.5	26.6	57.9	581#	-108	0.96 a	
Diethyl phthalate	--	2.33	5.87	9.72	15.8	57.2	43.1	0.84 d	
Butyl phthalyl butyl glycolate	--	3.75	12.2	23.8	46.0	273	19.8	0.85 c	
Di-(2-ethylhexyl) phthalate	--	4.36	14.9	30.0	58*	367	20.4	0.94 c	
<u>Adipates</u>									
Di-(1-methylethyl)	12	1.16	2.12	2.92	3.92	8.34#	104	0.85 a	
Di-(1-ethylpropyl)	14	1.56	3.09	4.58	6.31	15.7	98	0.83 d	
Di-(3-methylbutyl)	16	1.73	3.46	4.94	6.89	16.0	125	0.76 d	
Di-(1,3-dimethylbutyl)	16	1.79	3.78	5.64	8.27	22.8#	96	0.84 d	
Di-(2-ethylbutyl)	16	1.89	3.89	5.68	8.2*	20.1	123	0.77 d	
Di-(2-ethylhexyl)	20	2.38	5.34	8.22	12.4	37*	121	0.77 d	
Di-(2-(2-ethylbutoxy)ethyl)	22	2.68	6.01	9.23	14.0	41.9	144	0.76 d	
Di(undecyl) (1)	24	3.64	9.82	16.9	28.5	117*	111	0.77 d	
Di(tetradecyl) (2)	24	5.73	20*	40.5	78*	480	86	0.77 c	
Di(heptadecyl) (3)	24	6.81	23.8*	47.3	87*	485	107	0.71 c	
Di(2-(2-butoxyethoxy) ethyl)	28	3.29	7.85	12.2	19.1*	62*	158	0.73 d	

Identification	Chain length	Visc. in cs. at OF:					Kinematic V.I.	ASTM Slope
		210	130	100	77	32		
<u>Azelates</u>								
Di-(1-ethylpropyl)	17	2.10	4.50	6.66	9.62	25.8	126	0.77 d
Di-(3-methylbutyl)	19	2.29	4.83	7.03	9.9*	4.1	153	0.71 d
Di-(2-ethylbutyl)	19	2.51	5.4*	8.17	11.9*	31.8*	149	0.72 d
Di-(2-ethylhexyl)	23	3.06	7.20	11.4	17.4*	52*	146	0.72 d
Di-(2-butoxyethyl)	25	2.80	6.20	9.49	13.9	39.4	156	0.71 b
<u>Sebacates</u>								
Di-(1-methylethyl)	16	1.74	3.50	4.98	6.96	16.2#	125	0.76 b
Di-(1-ethylpropyl)	18	2.28	5.0*	7.38	10.9*	29.6	133	0.75 d
Diethyl	20	2.11	4.27	6.11	8.54	19.8	157	0.71 a
Di-(3-methylbutyl)	20	2.51	5.38	7.95	11.5	28.9	158	0.70 b
Di(1,3-dimethyl-butyl)	20	2.80	6.56	10.3	15.9	49.1	132	0.76 d
Di(2-ethylbutyl)	20	2.73	6.0*	9.05	13.3*	36.0*	158	0.70 b
Di(2-ethylhexyl)	24	3.32	7.96	12.6	19.5	60.9	154	0.71 d
Di(2-(2-ethylbutoxyl)ethyl)	26	3.59	8.40	13.3	20.4	63.5	175	0.70 d
Di(tetradecyl) (2)	28	6.55	22.8*	44.0	84*	455*	109	0.73 c

* interpolated
 ** extrapolated
 # supercooled

(1) undecyl or (1-methyl, 4-ethyloctyl)
 (2) tetradecyl or (1-(2-methylpropyl), 4-ethyloctyl)
 (3) heptadecyl or (1-(3-ethylamyl), 4-ethyloctyl)

a A-1M Slope 210 to 32°F
 b " " 210 to 0°F
 c " " 210 to -200°F

RESTRICTED

TABLE IV

Effect of Chain Length and Branching on the Viscosity
of Aliphatic Diesters

Compound	Chain Length No. atoms	Visc. cs. at t°F:				V.I.	ASTM Slope
		210	100	0	-40		
Di-(1-ethylpropyl):							
Adipate	14	1.56	4.58	40.3	255	98	0.83
Azelate	17	2.10	6.66	68.8	429	126	0.77
Sebacate	18	2.28	7.38	80	504	133	0.75
Di-(3-methylbutyl)							
Adipate	16	1.73	4.94	36.8	171	125	0.76
Azelate	19	2.29	7.03	58.5	286	153	0.71
Sebacate	20	2.51	7.95	71.4	--	158	0.70
Di-(1,3-dimethylbutyl)							
Adipate	16	1.79	5.64	67.9	623	96	0.84
Sebacate	20	2.80	10.3	154	1510	132	0.76
Di-(2-ethylbutyl)							
Adipate	16	1.89	5.68	51	297	123	0.77
Azelate	19	2.51	8.17	83.0	500	149	0.72
Sebacate	20	2.73	9.05	97.8	--	158	0.70
Di-(2-ethylhexyl)							
Adipate	20	2.38	8.22	107	807	121	0.77
Azelate	23	3.06	11.4	156	1190	146	0.72
Sebacate	24	3.32	12.6	187	1410	154	0.71

RESTRICTED

TABLE V

Effect of Branching on Viscosity

Compound	Chain length No. of atoms	Visc. cs. at °F				ASTM V.I. slope
		210	100	0		
Di-(undecyl) adipate (1)	24	3.6	16.9	508	111	0.77
Di-(tetradecyl) adipate (2)	24	5.7	40.5	3000	86	0.77
Di-(heptadecyl) adipate (3)	24	6.8	47.3	2630	107	0.71

(1) Undecyl is (1-methyl, 4-ethyloctyl)

(2) tetradecyl is (1-(2-methylpropyl), 4-ethyloctyl)

(3) heptadecyl is (1-(3-ethylamyl), 4-ethyloctyl)

TABLE VI

Effect of Position of Ester Groups on Viscosity and
Freezing Point

Compound	Chain length No. atoms	Viscosity (cs.) °F				ASTM V.I. slope	Freez- ing pt. °F
		210	100	32	0		
Di-(3-methylbutyl) adipate	16	1.73	4.94	16.0	36.8	125 0.76	-51
Di-(1-methylethyl) sebacate	16	1.74	4.98	16.2	37.6	125 0.76	-39

TABLE VII

Comparison of Boiling Points of Di-ethyl Esters with
those of the Normal Hydrocarbons of same Chain Length

Chain length	Boiling Point °C	
	Normal straight chain Hydrocarbon	Diester
8	125	185
9	151	190
10	174	218
11	196	237
12	216	240
13	236	253 (748 mm)
14	254	285
16	286	308

TABLE VIII

Evaporation Characteristics of Diesters at 150°F

Identification	Chain Length	Boiling Point °C**	Evaporation Loss 24 hrs	Evaporation Loss 48 hrs	Evaporation Loss 96 hrs	Wt. after 168 hrs	Neut. No. Increase	Visc. Incr. g
Phthalates								
Diethyl phthalate	-	-*	1.04	1.93	4.13	7.32	nil	0.3
Methyl phthalyl ethyl glycolate	-	-*	0.17	0.21	0.30	0.47	-	4.9
Ethyl phthalyl ethyl glycolate	-	-*	0.12	0.14	0.19	0.27	-	4.8
Diethyl phthalate	-	-*	0.09	0.14	0.31	0.58	-0.01	0.14
Butyl phthalyl butyl glycolate	-	-*	0.05	0.05	0.06	0.09	-	3.4
Di-(2-ethylhexyl) phthalate	-	-*	0.01	0.01	0.00	0.00	nil	0.1
Adipates								
Di-(1-methyl ethyl)	12	124-5/10 mm.	4.83	11.17	25.96	46.05	0.01	I.S.
Di-(1-ethylpropyl)	14	143/1.5 mm.	0.24	0.81	1.28	2.11	0.15	0.4
Di-(3-methylbutyl)	16	156/2-3 mm.	0.34	0.30	0.24	0.23	0.01	-
Di-(1,3-dimethylbutyl)	16	162.5/3 mm.	0.11	0.43	0.86	1.54	-0.29	0.1
Di-(2-ethylbutyl)	16	165.8/3 mm.	0.05	0.10	0.26	0.50	0.14	0.1
Di-(2-ethylhexyl)	20	196/2 mm.	0.02	0.03	0.05	0.09	0.01	nil
Di-(2-(2-ethylbutoxy) ethyl)	22	223/3-4 mm.	0.03	0.02	0.07	0.14	1.05	2.5
Di(undecyl) (1)	24	231.4/2-3 mm.	0.54	0.58	0.59	0.55	0.05	4.2
Di(tetradecyl) (2)	24	Vol. Dist.	I.S.	--	--	--	--	--
Di(heptadecyl) (3)	24	" "	0.03	0.03	0.03	0.04	nil	0.5
Di-(2-(2-butoxyethoxy) ethyl)	28	" "	I.S.	--	--	--	--	--
Azelates								
Di-(1-ethylpropyl)	17	192-3/5-6 mm.	0.06	0.12	0.24	0.40	0.02	nil
Di-(2-ethylbutyl)	19	196-8/3 mm.	0.07	0.11	0.12	0.28	0.03	1.3
Di-(2-ethylbutyl)	19	189-93/1 mm.	0.04	0.03	0.05	0.06	0.06	0.3
Di-(2-ethylhexyl)	23	233½-5/2.5 mm.	0.02	0.03	0.03	0.05	0.02	0.1

TABLE VIII (continued)

Identification	Chain Length	Boiling Point °C**	Evaporation Loss t. % after	Neut. No. Increase	Visc. Incr. %			
		24 hrs	48hrs	96hrs	168hrs			
<u>Azelates</u>								
Di-(2-butoxyethyl)	25	236-7/6 mm.	0.03	0.45	0.77	0.62	0.18	2.9
<u>Sebacates</u>								
Di-(1-methylethyl)	16	175/13 mm.	0.33	0.62	1.29	2.83	0.01	0.6
Di-(1-ethylpropyl)	18	202/7 mm.	0.03	0.07	0.10	0.20	0.01	0.1
Di(butyl)	20	179/2 mm.	0.00	0.04	0.09	0.18	0.02	0.3
Di-(3-methylbutyl)	20	191-3/3-4mm.	0.05	0.06	0.08	0.14	nil	-0.3
Di-(1,3-diemthylbutyl)	20	194/2-3 mm.	0.06	0.08	0.11	0.15	0.01	0.3
Di-(2-ethylbutyl)	20	202-6/1.5mm.	0.03	0.02	0.01	0.01	-0.02	0.3
Di-(2-ethylhexyl)	24	232/1-2 mm.	0.03	0.02	0.03	0.05	0.01	0.2
Di-(2-ethylbutoxyethyl)	26	255-6/3 mm.	0.04	0.04	0.02	0.00	-0.10	1.7
Di-tetradecyl(2)	28	sol. Dist.	0.04	0.05	0.05	0.04	-0.01	0.1

* Commercial Products

(1) Undecyl or (1 methyl, 4-ethyloctyl)

(2) Tetradecyl or (1-(2-methylpropyl), 4 ethyloctyl)

(3) Heptadecyl or (1-(3 ethylaryl), 4-ethyloctyl)

** Data from NRL Report 2573 (14)

I.S. = Insufficient Sample.

RESTRICTED

TABLE IX

Flammability Characteristics of Diesters

Identification	Visc. cs. at 100°F.	Cleveland Open Cup Flash Pt. °F.	Fire Pt. °F.	Spontaneous Ignition Temp. °F.	Spray Test % Oxygen
Di-(1-ethylpropyl) azelate	6.66	370	395	842	--
Di-(1-ethylpropyl) sebacate	7.38	380	410	798	--
Di-(1-ethylpropyl) sebacate: plus 1% Acryloid HF-880	9.84	-	-	778	--
plus 3% Acryloid HF-880	16.4	-	-	783	--
Di-(2-ethylhexyl) adipate	8.22	380	430	743	16
Di-(2-ethylhexyl) adipate: plus 0.1% 4-tert butyl, 2-phenyl phenol and 0.25% zinc di-(phenylstearate)	8.23	400	440	-	16
Di-(2-ethylhexyl) azelate	11.4	445	470	756	23
Di-(2-ethylhexyl) sebacate	12.6	450	495	765	18
Di-(2-ethylhexyl) sebacate plus 0.2% 4-tert butyl, 2-Phenyl-phenol: and 0.35% calcium di-(phenylstearate)	12.8	445	500	765	--
1.0% "	13.5	445	500	765	--
2.0% "	15.0	450	510	765	--
3.0% "	16.8	455	510	763	--

RESTRICTED

TABLE X

Densities and Specific Gravities of the Diesters

Identification	Density 25/4°C.	Specific Gravity 60/60°F.
<u>Phthalates</u>		
Diethyl phthalate	1.114	1.121
Methyl phthalyl ethyl glycolate	1.216	1.223
Dibutyl phthalate	1.043	1.050
Ethyl phthalyl ethyl glycolate	1.179	1.185
Butyl phthalyl butyl glycolate	1.095	1.102
Di-(2-ethylhexyl) phthalate	0.981	0.987
<u>Acipates</u>		
Di-(1-methylethyl)	0.959	0.965
Di-(1-ethylpropyl)	0.935	0.942
Di-(3-methylbutyl)	0.940	0.947
Di(1,3 dimethylbutyl)	0.919	0.926
Di(2-ethylbutyl)	0.940	0.947
Di(2-ethylhexyl)	0.922	0.929
Di(2-(2-ethylbutoxy),ethyl)	0.921	0.928
Di(undecyl)(1)	0.904	0.911
<u>Azelates</u>		
Di(1-ethylpropyl)	0.933	0.940
Di(2-ethylbutyl)	0.928	0.935
Di(2-ethylhexyl)	0.915	0.922
Di(2-butoxyethyl)	0.972	0.979
<u>Sebacates</u>		
Di(1-methylethyl)	0.931	0.938
Di(1-ethylpropyl)	0.922	0.929
Dibutyl	0.932	0.939
Di(3-methylbutyl)	0.921	0.928
Di(1,3-dimethylbutyl)	0.910	0.917
Di(2-ethylhexyl)	0.912	0.919
Di(2-(2-ethylbutoxy)ethyl)	0.951	0.958

(1) undecyl or 1-methyl, 4 ethyloctyl)

TABLE XI

Bomb Oxidation Tests of Typical Diesters at 212°F.*

Name of Ester	Pressure Decrease p.s.i.	Neut. No.		Viscosity		Description of Fluid After Test
		Before	After	Before	After	
Di-(1-ethylpropyl) adipate	4.5	0.02	0.66	4.45	4.75	clear - acidic odor
Di-(1-ethylpropyl) azelate	3.5	0.10	--	6.60	--	yellow - precipitate- alcohol odor
Di-(1-ethylpropyl) sebacate	11	10.7	17.5	8.02	8.35	yellow - cloudy
Di-(1,3-dimethylbutyl) sebacate	49	0.61	30.2	10.3	11.5	white - cloudy
Di-(2-ethylhexyl) adipate	28	0.03	10.6	8.23	8.81	clear - acidic odor
Di-(2-ethylhexyl) sebacate	25	0.08	10.0	12.6	13.2	yellow - clear

* Using oxygen at 125 pounds per sq. inch initial pressure at 212°F.

RESTRICTED

TABLE XII

The Effect of Various Inhibitors on Oxidation Stability* of di-(2-ethylhexyl) sebacate

Antioxidant	Conc. wt. %	AP. lbs.	Neut. Before	No. After	Visc. cs. Before	Visc. cs. After	Description of Appearance after Oxidation Test of Fluid of Copper of Aluminum of Steel
None	--	33	0.01	16.6	12.6	12.7	Cloudy Oxidized-Corroded No change No change No change No change
Aniline	0.10	0	0.01	0.22	12.6	12.5	Amber-slight sediment Oxidized No change No change No change No change
Diphenylamine	0.17	1.0	0.55	3.18	12.6	12.6	Dark green Oxidized No change No change No change No change
N-(p-tert-Amylphenyl) ethanol amine	0.10	2.5	0.01	0.34	12.6	12.6	Clear-slightly yellow Oxidized No change No change No change No change
2, 4' Dichlorobenzo-phenone	0.10	36.5	0.03	24.0	12.6	13.5	White-cloudy Oxidized Oxidized Oxidized Oxidized Oxidized
O-(cyclohexyl)phenol	0.10	0.5	0.01	0.08	12.6	12.6	Clear-slightly yellow Oxidized No change No change No change No change
p-Cyclohexylphenol	0.20	0.5	0.55	3.23	12.6	12.5	Light green None present Oxidized Oxidized Oxidized Oxidized
p-Hydroxydiphenyl	0.20	0	0.55	3.19	12.6	12.6	Light green Oxidized Oxidized Oxidized Oxidized Oxidized
4-tert-Butyl,2-phenyl-phenol	0.10	0	0.01	0.08	12.6	12.6	Clear-slightly yellow No change No change No change No change No change
p-tert-Butyl-o-cresol	0.10	0	0.01	0.12	12.6	12.6	Clear Oxidized No change No change No change No change
p-tert-Amylphenol	0.10	0.5	0.01	0.21	12.6	12.6	Clear-slightly yellow Oxidized Oxidized Oxidized Oxidized Oxidized
5-Methyl-2-isopropyl-phenol**	0.10	0	0.01	0.08	12.6	12.6	Clear-pale yellow Oxidized Oxidized Oxidized Oxidized Oxidized
4-tert-Butylcatechol	0.10	0.5	0.01	0.33	12.6	12.6	Clear-slightly green Oxidized Oxidized Oxidized Oxidized Oxidized

* Oxygen bomb test method

** Thymol

RESTRICTED

TABLE XIII

Modified Turbine Rust Test at 140°F.

Di(2-ethylhexyl) sebacate used as base fluid

A, Using Distilled Water				
Additive tested	Wt. % of additive	Rust Rating	Emulsion Broke	pH of Water
None	0	10	Less than 10 min.	6.7
Magnesium di-(xylylstearate)	0.35	0	Less than 30 min.	9.6
Calcium di-(phenylstearate)	0.35	0	Less than 30 min.	8.9
Calcium di-(xylylstearate)	0.35	0	Less than 30 min.	8.9
Barium di-(phenylstearate)	0.35	0	Less than 30 min.	8.3
B. Using Synthetic Sea Water				
None	0	10	Less than 10 min.	6.1
Magnesium di-(xylylstearate)	0.35	0	Less than 1 hr.	9.8
Calcium di-(phenylstearate)	0.35	3/4	Less than 1 hr.	8.6
Calcium di-(xylylstearate)	0.35	1/8	Less than 1 hr.	8.8
Barium di-(phenylstearate)	0.35	1/4	Less than 1 hr.	9.0

* Test run for 24 hours

RESTRICTED

Results of Static Water Drop Tests

Diester used	Additive tested	Distilled Water at 140°F.						Synthetic Sea Water at 100°F.					
		Conc. wt. %		Rust rating after		Rust rating after		Rust rating after		Rust rating after		Rust rating after	
		24 hrs	72 hrs	10 hrs	24 hrs	72 hrs	168 hrs	24 hrs	72 hrs	120 hrs	168 hrs	24 hrs	72 hrs
Di-(2-ethylhexyl) sebacate	-----	0	0	0	0	0	0	10	-	-	-	-	-
"	barium di-(phenylstearate)	0.25	0	0	0	0	0	1/64	1/64	1/2	2	1/64	1/2
"	calcium "	0.35	0	0	0	0	0	1/64	1/64	1/4	1	1/64	1/4
"	" "	1.0	0	0	0	0	0	1/64	1/64	1/16	1/2	1/64	1/16
"	" "	2.0	0	0	0	0	0	1/64	1/64	1/32	1/4	1/64	1/8
"	" "	3.0	0	0	0	0	0	1/64	1/64	1/64	1	1/64	1/8
"	di-(xyllyl stearate)	0.25	0	0	0	0	0	1/64	1/64	1/4	1	1/64	1/4
"	magnesium di(phenylstearate)	0.25	0	0	0	0	0	1/64	1/32	1/16	1	1/64	1/16
"	di-(xyllyl stearate)	0.25	0	0	0	0	0	1/64	1/64	1/64	1/16	1/64	1/16
"	strontium di-(phenylstearate)	0.40	0	0	0	0	0	1/64	1/64	1/8	1	1/64	1/8
"	zinc di-(phenylacetate)	0.50	0	0	0	0	0	1/64	1/8	1/2	2	1/64	1/2
"	di-(benzylacetate)	0.50	0	0	0	0	0	1/64	1/16	1/4	1	1/64	1/4
"	di-(2-ethylhexanoate)	0.50	0	0	0	0	0	1/32	1/2	2	4	1/32	2
"	di-(3-ethylheptanoate)	0.50	0	0	0	0	0	1/32	1/8	1/2	2	1/32	1/2
"	di-(4-ethyloctanoate)	0.50	0	0	0	0	0	1/64	1/64	1/32	1/8	1/64	1/32
"	di-(5-ethyl, 2-methyl, nonoate)	0.50	0	0	0	0	0	1/64	1/64	1/32	1/16	1/64	1/32
"	di-(6-ethyl, 3 methyl, decanoate)	0.50	0	0	0	0	0	1/64	1/64	1/64	1/32	1/64	1/32
"	di-(phenylundecanoate)	0.50	0	0	0	0	0	1/64	1/16	1/8	3/4	1/64	3/4
"	di-(phenylstearate)	0.35	0	0	0	0	0	1/64	1/32	1/16	1/4	1/64	1/4
"	di-(xyllyl stearate)	0.25	0	0	0	0	0	1/64	1/32	1/8	1/2	1/64	1/2
"	"naphthenate(14.5% solids)	0.5	0	0	0	0	0	1/64	1/16	1/4	1	1/64	1/4
"	sorbitan monooleate (G944)	1.0	0	0	0	0	1/16	1/2	2	4	6	1/2	4
"	cyclohexyl ammonium laurate	0.5	0	0	0	0	4	1/4	1	3	5	1/4	3
"	dicyclohexyl ammonium laurate	0.5	0	0	0	0	5	1/2	2	4	6	1/2	4
"	n-butyl ammonium xyllyl stearate	0.5	0	0	0	0	2	1/32	1	3	5	1/32	3
"	cyclohexyl-ammonium xyllyl-stearate	0.5	0	0	0	0	2	1/32	1/4	1	3	1/32	1

TABLE XIV (continued)

Results of Static Water Drop Tests

Diester used	Additive tested	Conc. wt. %	Distilled Water at 140°F.			Synthetic Sea Water at 100°F.		
			Rust rating after			Rust rating after		
			24 hrs	72 hrs	168 hrs	24 hrs	72 hrs	168 hrs
Di-(1-ethylpropyl) sebacate	calcium di-(phenylstearate)	0.25	0	0	0	1/64	1/32	1/16
"	magnesium di-(phenylstearate)	0.35	0	0	0	1/64	1/32	1/16
"	di-(xylylstearate)	0.30	0	0	0	1/64	1/64	1/16
"	zinc di-(phenylstearate)	0.45	0	0	0	1/64	1/32	1/8
Commercial sec. amyl sebacate	"	0.50	0	0	0	1/64	1/32	1/8
Di-(2-ethylhexyl) adipate	"	0.35	0	0	0	1/64	1/64	1/16
Di-(1-ethylpropyl) adipate	"	0.40	0	0	0	1/64	1/64	1/16
Di-(2-ethylhexyl) azelate	"	0.40	0	0	0	1/64	1/64	1/32
Di-(1-ethylpropyl) azelate	calcium di-phenylstearate)	0.25	0	0	0	1/64	1/32	1/8
"	di-(xylylstearate)	0.25	0	0	0	1/64	1/32	1/8
"	zinc di-(phenylstearate)	0.40	0	0	0	1/64	1/64	1/16

RESTRICTED

TABLE XV

Spray Cabinet Test at 100°F. with Distilled Water

Additive tested in di-(2-ethylhexyl) sebacate	Wt. % of ad- ditive	Rusting rating after:			
		24 hrs.	48 hrs.	72 hrs.	96 hrs.
None	--	10	--	--	--
Calcium di-(phenylstearate)	0.35	3	4	5	7
Calcium di-(phenylstearate)	1.0	1/2	1	2	3
Calcium di-(phenylstearate)	2.0	0	1/8	1/4	1/2
Calcium di-(phenylstearate)	3.0	0	0	0	0
Magnesium di-(xylylstearate)	0.75	1/4	2	4	5
Magnesium di-(xylylstearate)	1.0	1/8	1	2	3
Magnesium di-(xylylstearate)	1.5	0	0	1/2	1

RESTRICTED

TABLE XVI

Viscosity-Temperature Characteristics of Some Polymer Thickened Diesters

Identification	Viscosity in Centistokes at OF:						Kinematic V.I.	ASTM Slope
	210	130	100	77	32	0	-20	-40
Di-(2-ethylhexyl)sebacate	3.32	7.96	12.6	19.5	60.9	187	445	1410
plus Acryloid HF845, 1.0%	3.96	9.3	15.0	23.2	70.7	217	540	1640
plus Acryloid HF845, 3.0%	5.59	13.3	21.4	33.1	99.3	307	740	2320
plus Acryloid HF845, 5.0%	7.58	18.3	29.4	45.5	137	436	1060	3180
plus Acryloid HF845, 10.0%	14.5	37.2	58.6	92.1	290	894	2100	--
plus Acryloid HF845, 20.0%	39.7	106	179	291	1000	3290#	8700	--
plus Acryloid HF880, 1.0%	4.27	10.2	16.1	25.0	75.9	230	575	1760
plus Acryloid HF880, 3.0%	6.65	15.9	25.3	39.2	119	352	870	2680
plus Acryloid HF880, 5.0%	9.82	23.7	37.6	58.5	174	534	1320	3980
plus Acryloid HF880, 10.0%	21.0	52	84.0	131	405	1210#	2900	--
plus Acryloid HF880, 20.0%	65.5	179	291	469	1570	5310#	13000	--
plus Acryloid F-10, 1.0%	4.01	9.5	15.1	23.4	70.5	223	540	1610
plus Acryloid F-10, 3.0%	5.76	13.8	22.0	34.0	101	311	750	2240
plus Acryloid F-10, 5.0%	8.19	19.6	31.2	48.7	151	460#	1350	3450
plus Acryloid F-10, 10.0%	16.5	42.8	72.4	117	397	1470#	--	--
plus Acryloid F-10, 20.0%	57.1	184	360	695	4450	43100#	--	--
Di-(1-ethylpropyl)azelate	2.10	4.50	6.66	9.62	25.8	68.8	152	429
plus Acryloid HF845, 3.3%			13.3		51.5		826	
Di-(1-ethylpropyl)sebacate	2.28	5.0	7.38	10.9	29.6	80	182	504
plus Acryloid HF880, 1.0%			9.84		38.7			635
plus Acryloid HF880, 2.0%			12.8		50.1			828
plus Acryloid HF880, 2.23%			13.6		53.3	142		866
plus Acryloid HF880, 3.0%			16.4		64.0			1050

Non-Newtonian behavior
a ASTM Slope 210 to - 0°F.
b " " 100 to -40°F.
c " " 210 to -40°F.

RESTRICTED

TABLE XVII

Solubility of Water in Diesters at Room Temperature

Identification	Weight percent
Di-(1-ethylpropyl) adipate	0.19
Di-(1-ethylpropyl) azelate	0.12
	0.13
	0.12
	0.11
Di-(1-ethylpropyl) sebacate	0.13
	0.13
Di-(2-ethylhexyl) glutarate	0.08
	0.08
Di-(2-ethylhexyl) adipate	0.08
	0.08
Di-(2-ethylhexyl) azelate	0.06
	0.06
Di-(2-ethylhexyl) sebacate	0.06
	0.06
Di-(undecyl) adipate	0.08
	0.08
E-22a *	0.13
	0.13
E-25c *	0.06
	0.06
E-25d *	0.08
	0.08
E-33a *	0.06
	0.05

* See Table XVIII for oil composition.

RESTRICTED

TABLE XVIII

Some Diester Lubricating Oil Compositions

Code No.	Base stock	Rust inhibitor	Wt. conc.	Antioxidant	Wt. conc.	Polymer thickener	Wt. conc.
E-17a	Di-(2-ethylhexyl) adipate - 3 parts by vol.; di-(2-ethylhexyl) sebacate - 2 parts by vol.	zinc di-(xylol-stearate)	0.25	p-hydroxy diphenyl	0.20	none	
E-17c	"	zinc di-(phenyl-stearate)	0.25	4-tert-butyl, 2-phenylphenol	0.10	"	
E-17b	Di-(2-ethylhexyl) adipate	zinc di-(phenyl-stearate)	0.25	4-tert-butyl, 2-phenylphenol	0.10	"	
E-21b	Di-(1-ethylpropyl) azelate	calcium di-(phenyl-stearate)	0.25	"	0.20	Acryloid HF-880	3.0
E-22a	Di-(1-ethylpropyl) sebacate	"	0.35	"	0.20	"	2.5
E-25a	Di-(2-ethylhexyl) sebacate	zinc di-(xylol-stearate)	0.25	diphenylamine	0.20	none	
E-25c	Di-(2-ethylhexyl) sebacate	zinc di-(phenyl-stearate)	0.25	4-tert-butyl, 2-phenylphenol	0.10	"	
E-25d	"	calcium di-(phenyl-stearate)	0.35	"	0.20	"	

Code No.	Base stock	Rust inhibitor	Wt. conc.	Antioxidant	Wt. conc.	Polymer thickener	Wt. conc.
E-25d1	Di-(2-ethylhexyl) sebacate	calcium di-(phenyl-stearate)	1.0	4-tert-butyl, 2-phenylphenol	0.20	none	
E-25d2	"	"	2.0	"	0.20	"	
E-25d3	"	"	3.0	"	0.20	"	
E-25h	"	magnesium di-(phenyl-stearate)	0.37	"	0.20	"	
E-25h1	"	"	1.1	"	0.20	"	
E-25h2	"	"	2.0	"	0.20	"	
E-25h3	"	"	3.0	"	0.20	"	
E-25k3/4	"	magnesium di-(xylyl-stearate)	0.75	"	0.20	"	
E-25k1	"	magnesium di-(xylyl-stearate)	1.00	"	0.20	"	
E-25k1 $\frac{1}{2}$	"	"	1.50	"	0.20	"	
E-33a	di-(2-ethylhexyl) azelate	zinc di (phenyl-stearate)	0.35	"	0.15	"	

RESTRICTED

Characteristics of Some Diester Lubricating Oil Compositions (The Compositions are listed in Table XVIII.)

a = ASTM Slope 210 to 0°F.
b = ASTM Slope 210 to -40°F.
c = ASTM Slope 210 to -60°F.
n = Non-Newtonian behavior
* = interpolated
RESTRICTED

RESTRICTED

Table XX

Diester Lubricating Oils - Bomb Oxidation Tests at 212°F

Compositions are listed in Table XVIII

Diester oil com- position	ΔP psi	Neut. No.		Visc. in cs.		Description of appearance after oxidation test:	
		Before	After	Before	After	Of fluid	Of copper*
E-25c	0	0.30	0.73	12.6	12.6	faint green cast, clear	oxidized
E-25d	4	0.07	0.47	12.8	12.8	yellow, clear	"
E-25d ₁	1	0.02	0.32	13.5	13.5	light brown, clear	darkened
E-25d ₂	2	0.28	0.59	15.0	15.1	light brown, clear	"
E-25d ₃	2	0.28	0.75	16.8	16.7	" " "	"
E-25h ₁	0	1.23	1.60	13.0	13.0	pale yellow, clear	"
E-25h ₂	0	2.23	2.11	13.3	13.3	" " "	"
E-25h ₃	0	3.18	3.13	13.7	13.8	" " "	"

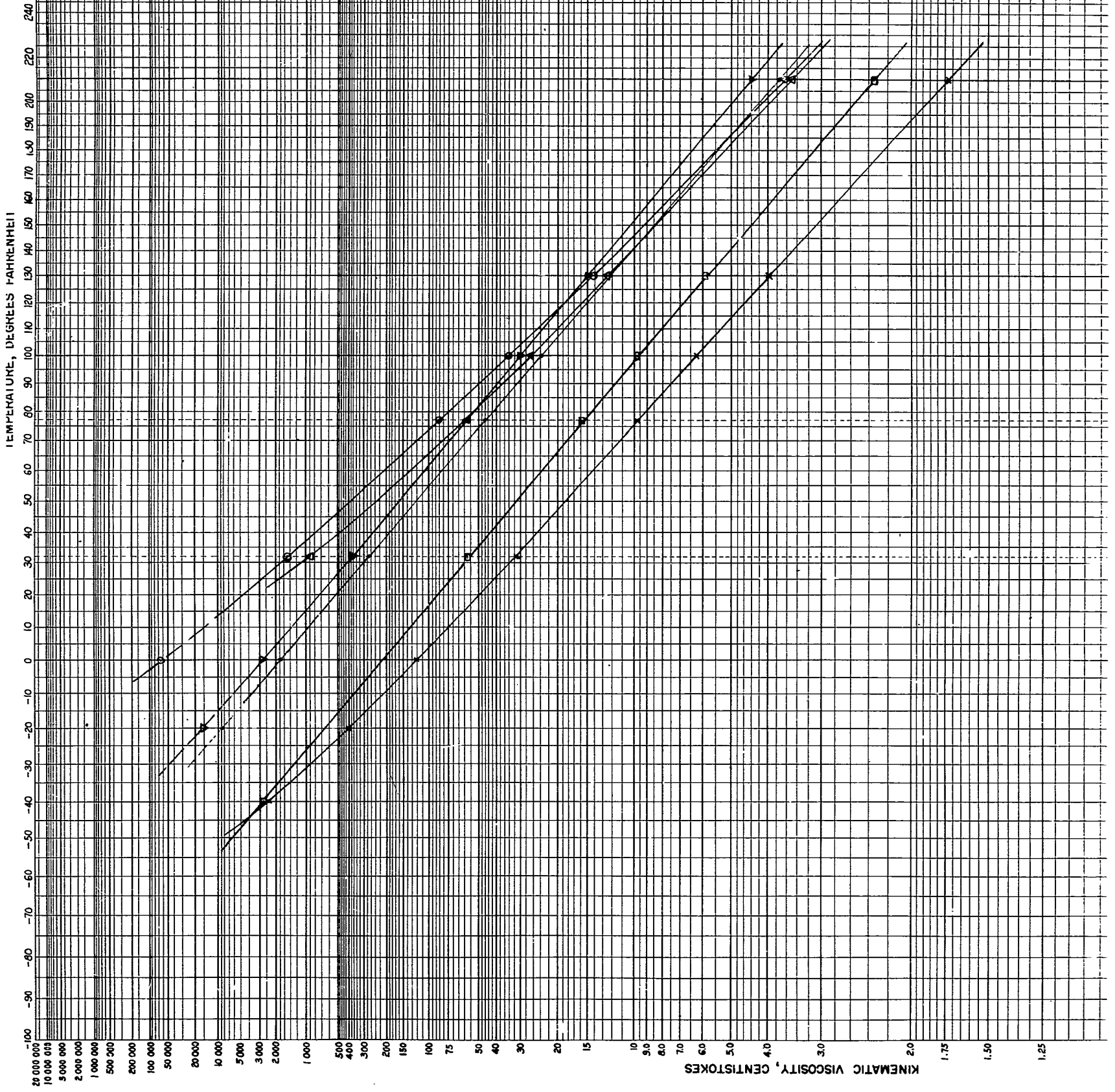
* No change in appearance of duralumin and cold-rolled steel.

TABLE XXI

Diester Lubricating Oils-Dynamic Oxidation Tests at 212°F. The Compositions are listed on Table XVIII.										
Diester Oil Composition	Neut. No. Before	Neut. No. After	Viscosity, c.s. Before	Volatile Acid 24hrs. After	Neut. No. After 100 hrs.	Neut. No. After 168 hrs.	Description of Fluid of Instrument Oils	Appearance After Oxidation of Copper	Appearance After Oxidation of Aluminum	Test of Steel
E-33a	0.42	0.61	11.0	0.88	1.72	3.56	6.08	Slight corrosion	n.c.*	oxidized
E-25c	0.30	0.50	12.6	0.72	2.04	4.16	6.70	light green - clear	n.c.	n.c.
E-25a	0.07	0.50	12.8	1.32	2.88	6.24	9.60	light green - clear	n.c.	n.c.
E-25d ₁	0.20	0.74	13.5	0.90	1.90	3.55	6.40	yellow - clear	n.c.	n.c.
E-25d ₂	0.51	0.10	15.0	1.00	2.20	3.95	6.80	yellow - clear	n.c.	n.c.
E-25d ₃	0.56	0.13	16.8	0.90	1.50	2.90	5.50	brown - clear	n.c.	n.c.
E-25h ₁	1.23	-	13.0	0.84	1.84	3.58	5.27	brown - clear	n.c.	n.c.
E-25h ₃	3.18	-	13.7	0.59	1.60	2.33	3.40	n.c.	n.c.	n.c.
E-22a	0.06	0.68	14.3	0.88	2.00	4.24	6.96	light - yellow	n.c.	n.c.

* n.c. = no change

RESTRICTED



VISCOSITY - TEMPERATURE CHARTS
MODIFIED FROM A.S.T.M. (D 341-39)
COMBINED C AND D CHARTS

- VISCOSITY-TEMPERATURE CHART OF
PHTHALIC ACID ESTERS
- X DI ETHYL PHTHALATE
 - DI BUTYL PHTHALATE
 - △ ETHYL PHTHALYL ETHYL GLYCOLATE
 - METHYL PHTHALYL ETHYL GLYCOLATE
 - BUTYL PHTHALYL BUTYL GLYCOLATE
 - ▽ DI [2 - ETHYLHEXYL] PHTHALATE

TEMPERATURE, DEGREES FAHRENHEIT

-100 -90 -80 -70 -60 -50 -40 -30 -20 -10 0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 220 240

VISCOSITY-TEMPERATURE CHARTS
MODIFIED FROM A.S.T.M. (D 341-39)
COMBINED C AND D CHARTS

VISCOSITY-TEMPERATURE CHART OF
ADIPIC ACID ESTERS

- X DI [1 - METHYLETHYL]
- DI [1 - ETHYLPROPYL]
- ▲ DI [1, 3 - DIMETHYLBUTYL]
- DI [2 - ETHYLBUTYL]
- DI [2 - ETHYLHEXYL]
- ▽ DI [2 - (2 - ETHYLBUTOXY) ETHYL]
- ⊗ DI [2 - (2 - BUTOXYETHOXY) ETHYL]
- ◇ DI [1 - METHYL, 4 - ETHYLOCTYL] or DIUNDECYL
- △ DI [1 - (2 - METHYLPROPYL), 4 - ETHYLOCTYL] or DITETRADECYL
- / DI [1 - (3 - ETHYLAUYL), 4 - ETHYLOCTYL] or DIHEPTADECYL

KINEMATIC VISCOSITY, CENTISTOKES

KINEMATIC VISCOSITY, CENTISTOKES

TEMPERATURE, DEGREES FAHRENHEIT

VISCOSITY - TEMPERATURE CHARTS
MODIFIED FROM A.S.T.M (D 341-39)
COMBINED C AND D CHARTS

VISCOSITY-TEMPERATURE CHART OF
AZELAIC ACID ESTERS

- X DI [1 - ETHYLPROPYL]
- O DI [2 - METHYLBUTYL]
- DI [2 - ETHYLBUTYL]
- ▽ DI [2 - BUTOXYETHYL]
- △ DI [2 - ETHYLHEXYL]

-100 -90 -80 -70 -60 -50 -40 -30 -20 -10 0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240

20 000 000
10 000 000
5 000 000
2 000 000
1 000 000
500 000
200 000
100 000
50 000
20 000
10 000
5 000
3 000
2 000
1 000
500
400
300
200
150
100
75
50
40
30
20
15
10
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.75
1.50
1.25

KINEMATIC VISCOSITY, CENTISTOKES

KINEMATIC VISCOSITY, CENTISTOKES

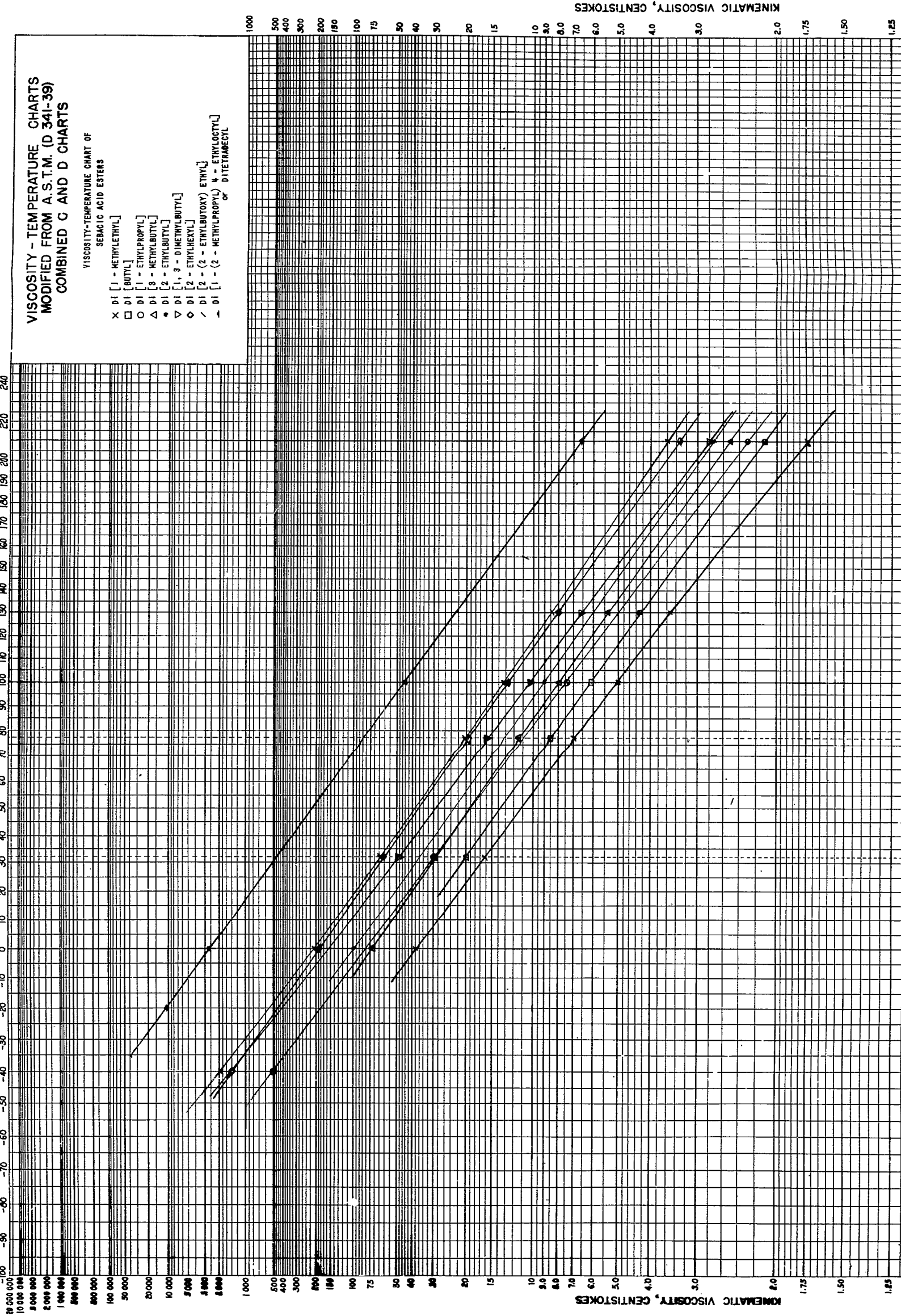
TEMPERATURE, DEGREES FAHRENHEIT

-100 -90 -80 -70 -60 -50 -40 -30 -20 -10 0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 220 240

VISCOSITY - TEMPERATURE CHARTS MODIFIED FROM A.S.T.M. (D 341-39) COMBINED C AND D CHARTS

VISCOSITY-TEMPERATURE CHART OF
SEBACIC ACID ESTERS

- X DI [1 - METHYLETHYL]
- DI [BUTYL]
- DI [1 - ETHYLPROPYL]
- △ DI [3 - METHYLBUTYL]
- DI [2 - METHYLBUTYL]
- ▽ DI [1, 3 - DIMETHYLBUTYL]
- ◇ DI [2 - ETHYLHEXYL]
- ∧ DI [2 - (2 - ETHYLBUTOXY) ETHYL]
- DI [1 - (2 - METHYLPROPYL) 4 - ETHYLOCTYL]
or DITETRADECYL



TEMPERATURE, DEGREES FAHRENHEIT

-100 -90 -80 -70 -60 -50 -40 -30 -20 -10 0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 220 240

20 000 000 10 000 000 5 000 000 2 000 000 1 000 000 500 000 200 000 100 000 50 000 20 000 10 000 5 000 3 000 2 000 1 000 500 400 300 200 150 100 75 50 40 30 20 15 10 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.75 1.50 1.25

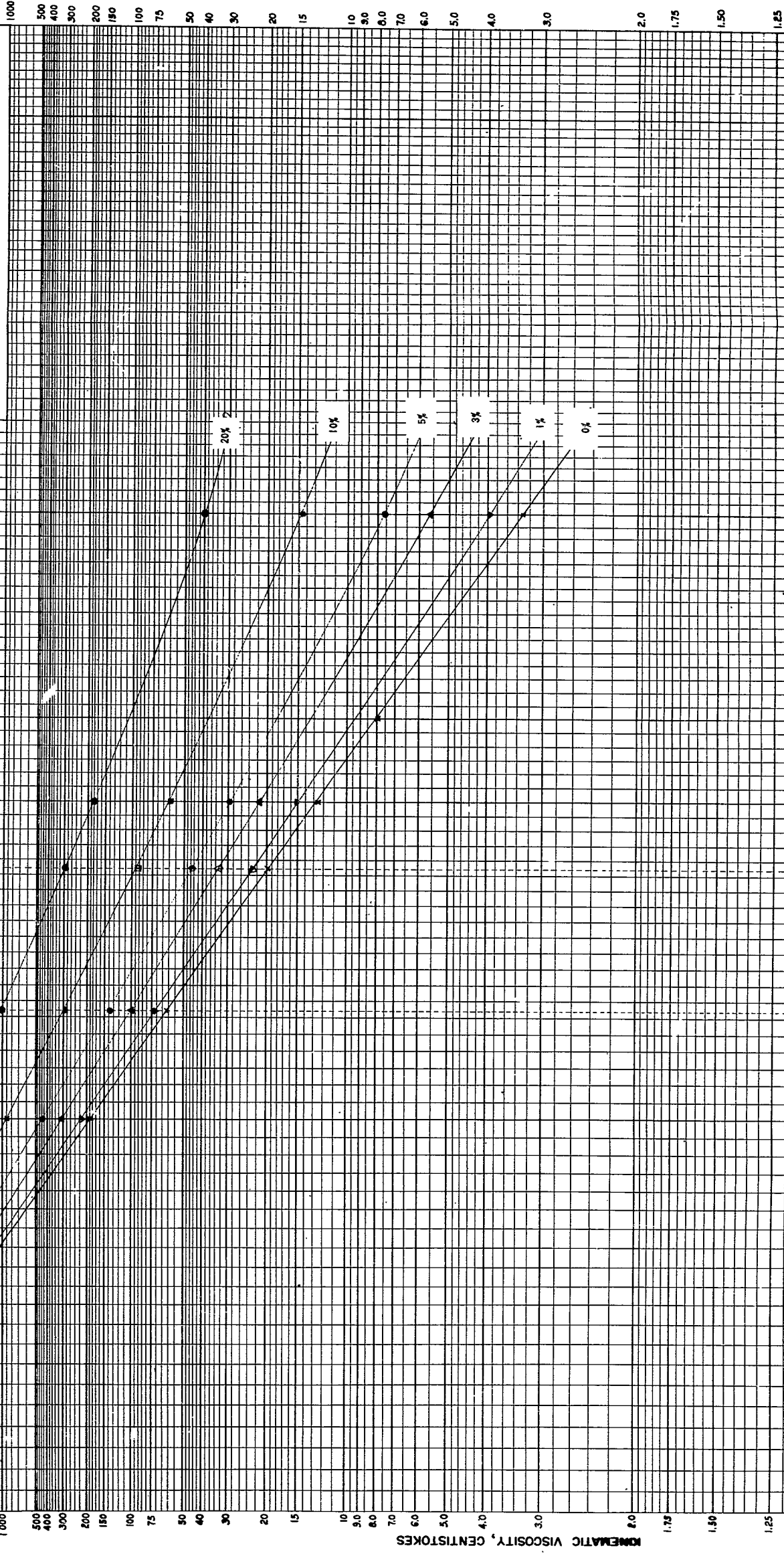
KINEMATIC VISCOSITY, CENTISTOKES

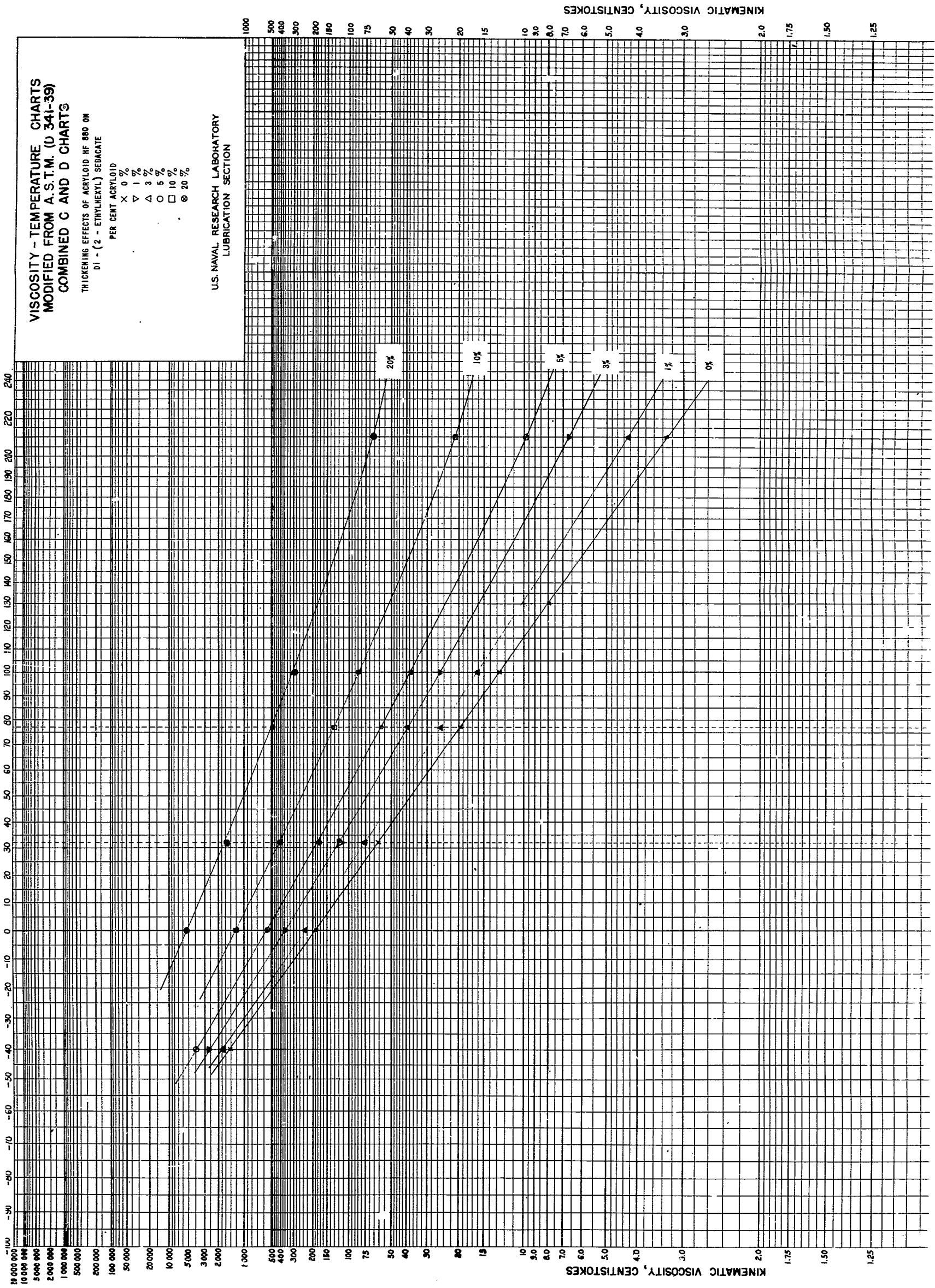
VISCOSITY - TEMPERATURE CHARTS
MODIFIED FROM A.S.T.M. (D 341-39)
COMBINED C AND D CHARTS

THICKENING EFFECTS OF ACRYLOID HF 845 ON
DI - (2 - ETHYLHEXYL) SEBACATE

- PER CENT ACRYLOID
- X 0 %
 - ▽ 1 %
 - △ 3 %
 - 5 %
 - 10 %
 - ⊗ 20 %

U.S. NAVAL RESEARCH LABORATORY
LUBRICATION SECTION





TEMPERATURE, DEGREES FAHRENHEIT

-100 -90 -80 -70 -60 -50 -40 -30 -20 -10 0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240

20 000 000

10 000 000

5 000 000

2 000 000

1 000 000

500 000

200 000

100 000

50 000

20 000

10 000

5 000

3 000

2 000

1 000

500

400

300

200

150

100

75

50

40

30

20

15

10

9.0

8.0

7.0

6.0

5.0

4.0

3.0

2.0

1.75

1.50

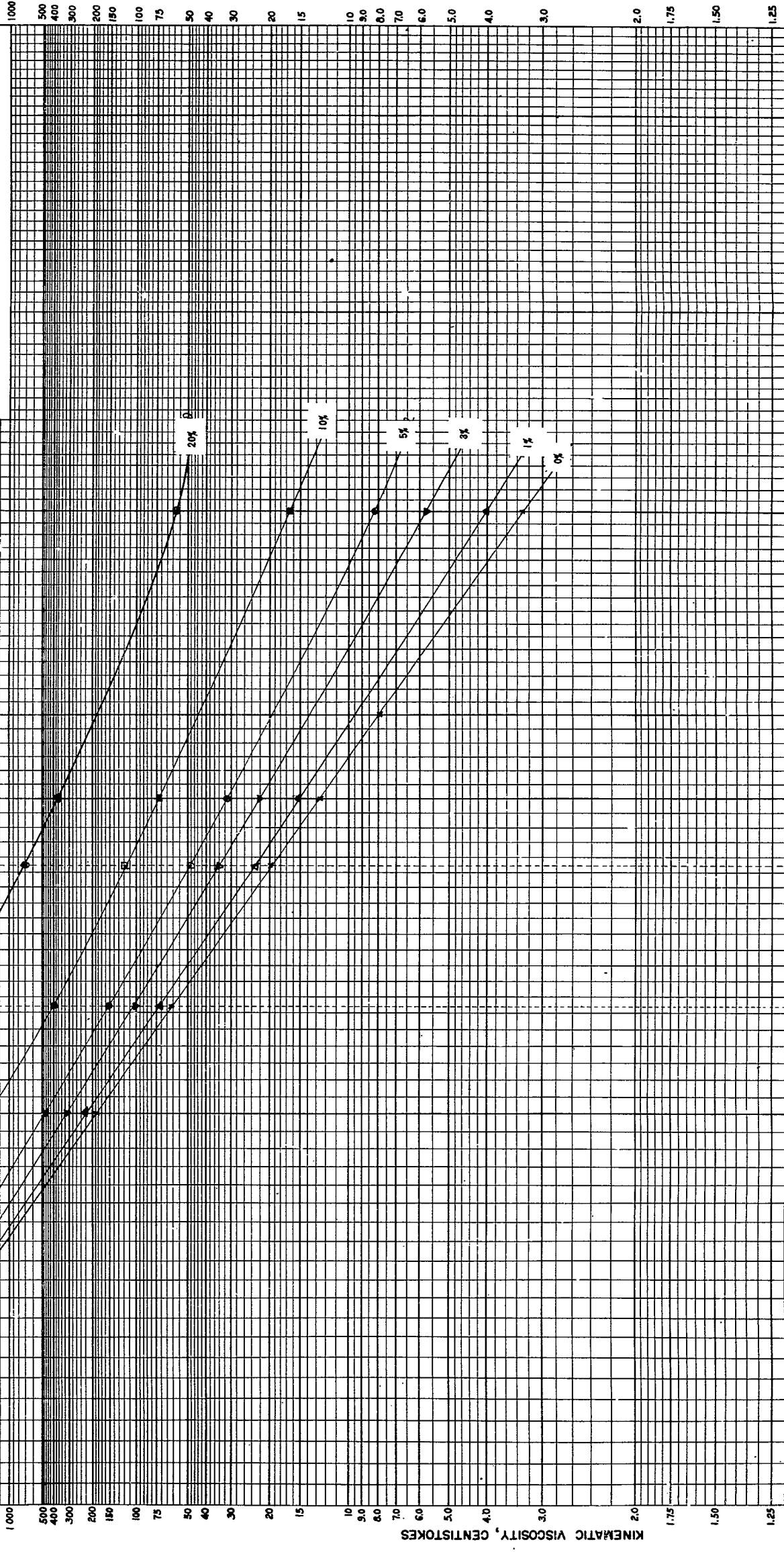
1.25

KINEMATIC VISCOSITY, CENTISTOKES

VISCOSITY - TEMPERATURE CHARTS
MODIFIED FROM A.S.T.M. (D 341-39)
COMBINED C AND D CHARTS

THICKENING EFFECTS OF ACRYLOID F10 ON
D.I. - (2 - ETHYLHEXYL) SEBACATE

PER CENT ACRYLOID
X 0 %
Δ 1 %
▽ 3 %
○ 5 %
□ 10 %
⊗ 20 %



DISTRIBUTION

BuAer	(5)
BuShips	(5)
BuOrd	(5)
OR&I	(2)

- e -

RESTRICTED

THE END

Microfilmed

by

*The Library of Congress
Photoduplication Service*
