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VAPOR PHASE OXIDATION AND SPONTANEOUS IGNITION OF ORGANIC COMPOUNDS

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by

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I. Introduction

A study of the spontaneous ignition characteristics of lubricating oils has been considered important by the National Advisory Committee for Aeronautics because the spontaneous ignition of lubricants by hot surfaces is a major factor in the initiation of fires in aircraft. For this reason the National Advisory Committee for Aeronautics has sponsored a series of research projects at the Applied Science Research Laboratory to pursue a study of this problem. The study conducted at this laboratory may be divided into three principle phases.

First, spontaneous ignition temperatures of a number of pure chemical compounds have been determined. In the selection of these compounds attention was given to simple molecules which would compare with the structural units found in fuels and lubricants. The effect of metals and additives on some of these pure compounds was studied. Definite correlation was observed between spontaneous ignition and chemical structure of these compounds.

Second, the test procedure was extended to a wide variety of lubricants to observe whether or not the lubricants behaved as would be predicted from a comparison of the structural unit of the lubricant with simple compounds of similar structure. A factor of low volatility obscured this comparison in the case of the more viscous oils. This difficulty prompted the use of a spray injector for the introduction of the oil into the ignition chamber. With this modification in procedure the correlation of spontaneous ignition with chemical structure was extended to lubricants of high viscosity.

Third, consideration was given to the reaction processes leading to the spontaneous ignition of organic compounds. The procedure consisted of passing a definite fuel-oxygen mixture through a hot tube and condensing and analyzing the resultant reaction mixture. The use of a smaller diameter reaction tube and shorter contact times than previously reported in the literature permitted a clearer understanding of the initial reaction processes than had previously been obtained.

II. Historical Background

Just what is meant by spontaneous ignition temperature may be illustrated in general fashion in the following way. When any volatile combustible material is heated in an atmosphere containing oxygen the rate of oxidation increases with temperature. As the temperature continues to rise, a temperature may be reached where due to the exothermic oxidation reaction the rate of generation of heat just balances the rate of dissipation of heat. This temperature may be referred to as the spontaneous ignition temperature because at temperatures just above this heat equilibrium temperature the reaction rapidly accelerates and the vapor ignites. Certain modifications of this definition of spontaneous ignition temperature became necessary as this investigation proceeded; these will be discussed at appropriate places later in the report.

No doubt the early workers in this field considered the possibility of spontaneous ignition temperature being as much of a characteristic property of a compound as melting point or boiling point. However, it soon became evident that this was not so and the spontaneous ignition temperature of a compound may vary widely according to a variety of variable conditions. Such conditions include material of ignition vessel, concentration of oxygen in the vapor mixture, volume of ignition chamber, time lag before ignition, pressure, amount of combustible material charged into ignition chamber.

According to a review of spontaneous ignition temperature by W. Helmore[1] in 1938, H. Holm in 1913 was the first to report spontaneous ignition temperature determinations by dropping combustible material on a heated porcelain surface. H. Moore in 1917 used a

platinium crucible inbedded in a steel block heated by a gas burner to determine spontaneous ignition temperatures. Dry preheated air or oxygen was delivered to the crucible. His work represented the first positive attempt to correlate ignition temperatures and engine behavior; he concluded that fuels for spark ignition engines should have high spontaneous ignition temperatures and fuels for compression ignition engines should have low ignition temperatures.

From the work done before 1938 Helmore was able to compile the following generalizations relative to spontaneous ignition of pure compounds:

(1) Open chain paraffinic hydrocarbons have low spontaneous ignition temperatures which decrease with rise in molecular weight of the hydrocarbon.

(2) Branched chain paraffins have much higher spontaneous ignition temperatures than corresponding paraffins.

(3) Olefins have variable spontaneous ignition temperatures but often higher than corresponding paraffins.

(4) Napthenes have in general higher spontaneous ignition temperatures than those of n-paraffin and olefins.

(5) The aromatic hydrocarbons have much higher spontaneous ignition temperatures than other hydrocarbons.

(6) Alcohols possess higher spontaneous ignition temperatures than corresponding hydrocarbons.

(7) Aldehydes have much lower spontaneous ignition temperatures than corresponding hydrocarbons.

(8) Introduction of bromine or chlorine atoms or nitro groups leads to reduction in spontaneous ignition temperature; introduction of amino group causes increase in spontaneous ignition temperature.

In 1941 Sortman, Beatty and Heron[2] reported the existence of zones of nonignition for some n-paraffins and decalin using a Moore type apparatus. They also observed a remarkable inhibition of spontaneous ignition of paraffins by tetraethyl lead.

Emphasis has been placed upon the crucible method for determination of ignition temperatures because it is the most convenient and it is the method used in this investigation. Among other methods that have been used for determining ignition temperatures are dynamic tube methods, bomb methods, and methods involving adiabatic compression.

A rather detailed example of the effect of branching in the hydrocarbon chain on the rate of oxidation was reported by Cullis and Mulcahy[3] on isomeric hexanes.

Paraffin structure	Relative oxidation rate
C-C-C-C-C-C	1590
C-C-C-C-C C	560
C-C-C-C-C C	60
C C-C-C-C C	12
C-C-C-C C C	1

Some work has been done on determining the compounds formed in the sequence of oxidation steps. However, many different products have been obtained and it has been extremely difficult to fix them into a definite reaction mechanism. As yet an established reaction mechanism describing spontaneous ignition is lacking. Perhaps the best starting point is the mechanism of hydroperoxide formation advanced by Walsh[4]:

(a) Formation of a free radical

$$RH \rightarrow R\cdot$$

(b) Reaction with oxygen

$$R\cdot + O_2 \rightarrow R\text{-}OO\cdot$$

(c) Abstraction of a hydrogen atom

$$R\text{-}OO\cdot + R\,H \rightarrow ROOH + R\cdot$$

(d) Chain branching through decomposition of hydroperoxide

$$ROOH \rightarrow RO\cdot + HO\cdot$$

III. Description of Apparatus

1. The Spontaneous Ignition Cup

The spontaneous ignition cup and accessories were modeled after the equipment of Sortman, Beatty and Heron[2]. This consisted of a cavity in a metal block housed in an electric crucible furnace. A convenient modification for the present investigation was the construction of metal cup assemblies which could be placed in the cavity of the metal block. Complete cup assemblies of seven different metals were made so that the effects of metals on spontaneous ignition could be observed. Each cup assembly consisted of a base plate, a sleeve, and a lid which were accurately machined to fit tightly into the cavity in the metal block. An arrangement was made for air to be preheated and enter the chamber through four small openings at the base of the sleeve. A thermocouple was placed in a recess in the bottom of the base plate. The temperature of the cup was obtained directly from this thermocouple by use of a Leeds and Northrop potentiometer. The details of the apparatus are shown in figures 1 and 2.

Throughout this investigation two units were used, one with a stainless steel block, the other with a copper block, and the metal cup assemblies used interchangeably. These two units gave parallel spontaneous ignition results. However, the copper block unit was not used at high temperatures because of the rapid formation of a heavy copper-oxide layer.

2. The Spray Injector

In an effort to reduce the influence on the ignition temperature of the slow rate of volatization of higher molecular weight materials a spray injector was constructed. The details of this construction

Figure I

Cross Sectional View of Ignition Apparatus - Showing Arrangement of Metal Block in Furnace but not Including the Cup Assembly

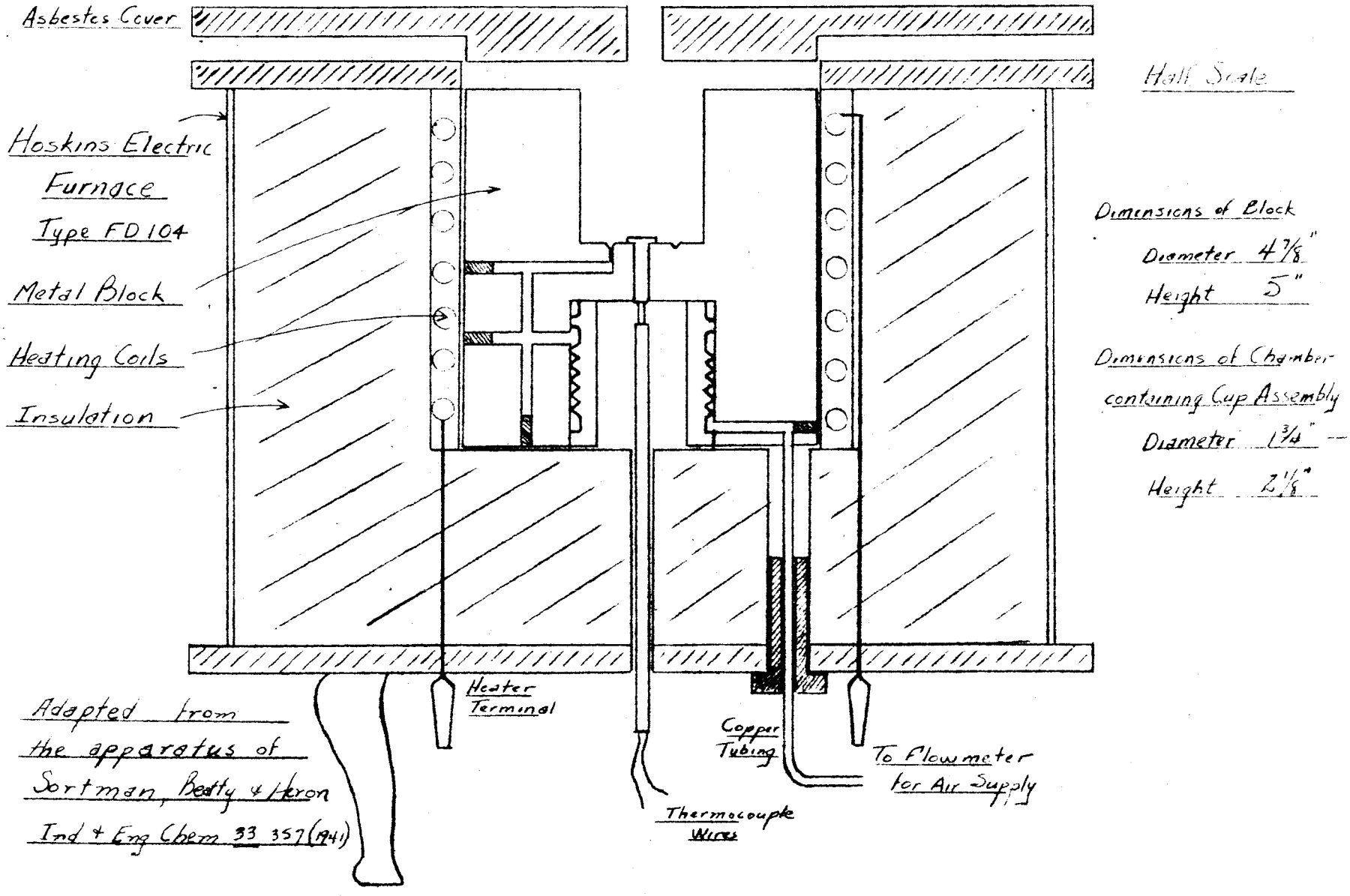
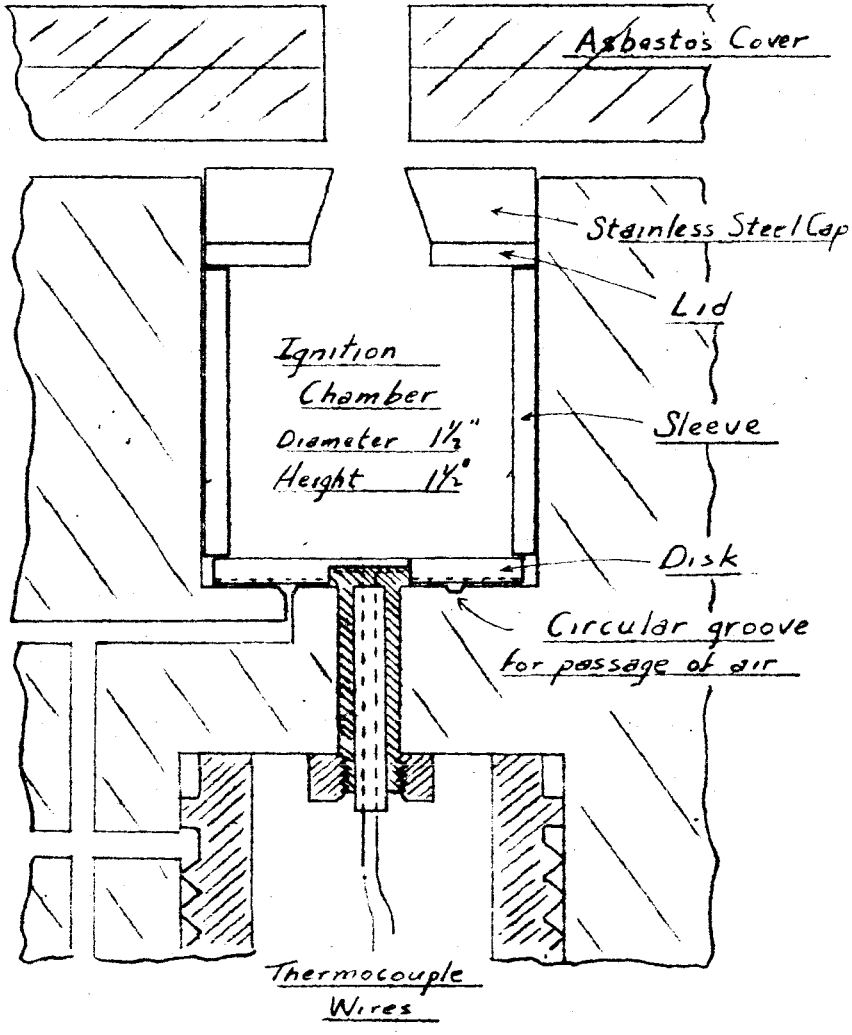
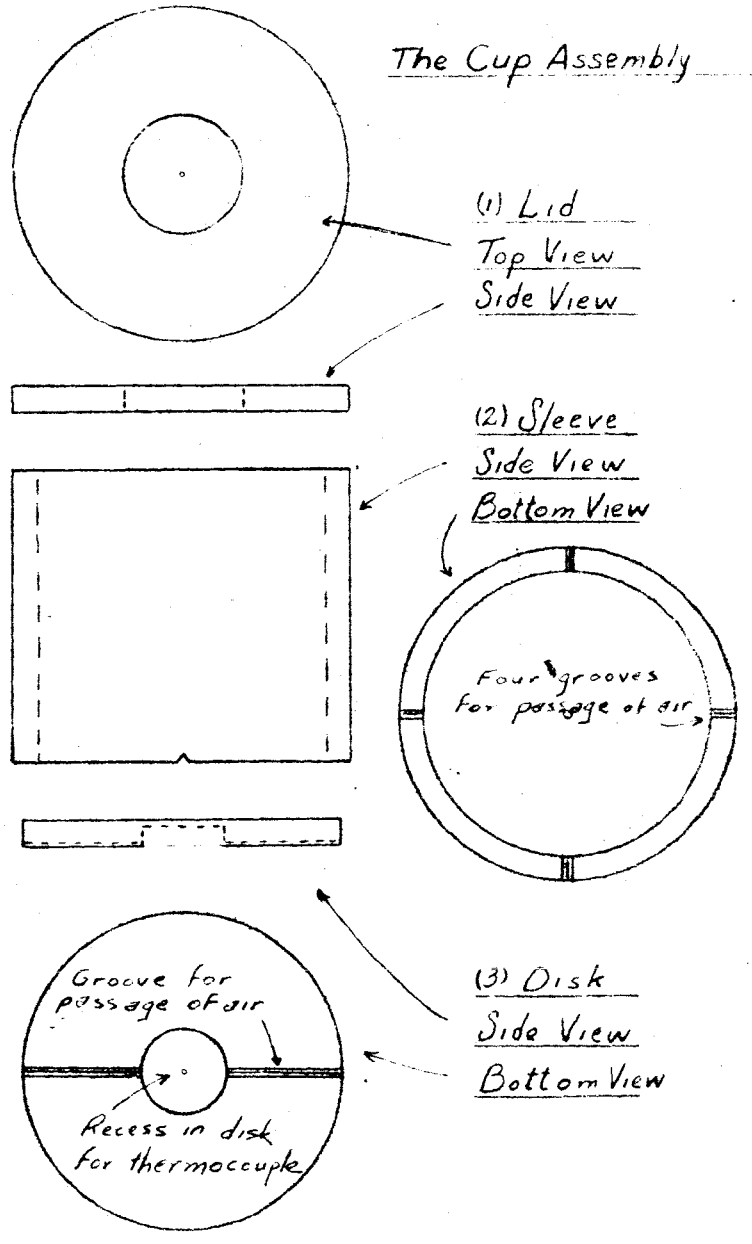


Figure II

Cross Sectional View of Metal Block
Showing the Ignition Cup Assembly



The Cup Assembly



Full Scale

are shown in figures 3 and 4. The apparatus consists of a hand operated piston which ejects the liquid through a small opening (approximately eight thousandths of an inch in diameter) from a cylinder 0.125 inches in diameter. Some asbestos packing in the cylinder prevents leakage of oil. This injector worked satisfactorily with oils of viscosities up to about 500 SSU at 100°F. For more viscous oils it would be necessary to construct an injector which would permit still higher piston pressures; this was considered beyond the scope of this investigation.

3. The Vapor Phase Oxidation Apparatus

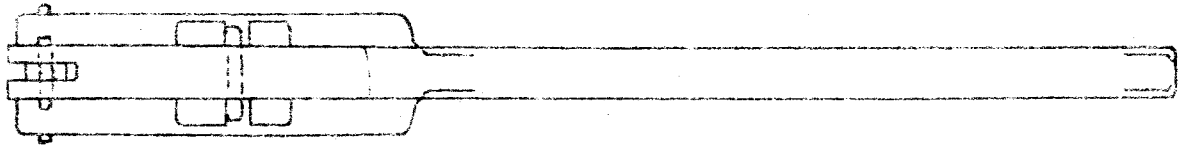
The apparatus comprises essentially three stages: (1) the hydrocarbon-oxygen mixing tube, (2) the oxidation chamber, and (3) cold traps and gas analyzer. These are illustrated in figure 5.

(1) Tank oxygen is first dried by passing through sulfuric acid. It is then passed through a flowmeter and bubbled into the hydrocarbon, held at a constant temperature by a vapor bath to secure a constant fuel/oxygen ratio. The fuel/oxygen mixture enters the oxidation chamber through a glass tube heated to a temperature slightly higher than the vapor bath to prevent any condensation.

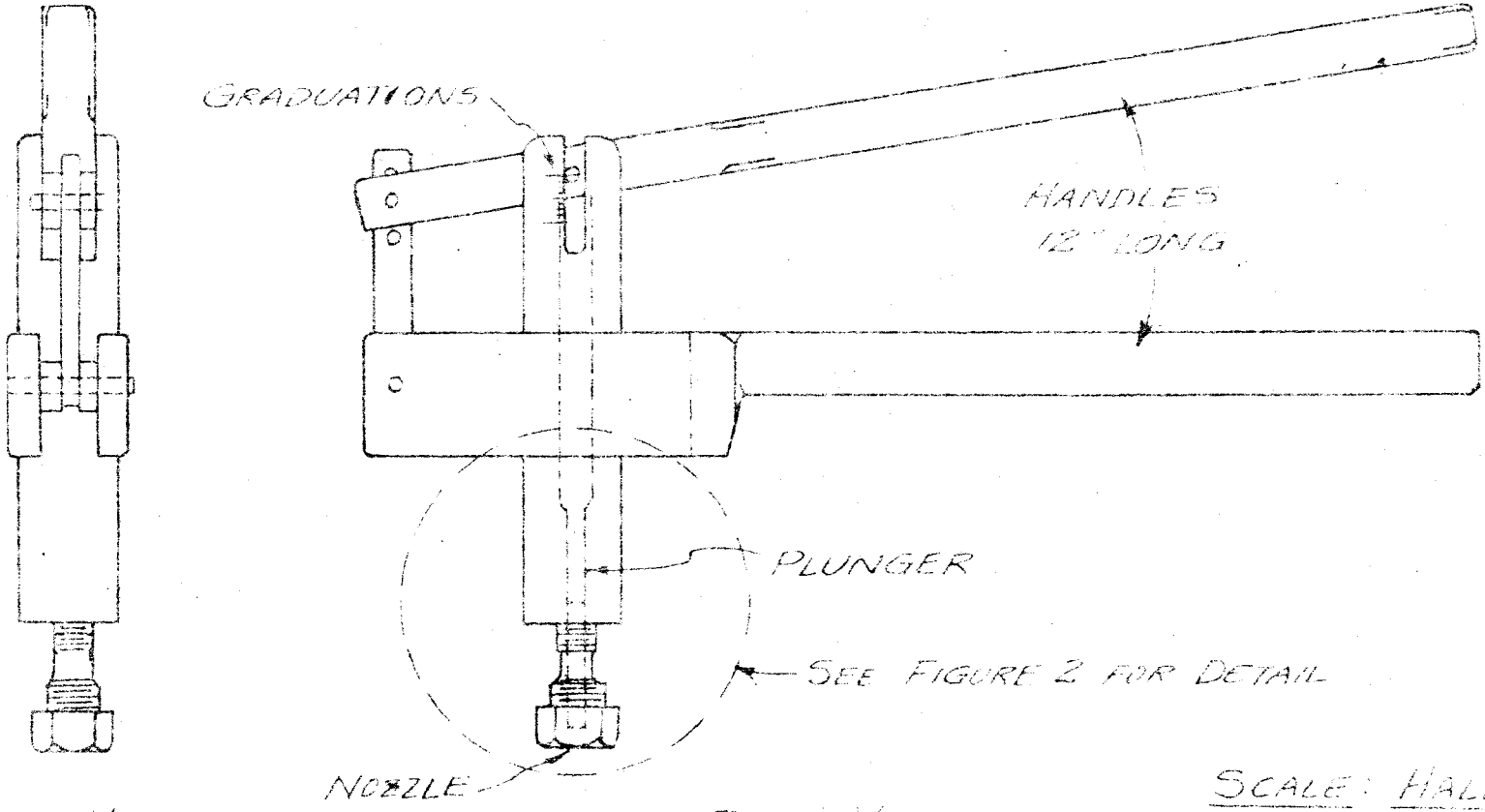
(2) The oxidation thus far has been conducted in a glass tube of about 1/16" I.D. This tube passes through a heating unit comprising a steel rod 1" in diameter and 12" long heated in an electric furnace. The rod is drilled lengthwise to provide a close-fitting jacket about the glass tubing. This rod also contains a smaller hole into which the thermocouple is inserted. The distribution of temperature through the reaction tube was determined for various peak temperatures; the results are shown in figure 6.

FIGURE 3

SPRAY INJECTOR APPARATUS (ASSEMBLY)



TOP VIEW



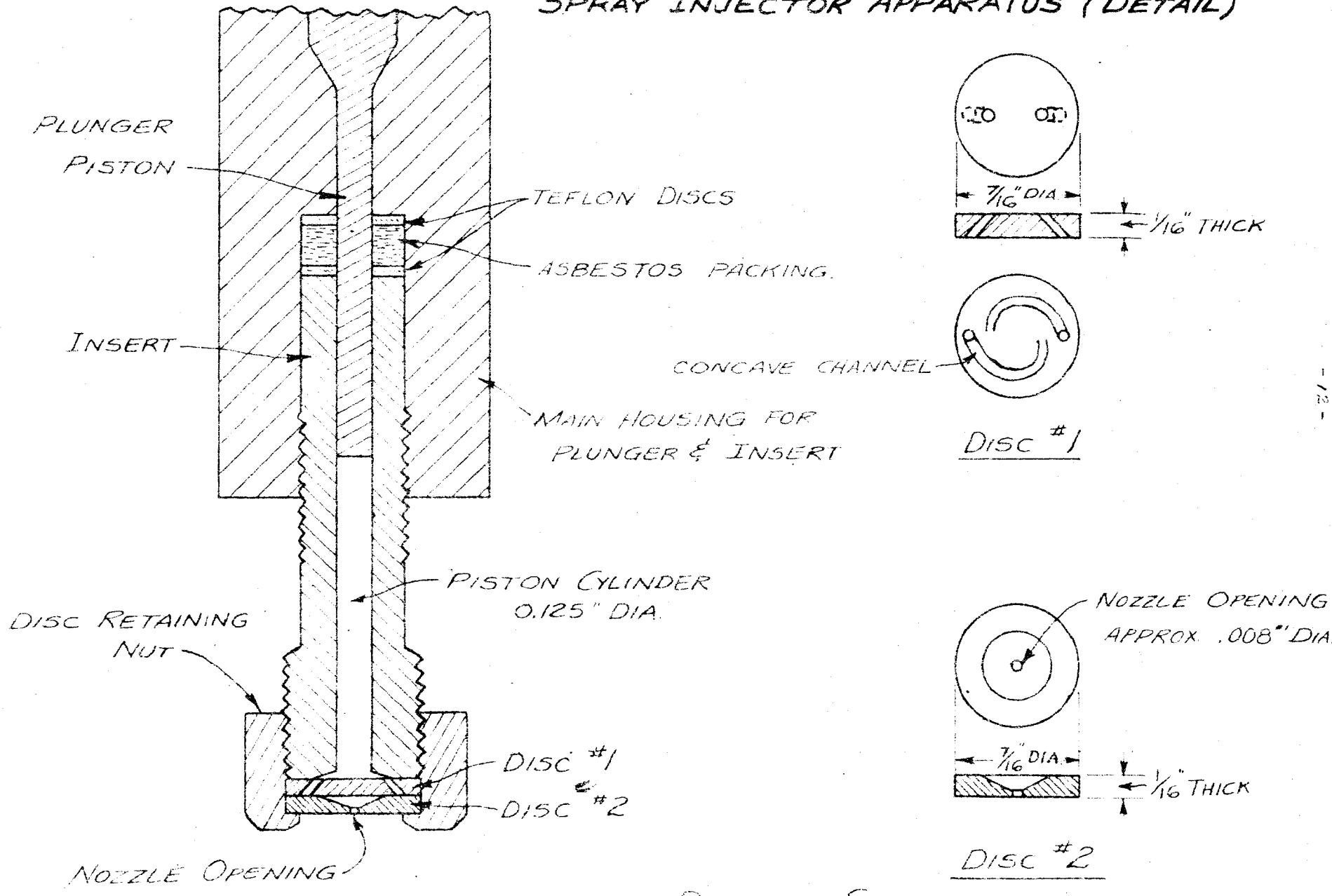
FRONT VIEW

SIDE VIEW

SCALE: HALF SIZE

FIGURE #4

SPRAY INJECTOR APPARATUS (DETAIL)

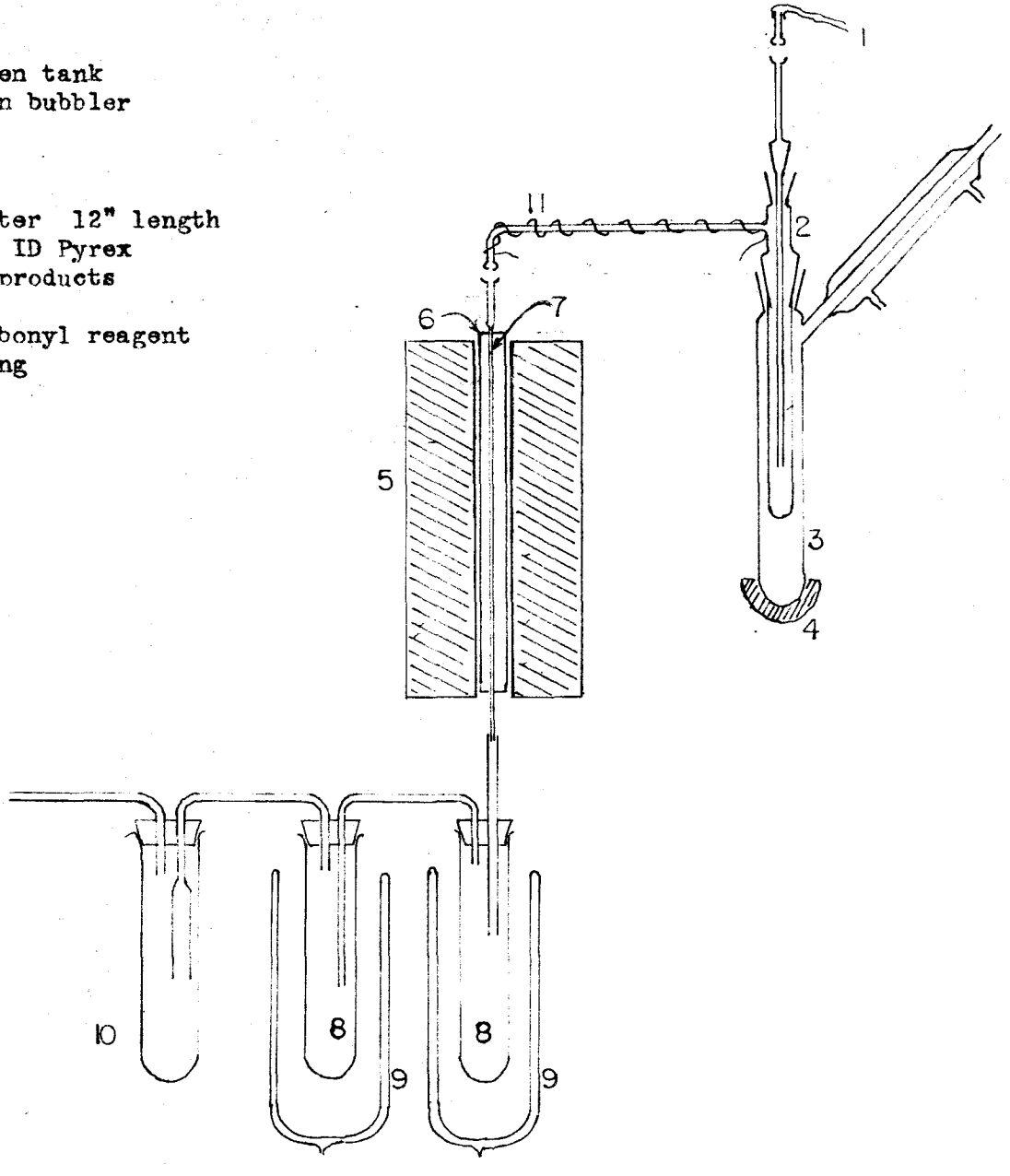


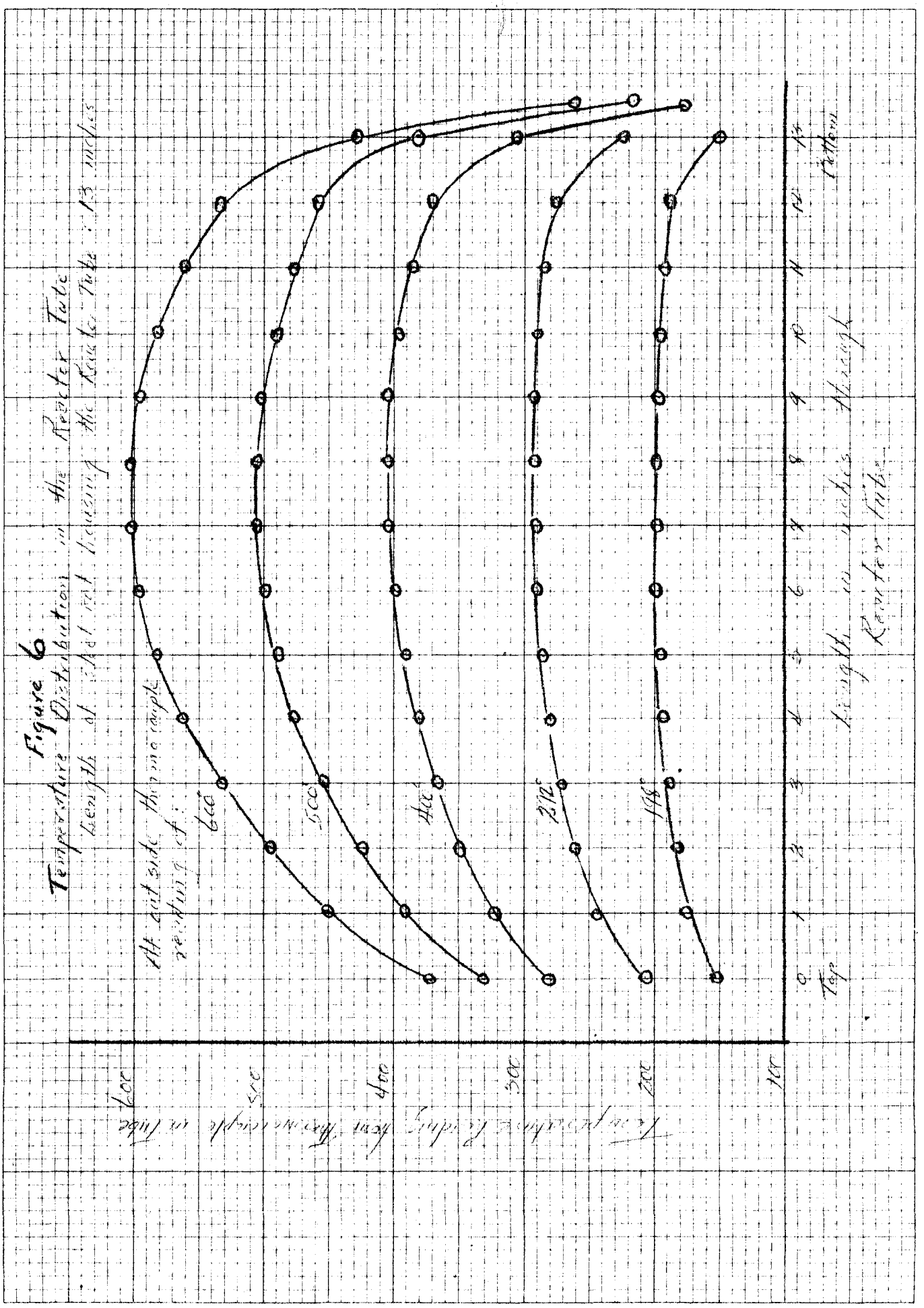
DOUBLE SIZE

Figure 5

The Apparatus

1. To flowmeter & oxygen tank
2. Hydrocarbon - oxygen bubbler
3. Vapor bath
4. Heating Mantle
5. Combustion Furnace
6. Steel Rod $1\frac{1}{4}$" diameter 12" length
7. Reaction Tube 1/16" ID Pyrex
8. Traps for reaction products
9. Dewar Flasks
10. Trap containing carbonyl reagent
11. Coil for mild heating





(3) The third stage consists of a series of two dry ice-acetone cold traps, and a 2,4-dinitrophenylhydrazine solution through which the gas is bubbled after leaving the traps. The final exit gas is checked periodically for carbon monoxide, carbon dioxide, hydrogen, oxygen, and volatile hydrocarbons by means of a Burrell "Industro" gas Analyzer.

To permit the collection of a larger sample, a six-tube reaction chamber was constructed. Six tubes, each of 0.125 inch diameter were supported by rubber stoppers within a large glass tube of one inch diameter. Iron powder was placed inside the large tube and around the smaller ones to serve as a heat conducting medium. This reactor, therefore, merely replaced the single tube reactor when larger samples were desired.

IV. Test Procedure and Precision

1. Determination of Spontaneous Ignition Temperatures

Spontaneous ignition temperatures were determined for a selected series of organic compounds of high purity including n-paraffins, branched paraffins, α-olefins, aromatic hydrocarbons, alcohols, ethers, and esters. The methods of purification and the physical properties of these compounds are given in table I.

To determine the spontaneous ignition temperature, the electric furnace is heated rapidly to the desired temperature range of operation. Then the furnace rheostat is adjusted so the furnace will cool at a desired rate. One drop of the material to be tested is introduced into the ignition chamber. If an ignition occurs the induction period is recorded (measured with a stop watch); also recorded is the temperature of the chamber just prior to the addition of the drop. If no ignition occurs this procedure is repeated with two or more drops after a time interval of at least two minutes to allow the oxidized gases to be flushed out by the incoming air. As the furnace cools this procedure is repeatedly followed, using more drops when necessary to effect the ignition, until a temperature is reached where no amount of material added will result in an ignition. The temperature of the preceding ignition is taken as the spontaneous ignition temperature. In this lower range the rate of cooling is reduced by approximately $1^{\circ}C$ per 2 to 5 minutes so that the spontaneous ignition temperature can be observed to the nearest degree.

The rate of air flow most generally used in these experiments has been 125 cubic centimeters per minute. At this rate, the ignition chamber is flushed out during the 2-minute time interval between additions. In some experiments, a 25 cc/minute rate of flow was used.

Table. I

Purification and Physical Constants of Compounds

Compound	Source	Purity designation	Additional Purification	Refractive Index				Density				Freezing Point			Boiling Point	
				Temp	Observed	Literature	Ref.	Temp	Obs.	Lit.	Ref.	Obs.	Lit.	Ref.	Pressure	Temp.
n-Paraffins																
n-Heptane	D	Pure grade 99%	N	25	1.3851	1.38511	22	25	.6793	.67951	22				740	97.0
n-Decane	A	Eastman	MN	25	1.4098	1.40986	18	25	.7263	.72643	18				20	72.8
n-Dodecane	B	> 95%	N	25	1.4196	1.41945	17	25	.7449	.74512	17				10	92.8
n-Tetradecane	A	Eastman	MN	25	1.4268	1.42681	17	25	.7590	.75913	17				10	124.2
n-Hexadecane	B	> 95%	N	25	1.4324	1.43248	17	25	.7695	.76993	17				9	148.0
n-Octadecane	A	Eastman	MN	28	1.4358	1.43582	17	28	.7771	.77646	17	28	28	19	29	202
n-Nonadecane	C		SMN									32.0	32	23	10.9	189.4
n-Eicosane	C		SMN									36.8	36-7	23	10.8	198-9
Branched Paraffins																
2,2,4-Trimethylpentane	D	Pure grade 99%	N	20	1.3914	1.39157	24									
2,3,5-Trimethylheptane	E	> 95%	O	20	1.4148	1.4149	25									
4,5-Dimethyloctane	E	> 97%	O	20	1.4189	1.4190	25									
4-Isopropylheptane	E	> 97%	O	20	1.4170	1.4171	25									
3-Ethyloctane	E	> 98%	O	20	1.4148	1.4150	25									
2-Methyldecane	E	> 99%	O	20	1.4153	1.4154	25									
Olefins																
1-Decene	B	> 95%	N	20	1.4212	1.4213	20	25	.7374	.7369	20				9.0	55.0
1-Dodecene	B	> 95%	N	20	1.4300	1.4301	20	25	.7552	.7553	20				5.2	77.8
1-Tetradecene	B	> 95%	N	20	1.4360	1.4365	19	25	.7647						5.0	106.2
1-Hexadecene	B	> 95%	N	20	1.4411	1.4410	20	25	.7779	.7777	20				6.1	137
1-Octadecene	B	> 95%	N	20	1.4450	1.4449	20	25	.7856	.7857	20				10.0	174.3
Ethers																
Diethyl Ether	G	C.P., Abs.	QT													
Diisopropyl Ether	F		QT	20	1.3691											
Dihexyl Ether	A	Eastman	NT	25	1.4186										14.5	107.5
Dioctyl Ether	B	> 95%	NT	25	1.4312										6.2	149
Didecyl Ether	B	> 95%	NT	25	1.4393										4.7	188

Table I (cont'd)

Compound	Source	Purity designation	Additional Purification	Refractive Index				Density				Freezing Point			Boiling Point	
				Temp	Obs	Lit	Ref.	Temp	Obs	Lit	Ref	Obs	Lit	Ref.	Pressure	Temp
Aromatic Hydrocarbons																
Benzene	G	C.P.	Q	25	1.4972	1.49792	21	25	.8727	.87319					740	79.4
Toluene	G	C.P.	N	25	1.4939	1.49413	21								740	109.6
o - Xylene	A	Eastman	N	20	1.5020	1.50545	21								740	143.8
m - Xylene	A	Eastman	N	20	1.4971	1.49722	21								740	139.8
p - Xylene	A	Eastman	N	20	1.4957	1.49582	21								740	138.5
1,2,3 - Trimethyl benzene	A	Technical	N	25	1.5078	1.51150	21								740	162-3
1,2,4 - Trimethylbenzene	A	Mixture	N	25	1.4994	1.50237	21								740	168-9
1,3,5 - Trimethylbenzene	A		N	25	1.4933	1.49684	21								740	164-6
1,2,4 - Triethylbenzene	A	Technical	N	20	1.4970	1.4968	24									
1,3,5 - Triethylbenzene	A	Mixture	N	20	1.4958	1.4951	24									
α-Methyl naphthalene	A	Practical	NP	20	1.6088	1.6157	24								12	113
Alcohols																
Ethanol		Absolute	R	18.4	1.3622	1.36242										
Propanol	G	C.P.	N	20	1.3858	1.38543										
Isopropanol	F	99%		20	1.3773	1.37757	23									
1 - Decanol	B	>90%	N	20	1.4370	1.4372	19					5.8	6-7	19	7.2	111
1 - Decanol	B	>90%	N	24.5	1.4408	1.4408	19					23.9	24.0	19	5	129.8
1 - Tetradecanol	B	>90%	N									37.5	38-9	19	68	156.2
1 - Hexadecanol	B	>90%	N									48.9	49	23	n/	148
1 - Octadecanol	B	>90%	N									57.7	57.95	23	n/	167
Esters (listed in Table IX)	H	High Purity	P													

Source

A - Eastman Kodak Company
B - Humphrey-Wilkinson Company
C - Atlantic Petroleum Company
D - Phillips Petroleum Company
E - A.P.I. Project #45 courtesy C.E. Boord
F - Carbide + Carbon Chemicals Company
G - Colemian + Bell Company
H - Naval Research Laboratory courtesy W.A. Zisman

Additional Purification

M - Chlorosulfonic acid treatment (Reference 18)
N - Fractionation through 90cm. glass helices packed column taking center cut of fractionation for experimental use
O - Percolation through silica gel
P - Percolation through alumina
Q - Refluxing with sodium and simple distillation
R - Refluxing with magnesium ethoxide + simple distillation
S - Fractionation of a C_{20} st-chain paraffin hydrocarbon sample
T - Test for peroxides before use; if necessary percolation through alumina

Here it was necessary to increase the air flow after each ignition to flush the chamber, and then to readjust the rate to 25 cc/minute at the end of the 2-minute time interval. The 25 cc/minute air flow rate gave readings that were generally some 3° to 8° C lower than the 125 cc/minute rate.

Three different types of oxidation phenomena have been observed and classed as ignitions in determining the spontaneous ignition temperature:

(1) A visible flame or flash, blue or yellow in color.

(2) A visible glow within the chamber, usually green or blue (sometimes yellow) which may or may not be followed by a puff of smoke ("cool flame" ignition).

(3) A definite puff of smoke after a reasonable induction period.

The last two types are usually observed at the spontaneous ignition temperature and temperatures slightly above. In this range the optimum fuel-air ratio to produce a flame is quite sensitive; if slightly exceeded, a glow or puff of smoke results instead of the flame.

For the hydrocarbons, alcohols, and olefins, the maximum amount required to effect an ignition was 30 to 40 milligrams (10 drops) at the spontaneous ignition temperature; the induction period was 30 to 60 seconds. The addition of larger than 40 milligram quantities of material did not lower the spontaneous ignition temperature more than a degree or two.

For the ethers, it was necessary to add much larger amounts of material to produce an ignition in the temperature range just above the spontaneous ignition temperature. The induction period remained quite short in this range and, even at the spontaneous ignition

temperature, it was only 8 to 12 seconds. Apparently the large amount of material was needed so that a high ether concentration in the vapor phase could be achieved very soon after the addition; otherwise, on addition of a smaller amount of material, the rate of oxidation would be faster than the rate of vaporization and, accordingly, sufficient concentration of ether for normal ignition could not be attained. The maximum amount of any ether added at the spontaneous ignition temperature was 100 milligrams (in the case of didecyl ether). Because of the very short induction period with the ethers, the material was added all at once rather than dropwise.

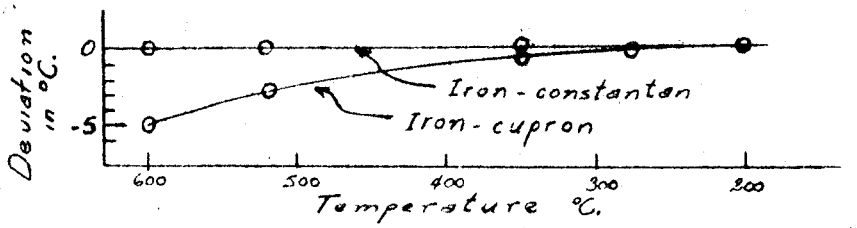
For some aromatic compounds tested the optimum amount of material for ignition did not exceed 3 to 5 drops (about 9 to 15 mg) even at the spontaneous ignition temperature. More than this amount failed to give ignition in the range just above the spontaneous ignition temperature. This probably results from a rapid rate of vaporization which volatilizes the material before the rate of oxidation becomes significant.

Spontaneous ignition temperature readings below 300°C have been reproducible generally within 1°C; at higher temperatures the accuracy is in the range of 3° to 5°C. The temperature actually observed (at thermocouple in recess of base plate) agrees within not more than 2°C with the temperature at the surface of the base plate where ignition would be expected to occur; in the lower range, this agreement is within 1°C. To obtain a complete picture of the heat distribution throughout the ignition chamber, thermocouples were placed in other parts of the ignition assembly and observations were made at various temperatures during both heating and cooling periods. These results are summarized in figure 7. The temperature differentials observed

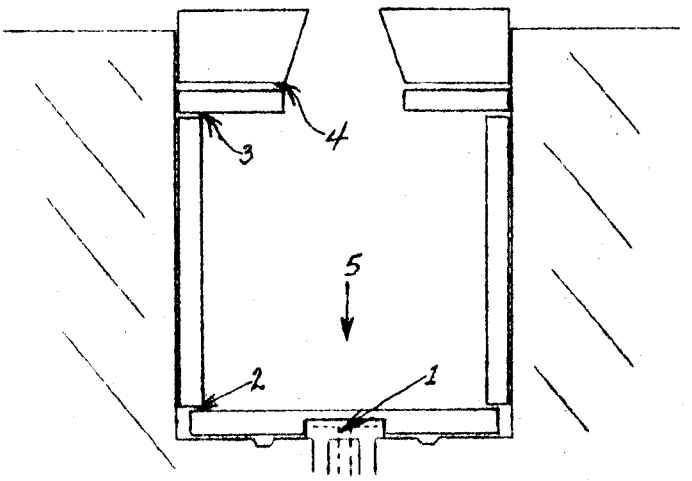
Figure VII

Temperature Distribution in the Metal Cup Assembly

Part (a) Calibration of an iron - cupron thermocouple (like those permanently located in the metal blocks) with an iron-constantan thermocouple. A Leeds-Northrup potentiometer calibrated for iron constantan thermocouples was used.



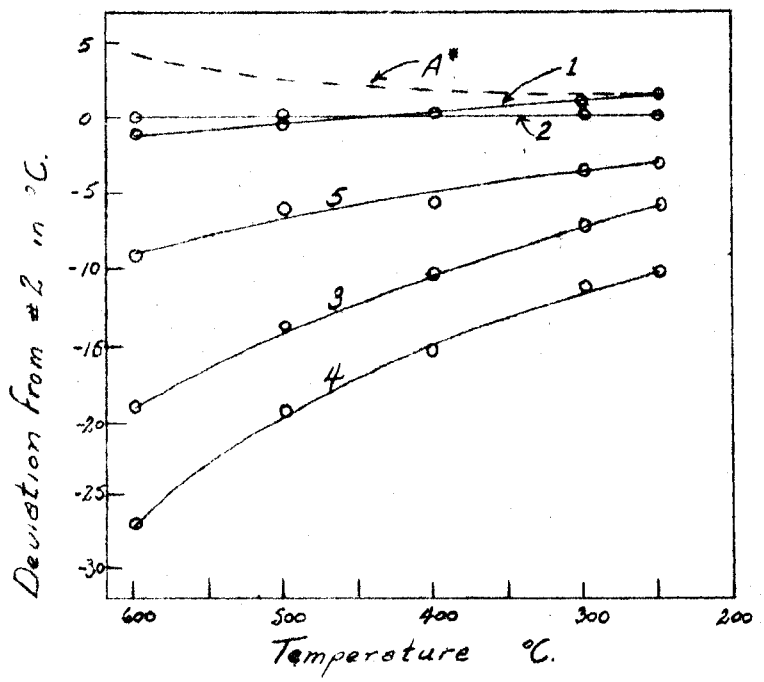
Part (b) A sectional view of the cup assembly showing the position of five thermocouples.



1 Iron-cupron thermocouple

2, 3, 4, 5 Iron-constantan thermocouples

Part (c) The distribution of heat in the ignition cup as it cools from 600° C. to 200° C.



In reporting the S.I.T. the direct reading of #1 thermocouple is used.

A* The iron-constantan equivalent reading of #1 obtained by using data in part (a)

are probably somewhat higher than those in actual operation, since insertion of the thermocouples necessitated some break in the thermal contact of the parts of the ignition cup assembly. It is of interest to note that the temperature differentials observed here are considerably less than those recently reported for the A.S.T.M. apparatus[5].

2. Spray Injection versus Dropwise Addition

At first the same general procedure as described in the previous section was used for the lubricants. It was soon observed that with much larger charge sizes (100-200 mg) and adding the material rapidly and all at once the spontaneous ignition temperatures of the lubricants could be considerably lowered. Therefore, dropwise addition in the case of the lubricants may refer to a very large "drop." Only a small portion of this 50-200 mg "drop" of oil is consumed in the spontaneous flame; the rest smolders in the bottom of the cup and may deposit a lacquer like residue. For the high viscosity oils five or ten minutes may be required for the stream of air to sweep out the ignition cup. Spontaneous ignition temperatures at both 125 cc/minute and 0 cc/minute airflow were determined for the lubricants in an effort to obtain as nearly as possible optimum fuel/air ratios. In general lower results were obtained at the zero airflow rate.

Some special determinations were made of open-cup spontaneous ignition temperatures. In these cases the lid and cap of the ignition cup assembly were removed leaving an open cup. The lubricant was added in amounts up to 500 mg. and a spontaneous flame was observed. In these determinations air flow into the cup was permitted at a rate of approximately 125 cc/minute. The precision of these spontaneous ignition temperatures was probably $\pm 5^{\circ}$ to 8°C. The main purpose of these open cup determinations was to illustrate that a rather simple

change in the ignition cup would give widely different ignition temperatures.

By injecting the charge into the cup in a fine spray a more efficient utilization of the oil could be obtained. Spray injection permitted a more rapid attainment of optimum vapor concentrations for flame ignitions. The general procedure for spray injection is the same as for dropwise ignition. A range of different charge sizes from the injector were used so as to give the lowest ignition temperature possible. The lower limit for injection was about 5 mg. For representative volatile compounds dropwise addition and spray injection give substantially the same results.

The precision of the dropwise addition and spray injection for lubricants may be summarized by the following table:

Properties of the Compound		Method of Addition	Precision, °C
Boiling Point, °C	Spontaneous Ignition Temperature, °C		
< 280	< 300	Dropwise	1-2
< 280	> 300	Dropwise	3-5
280 to ?	< 300	Spray Injection	2-3
280 to ?	>300	Spray Injection	3-6

Spray injection will give a much higher surface area to bulk volume ratio. The rate of achieving the equilibrium vapor pressure of the oil will be a function of this area to volume ratio. But there is an additional factor in obtaining the optimum vapor concentration for spontaneous ignition of relatively non-volatile oils. This factor is that the smaller the particle size of the droplets the higher will be the equilibrium vapor pressure according to the equation:

$$\ln \frac{p_r}{p_0} = \frac{2M}{RT} \frac{\gamma}{rd}$$

r - radius of droplet

γ - surface tension

d - density

M - molecular weight

p_r - vapor pressure of bulk liquid

p_0 - vapor pressure of droplet of radius r

The upper molecular weight limit of usefulness of spray injection, therefore, will depend upon the vapor pressure of very small droplets. However, with the present injector, the practical limit is determined by the viscosities and lies in the range of 300-600 SSU at 100°F dependent to some extent on the structure involved.

3. The Slow Vapor Phase Oxidation of Organic Compounds

The bubbler tube is first filled with the compound to be tested. From the vapor pressure data of the compound the temperature is determined which will permit the desired vapor ratio of compound to oxygen as the oxygen is bubbled through the compound. This temperature is then maintained by an appropriate vapor bath around the bubbler. The flow of the fuel-oxygen mixture is started and the furnace is heated to the desired temperature. This temperature is maintained by adjusting a variable transformer. The reaction is continued until a sufficient amount of reaction product is collected in the dry ice-acetone cooled traps. The reaction mixture is then separated into two parts: (1) the liquid organic phase, (2) the solid ice like phase adhering to the walls of the trap. The liquid organic phase is analyzed for total peroxide, hydrogen peroxide, carbonyl, olefin, and acid content. It is necessary to remove all of the peroxide and carbonyl to determine the olefin. The solid ice like phase is allowed to melt and then is washed down with water and analyzed for peroxide,

hydrogen peroxide, carbonyl, and acid content. With this simple type of procedure a series of runs is made varying the conditions of fuel/air ratio, contact time, and temperature. From this information a much more detailed analysis is carried out under a few particularly promising conditions. This detailed analysis may include the separation of any organic peroxides by low temperature distillation, chromatographic separation of the dinitrophenyl hydrazones of the various carbonyl compounds, and preparation and separation of the dibromo or monobromo derivatives of the olefins.

4. Analytical Procedures Used in the Characterization of the Oxidation Intermediates

Peroxides were determined iodometrically. A piece of dry ice was added to 10 cc of glacial acetic acid in the titration flask to sweep out the air. The potassium iodide solution and the sample then were added, the flask was loosely stoppered and allowed to stand one half hour at room temperature in the dark. The liberated iodine was titrated with 0.1 N sodium thiosulfate. The blank in most cases remained colorless. The value calculated from this titration was taken as total peroxides.

Hydrogen Peroxide was determined colorimetrically by the reaction with titanium sulfate reagent[6]. The per cent absorption of 410μ light is measured with a Coleman Universal Spectrophotometer and with this value the hydrogen peroxide is read directly from a calibrated chart.

Carbonyl compounds were determined by precipitation of the 2,4-dinitrophenylhydrazones using the reagent solution described by Shriner and Fuson[7]. The precipitate was filtered, washed with water, and transferred into a weighing beaker after dissolving in

ether. The ether then was evaporated, the product dried under reduced pressure and weighed.

The chromatographic procedure of Roberts and Green[8] and modifications by Gordon, et.al.[9] were used for the separation of the 2,4-dinitrophenylhydrazones. This involves the development of the chromatogram on a silicic acid-Super Cel column with a 4% solution of ether in petroleum ether.

Olefins were determined according to the procedure of Lucas and Pressman[10]; however, the mercuric sulfate catalyst was omitted. Ten or twenty-five milliters of 0.1N bromate-bromide solution are added to the titration flask which is then evacuated. The remaining reagents and sample are forced into the flask by excess atmospheric pressure. In this way the generated bromine is not lost. About 5 ml. 6N sulfuric acid liberates the bromine, the sample as a carbon tetrachloride solution is added and washed into the flask with glacial acetic acid. The flask is shaken about 2 minutes in the dark, potassium iodide solution is added, and the liberated iodine titrated with 0.1N sodium thiosulfate.

The olefin dibromides were prepared either by direct addition of bromine to the olefin-paraffin mixture or by addition of an aqueous bromine solution to the olefin-paraffin mixture.

The monobromo derivatives of the olefins were prepared by bubbling dry hydrogen bromide through the olefin paraffin mixture. The hydrogen bromide was obtained by dropping bromine on boiling tetralin.

Acids were determined by titration with -.1N sodium hydroxide, using either a Beckmann pH meter or phenolphthalien as the indicator.

Non-condensable gases were determined by means of the Burell "Industro" gas analyzer. These gases include carbon monoxide, carbon dioxide, oxygen, methane, nitrogen.

Formaldehyde was determined in some cases more specifically by the formation of a white crystalline precipitate with methane (5,5-dimethyl dihydroresorcinol)[11].

V. Results and Discussion

1. Spontaneous Ignition Temperature of Pure Compounds in Stainless Steel Chamber; Non-ignition Zone.

n-Paraffins. The series of normal paraffins from C_{10} to C_{20} gave spontaneous ignition temperatures in the range 232° to 240°C using an airflow rate of 125 cc/minute. Heptane under similar conditions gave a spontaneous Ignition temperature of 250°C. Other workers have reported higher values for the lower members of the homolous series. The most obvious generalization, therefore, is that as the length of the hydrocarbon chain increases the spontaneous ignition temperature decreases, rapidly at first but tending to level off with increasing chain length. This generalization holds up to hexadecane and then the spontaneous ignition temperature starts to rise with further increase in chain length. The reason for this rise is considered to be the result of the reduced volatility of the higher paraffins.

Compound	Spontaneous ignition temperature (°C)		
	Air flow 125 cc/min	Air flow 25 cc/min	From literature
n-Heptane	250	244	230 (5) 259 (2)
n-Decane	236	231	252 (2)
n-Dodecane	232	229	
n-Tetradecane	232	227	
n-Hexadecane	232	225	241 (12) 235 (2)
n-Octadecane	235	227	
n-Nonadecane	237	230	
n-Eicosane	240	232	

When the air flow rate is reduced to 25 cc/minute the spontaneous ignition temperatures decreased 3-8°C for each in this series of paraffins. Under these conditions higher fuel/air ratios are

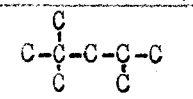
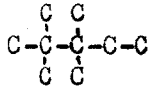
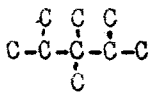
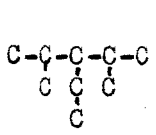
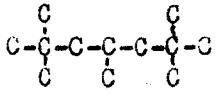
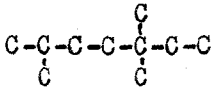
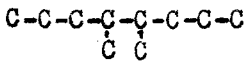
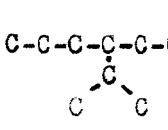
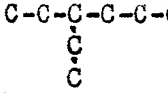
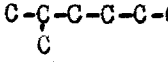
obtained which permit ignition at lower temperatures. At the lower air flow rate the spontaneous ignition temperature also begins to rise with the C_{18}-C_{20} paraffins indicating the reduced volatility of these compounds. Therefore, it appears that if volatility were not a factor the ignition temperatures of normal paraffins would continue to slowly drop with increasing chain length, approaching some asymptotic lower limit at much higher chain lengths.

Further indication of this is found by comparing the ignition behavior of dodecane and hexadecane under three different conditions. At the air flow rate of 125 cc/minute both compounds have ignition temperatures of 232°C. At the air flow rate of 25 cc/minute dodecane has the value 229 and hexadecane the value of 225°C. By going to still better conditions for diminishing the volatility effect, such as the conditions of rapid vaporization in determining cetane numbers of fuels, it is observed that the cetane number of dodecane is 80 and that of hexadecane is 100 (by definition). The inverse relationship of cetane number to spontaneous ignition will be shown later in the report.

Therefore, a more complete generalization is this: For the normal paraffins the spontaneous ignition temperature decreases with increasing chain length until the factor of reduced volatility begins to dominate and causes a rise in ignition temperature with the still higher molecular weight members.

Branched paraffins. Spontaneous ignition temperatures have been determined for ten branched paraffins of a high degree of purity. These values are listed in the table on the following page. Five of these compounds were obtained through the courtesy of Dr. C. E. Boord, Ohio State University. Three of them were obtained through the courtesy of the N.A.C.A.

Branched Paraffins

Compound	Structure	Number of Hydrogens 1°	2°	3°	Spontaneous Ignition Temperature Dropwise Addition 125 cc/min	25 cc/min	0 cc/min	Literature
2,2,4-Trimethyl pentane		15	2	1	515	502		
2,2,3,3-Tetramethyl pentane		18	2	0	516		505	452 (13)
2,3,3,4-Tetramethyl pentane		18	0	2	514		497	437 (13)
2,4-Dimethyl-3-Ethyl pentane		15	2	3	510		472	390 (13)
1,1-Dineopentyl ethane		21	4	1	500	486		
2,5,5-Trimethyl heptane		15	6	1	485	463		
4,5-Dimethyl octane		12	8	2	388	290		
4-Isopropyl heptane		12	8	2	288	275		
3-Ethyloctane		9	12	1	235	231		
2-Methyl decane		9	14	1	231	225		

A rather quick study of the table shows that the spontaneous ignition temperature rises with increasing degree of branching, that is, with decreasing number of methylene groups and increasing number of methyl groups. This observation fits in very well with the general postulate that primary hydrogen atoms are more resistant to oxidation than secondary hydrogen atoms which in turn are more resistant than tertiary hydrogen atoms. The three isomeric nonanes confirm this postulate much better at the zero air flow rate than at the 125 cc/minute air flow rate. Also it is observed that the values of Jackson[13] for these three compounds are much lower than our values although the order is the same. The major difference between the two procedures is Jackson's use of a 125 cc quartz flask and our use of a 43 cc stainless steel cup. This would suggest that a pronounced chain-breaking action is exerted by a higher surface:volume ratio. The differences in spontaneous ignition temperatures between these two procedures are greatest with these branched paraffins; for the normal paraffins igniting in the low temperature range the agreement is quite good. Accordingly, it appears that the high temperature reaction involving simple radical intermediates is more sensitive to wall effects than the low temperature reaction involving peroxide intermediates[14].

Further consideration should be given to 4,5-dimethyloctane and 4-isoprophylheptane. These isomers have the same number of primary, secondary, and tertiary hydrogen atoms, yet the spontaneous ignition temperatures at the 125 cc/minute rate are different by one hundred centigrade degrees and only fifteen degrees different at the 25 cc/minute rate. To obtain a clearer understanding of these results, it is suggested that reference be made to figure 10 page 42. Here it is seen that a 53% isooctane-in-heptane-mixture would ignite in the low

temperature range but a 58% mixture would not ignite in this range at the 125 cc/minute air flow rate. However, by considering the extension of the ignition curve at the 25 cc/minute rate both the 58% and 53% would ignite in the low temperature range. Therefore, it is suggested that in a rather qualitative fashion 4,5-dimethyloctane behaves as the 58% mixture and 4-isoprophylheptane behaves as the 53% mixture. These two compounds seem to represent structures rather sensitive to the competition between the low and high temperature mechanisms of oxidation under these particular conditions.

Both 3-ethyloctane and 2-methyldecane have ignition temperatures close to those of the comparable normal paraffins. Therefore, for higher molecular weight paraffins introduction of a single branch in the molecule does not markedly alter the ignition temperature. This may be due to somewhat of a balance between the extra methyl group making the molecule more resistant to oxidation and the tertiary hydrogen atoms making the molecule more susceptible to oxidative attack.

Paraffin combinations. The ignition temperatures of 7-phenyltridecane and 7-cyclohexyltridecane were determined for comparison with normal paraffins. These two compounds were obtained through the courtesy of Dr. Robert Schiessler, Pennsylvania State College.

Compound		Spontaneous Ignition Temperature Dropwise Addition Air flow		
		125 cc/min	25 cc/min	0 cc/min
7-Phenyltridecane	$C_6-C(C_6H_5)-C_6$	239		236
7-Cyclohexyltridecane	$C_6-C(C_6H_{11})-C_6$	237		234
n-Octadecane	$C_6-C_6-C_6$	235	227	

Although it was expected that aromatic rings and cycloparaffinic rings would have a pronounced effect on the ignition temperature, the length of the uninterrupted polymethylene chain is the dominating factor in the ignition of these compounds. This information would seem to indicate that the ignition temperatures of paraffin lubricating oils should be low in spite of the aromatic and naphthenic content of these oils. That this is the case will be shown in a later section.

α-Olefins. The straight chain α-olefins examined from 1-decene to 1-octadecene all have higher spontaneous ignition temperatures than the normal paraffins.

Compound	Spontaneous Ignition Temperature Dropwise Addition 125 cc/minute Airflow
1-Decene	265
1-Dodecene	257
1-Tetradecene	255
1-Hexadecene	253
1-Octadecene	251

This is in line with the cetane values of α-olefins as compared with normal paraffins. 1-Hexadecene has a cetane value of 88 while n-hexadecane has the defining value of 100. This greater resistance to spontaneous ignition of the α-olefins may be explained by the greater ease with which the olefins undergo free-radical attack and the correspondingly greater stability (lower reactivity) of the resultant peroxides or intermediate radicals formed. As the paraffinic portion of the olefin molecule is increased the ignition temperature becomes nearer to that of the corresponding normal paraffin. This is no doubt due to the lessening contribution of the double bond as the polymethylene chain increases in length. There has been some disagreement as to why the olefins behave as antiknock agents.

Badin[15] proposes that olefins behave as antiknocks because of their ready ability to form peroxides and thereby to act as chain initiators. The spontaneous ignition temperature data, however, are evidence for the more prevailing theory (outlined by Walsh in the "Discussion" following reference 15) that antiknock action is the result of chain inhibition rather than chain initiation.

Branched olefins. Some mention should be made of the spontaneous ignition characteristics of highly branched olefins because the comparison with corresponding paraffins is reversed for these compounds. Reference is made to table II page 52, where diisobutylene has a much lower ignition temperature than isooctane and 1,1-dineopentylethylene has a lower value than 1,1-dineopentylethane. The reason for this reversal probably ties in with the difference between the low and high temperature mechanisms of oxidation.

Aromatic hydrocarbons. The aromatic nucleus is very resistant to spontaneous ignition. Ignition temperatures are shown for a number of aromatic hydrocarbons in the following table.

Compound	Spontaneous Ignition Temperature (°C)		
	Air flow 125 cc/min	Air flow 25 cc/min	From literature
Benzene	645	639	702 (12) 580 (16) 652 (2)
Toluene	635	630	629 (2)
o-Xylene	551	547	591 (2)
m-Xylene	652	645	689 (2)
p-Xylene	657	650	690 (2)
1,2,3-Trimethylbenzene	510		
1,2,4-Trimethylbenzene	528		
1,3,5-Trimethylbenzene	577		
Triethylbenzenes			
Predominately 1,3,5 isomer	446		
Predominately 1,2,4 isomer	439		
α-Methylnaphthalene	553	547	565 (2)

In comparing the various methylated benzenes, the relative positions of the methyl groups on the aromatic nucleus is a more significant factor in altering the spontaneous ignition temperature than the actual number of methyl groups. Two methyl groups ortho to each other seems to make the molecule more susceptible to oxidative attack than do methyl groups meta or para to each other. In fact, meta and para xylene are more resistant than benzene. Larger alkyl groups (presence of secondary hydrogen atoms) in an aromatic hydrocarbon produce a sharp drop in spontaneous ignition temperature as demonstrated with the triethylbenzenes, and, as was shown earlier, a long polymethylene chain on an aromatic nucleus gives a compound with an ignition temperature near that of a normal paraffin (page 30). Puckett and Caudle[26] note that acceptable cetane numbers are observed only in alkylbenzenes possessing long side chains with little or no branching.

Alcohols. The spontaneous ignition temperatures for eight alcohols are listed in the following table.

Compound	Spontaneous Ignition Temperature °C.	
	Air flow 125 cc/min	From Literature
Ethanol	425	392 (5)
Propanol	441	439 (5)
Isopropanol	498	456 (16)
1-Decanol	291	
1-Dodecanol	283	
1-Tetradecanol	279	
1-Hexadecanol	273	
1-Octadecanol	269	

The series of straight chain alcohols from decanol to octadecanol show ignition temperatures higher than those of both the corresponding α-olefins and n-paraffins. Here also the effect of

the hydroxyl group decreases as the polymethylene chain is lengthened in progressing from decanol to octadecanol. The reason for the higher values for the alcohols than for the paraffins is probably the formation of less energetic radicals, R-$\dot{C}$HOH, tending to subdue the rapid oxidative chain reactions.

The lower alcohols have higher spontaneous ignition temperatures as would be expected. The more highly branched isopropanol has a value considerably higher than that of normal propanol. However, it is not apparent why ethanol has a lower value than normal propanol.

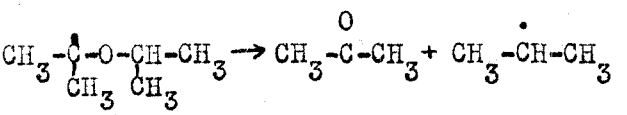
Ethers. Spontaneous ignition temperatures have been determined for five ethers.

Compound	Spontaneous Ignition Temperatures (°C)		
	Air flow 125 cc/min	Air flow 25 cc/min	From literature
Diethyl ether	193	190	193 (16)
Diisopropyl ether	500	495	443 (27)
Dihexyl ether	200	197	
Dioctyl ether	210	210	
Didecyl ether	217	217	

With the exception of diisopropyl ether the ignition temperatures of these ethers are extremely low. Ethers like the olefins are easily peroxidizable. This factor alone connotes a lesser degree of reactivity of the radicals formed. The difference, therefore, between the olefins and ethers must be due to the difference in stability of these radicals. That is, the radical R-$\dot{C}$H-CH=CH_2 is both more stable and less reactive than R-$\dot{C}$H-CH_2-CH_3; the radical R-$\dot{C}$H-O-R is probably less reactive, but it is very unstable and tends to decompose to R-CHO and R·[28]. It is significant that the odor of acetaldehyde is quite noticeable on ignition of diethyl ether (CH_3-$\dot{C}$H-O-CH_2-CH_3 → CH_3-CHO + CH_3-CH_2·). The aldehydes are very susceptible to further oxidation and the n-alkyl

radicals are the most reactive in comparison with secondary and tertiary alkyl radicals.

This same line of reasoning may be extended to diisopropyl ether to explain the high ignition temperature of this compound. Oxidative attack would be expected to yield acetone and the isopropyl radical.



Acetone is less susceptible to oxidative attack than aldehydes and the isopropyl radical is more stable than n-alkyl radicals.

As the molecular weight of the n-ethers increases, the spontaneous ignition temperatures progressively rise toward the values of the n-paraffins. Thus the spontaneous ignition temperature of alcohols, α-olefins and n-ethers seem to tend toward the values of the n-paraffins as one goes to higher molecular weights. This is graphically shown in figure 8.

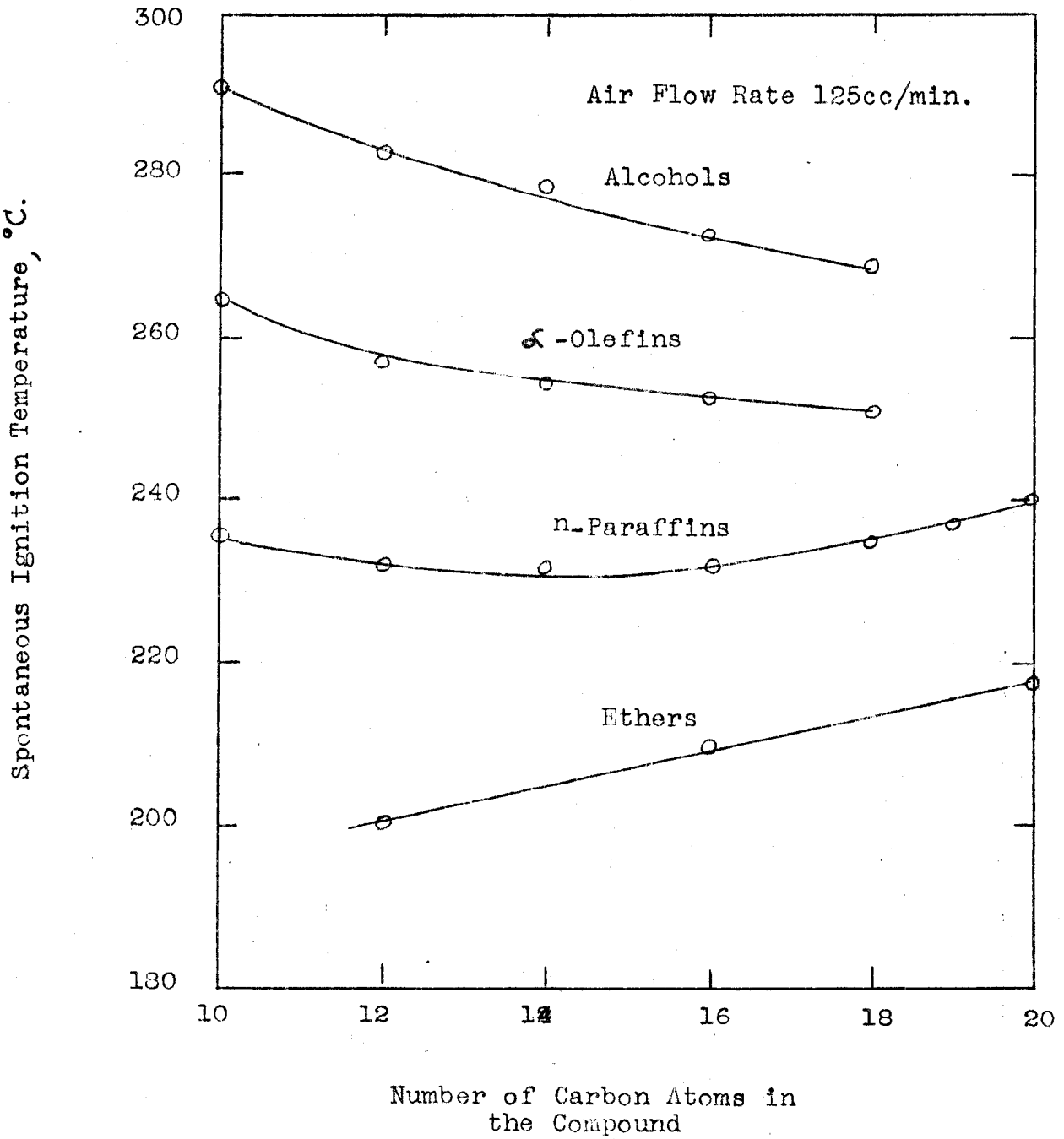
Esters. The spontaneous ignition temperatures for seven esters have been determined. These esters were obtained through the courtesy of Dr. W. A. Zisman of the Naval Research Laboratory.

Compound	Spontaneous Ignition Temperature (°C)			
	Air flow 125 cc/min	Air flow 25 cc/min	Air flow 0 cc/min	From Literature
Di(1-ethylpropyl) adipate	436	432		443 (29)
Di(1-ethylpropyl) azelate	420	419		443 (29)
Di(1-ethylpropyl) sebacate	412	410		426 (29)
Di(2-ethylhexyl) adipate	385 (265)	384		395 (29)
Di(2-ethylhexyl)-ortho-phthalate	395		400	
Di(2-ethylhexyl)-meta-phthalate	407		413	
Di(2-ethylhexyl)-para-phthalate	414		418	

The relatively high spontaneous ignition temperatures of an ester apparently result from the formation of an inactive radical ($\dot{R}CHCOOR'$)

Figure 8

Relationship of Spontaneous Ignition Temperature to Length of the Carbon Chain for some Alcohols, α-Olefins, n-Paraffins, and Ethers.



which is unable to propagate the cool flame process. It is of interest to note that results obtained herein with the 1-ethylpropyl esters of adipic, azelaic, and sebacic acids show the expected decrease in spontaneous ignition temperature value with increasing length of the uninterrupted hydrocarbon chain. The presence of relatively long alkyl groups as in di(2-ethylhexyl) adipate produces a somewhat larger drop in the spontaneous ignition temperature value just as would be predicted.

In fact, under rather extreme conditions di(2-ethylhexyl) adipate ignited in the low temperature range as indicated by the value in parenthesis. More detail of this development will be given in the next section.

The three phthalate ester isomers show the same order of stability toward oxidation, para > meta > ortho, as did the isomeric xylenes.

Nonignition Zone

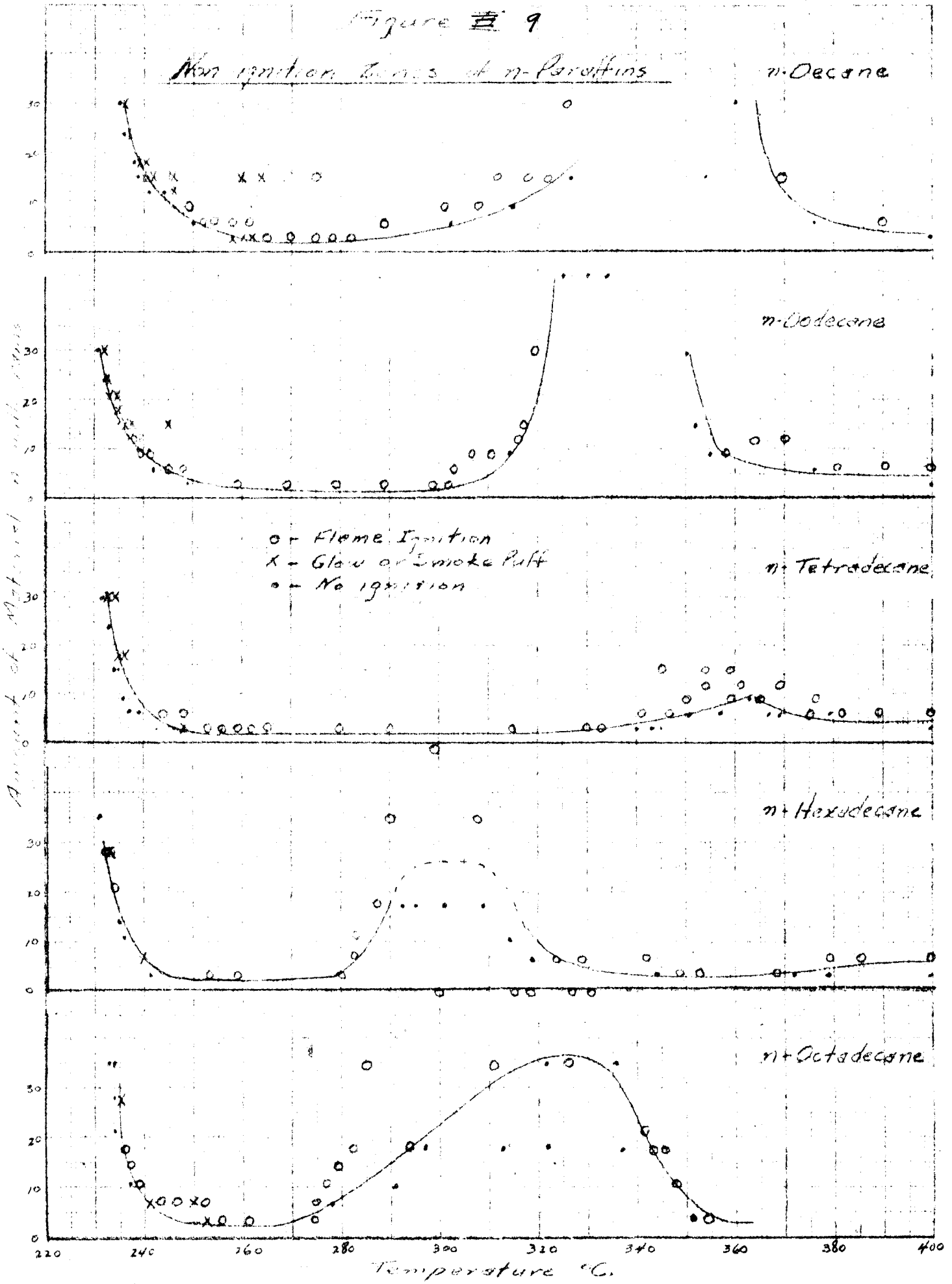
Zones of nonignition for normal paraffins were observed by Sortman, Beatty, and Heron[2] in an ignition cup similar to that used in this investigation. In this work also, zones of nonignition were observed for the normal paraffins; however, quantitative agreement between the contour curves of the zones was not obtained. As this investigation continued it soon became apparent that the boundary of the zones of nonignition was very sensitive to the test procedure. The rapid addition of a given charge size would cause the zone of nonignition to shrink somewhat as compared with the slower dropwise method of addition. Figure 9 shows a series of contour curves obtained for the normal paraffins. No significant trend was observed with these compounds and a tentative conclusion seemed to be that these zones of nonignition were a result of an interplay between the rate of vaporization and the rate of oxidation of the compound and not a direct

function of the chemical structure. The spray injection procedure gave support to this conclusion because the zone of nonignition was blotted out in the case of hexadecane by using this method of addition.

In addition to the normal paraffins, the long chain α-olefins, alcohols, ethers, and esters showed these nonignition zones. Accordingly this phenomenon appeared to result from a polymethylene chain in these higher molecular weight compounds rather than from any particular functional group. The best explanation for the zones of nonignition is that they represent a temperature range where the low temperature mechanism of oxidation has faded out and the high temperature mechanism has not yet begun[14]. Accordingly only compounds which can oxidize by both high and low temperature mechanisms exhibit this phenomenon.

Figure 9

Ignition Lags of n-Paraffins



2. (a) Correlation of Spontaneous Ignition Temperatures with Octane and Cetane Ratings.

Helmore[1] in his review of spontaneous ignition noted a good agreement between ignition temperatures and antiknock ratings. Octane numbers, cetane numbers, and critical compression ratios are different ways of expressing the antiknock properties of a particular fuel. One of the objects of this investigation was to extend the correlation between antiknock behavior and spontaneous ignition characteristics and place it on a more quantitative basis.

The aromatic hydrocarbons show a striking parallel between spontaneous ignition temperature and critical compression ratio.

Compound	Spontaneous Ignition Temperature (°C)	Critical compression Ratio (30).
p-Xylene	657	11.5
m-Xylene	652	11.5
Benzene	645	Approx. 12
Toluene	635	11.3
1,3,5-Trimethylbenzene	577	10.6
o-Xylene	551	8.3
1,2,4-Trimethylbenzene	528	8.7
1,2,3-Trimethylbenzene	510	7.9

The results of these amine additives correlate well with the effect of amine additives on antiknock ratings. Boyd[31], in discussing antiknock, reported the marked effectiveness of primary and secondary aromatic amines. The following table shows an interesting comparison of corresponding antiknock and spontaneous ignition temperature ratings.

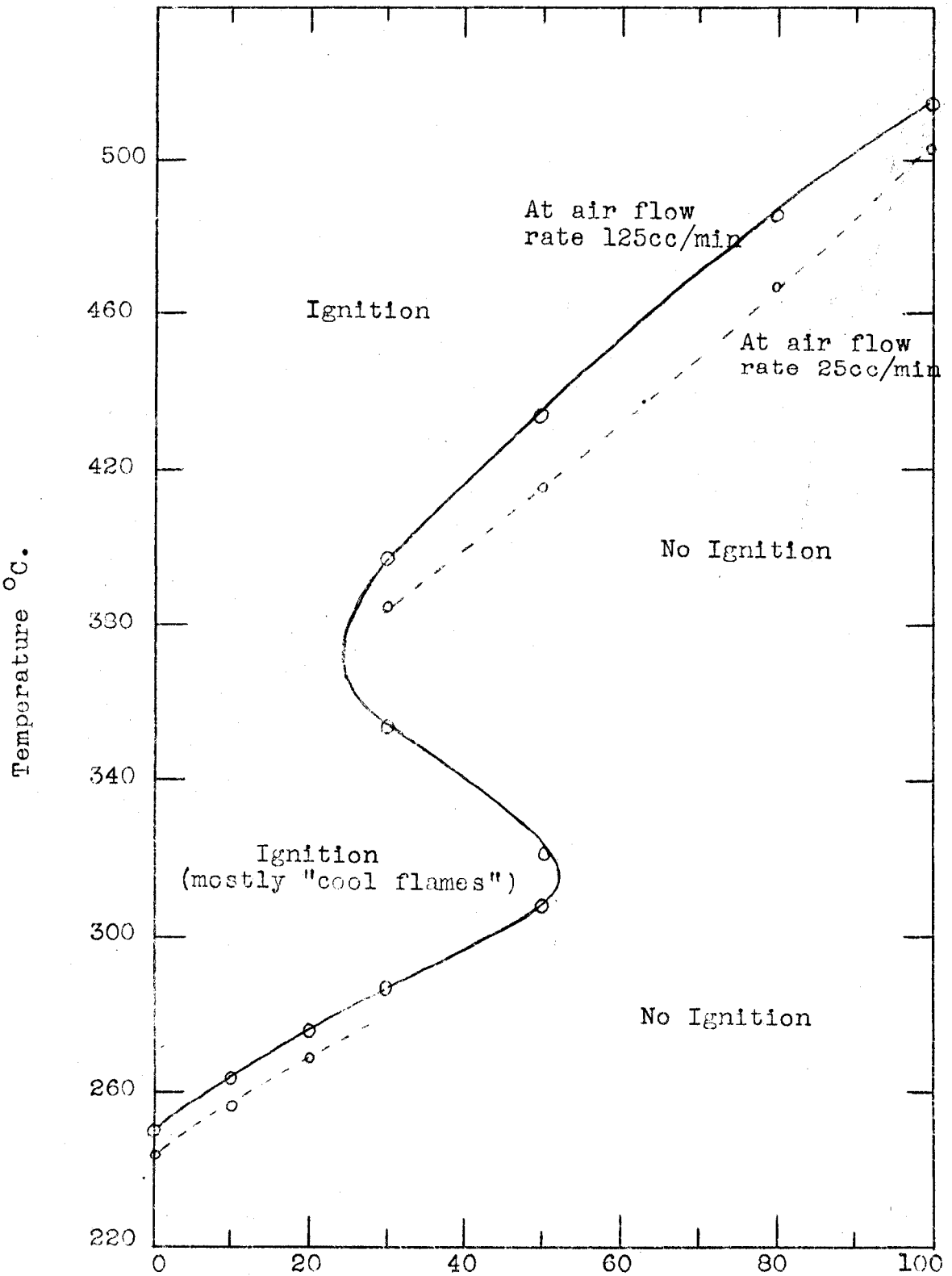
Amine	Reciprocal of Moles Required to Give Antiknock Effect Equivalent to 1 Mole of Aniline (31)	Rise in Spontaneous Ignition Temperature of Dodecane Employing 5 Mole % Additive °C
Diphenylamine	1.5	40
N-Methylaniline	1.4	36
Toluidines (average)	1.2	26
Aniline	1.0	11
Diethylamine	0.5	16
Dimethylaniline	0.2	2

To explore the range of octane numbers more completely, the spontaneous ignition characteristics of a series of isooctane-heptane mixtures were determined and plotted as shown in figure 10. The solid curve represents the maximum extension of the ignition boundary under the optimum conditions of fuel/air ratio obtainable with an air flow rate of 125 cc/minute. Between 25% and 50% isooctane in heptane, a non-ignition zone is observed above the low temperature ignition peninsula. If critical compression ratio were plotted against octane number the curve would not be S-shaped like this one, and the claim of close correlation of critical compression ratio and spontaneous ignition may be questioned. However, under the conditions of determining critical compression ratios much higher pressures than atmospheric pressure are encountered. Increased pressure would have the effect of extending the ignition boundary until ignition in the low temperature range could be obtained for all compositions of isooctane and heptane. This would compare more directly with the critical compression ratio data. The claim of correlation is based on the idea that the various antiknock ratings and spontaneous ignition characteristics depend upon the same fundamental property of molecules. Just what this property is is not yet known but it, of course, will be intimately connected with chemical structure. Therefore, the same structural influences are observed on both antiknock ratings and spontaneous ignition such as branching in hydrocarbons produces high spontaneous ignition temperatures as well as increased compression ratios and higher octane numbers. Both antiknock ratings and spontaneous ignition are quite sensitive to the conditions employed in the test procedure. For this reason it is important that the conditions be accurately stated to give the results their greatest significance.

Figure # 10

Spontaneous Ignition Characteristics of Various

2,2,4-Trimethyl pentane - n-Heptane Mixtures



A similar S-shaped curve is obtained for various cetane- methyl naphthalene mixtures (figure 11). It must be remembered that the cetane scale bears an inverse relationship to the octane scale and therefore to spontaneous ignition. Thus, the fuels with highest cetane numbers are the most susceptible to spontaneous ignition. The following table shows excellent qualitative correlation between cetane ratings and ignition temperatures.

Compound	Spontaneous Ignition Temperature (°C)	Cetane number (26)
n-Hexadecane	232	100
n-Dodecane	232	80
n-Heptane	250	57
1-Hexadecene	253	88
1-Tetradecene	255	79
2,2,4-Trimethylpentane	515	12
α-Methylnaphthalene	553	0
Toluene	635	-5

(Data taken for air flow rate of 125 cc/minute)

(b) Other S-shaped Curves Observed.

These S-shaped curves obtained for isooctane-heptane mixture and cetane -α-methylnaphthalene suggested an interesting avenue for further investigation of ignition characteristics. Accordingly a series of cetane-di(2-ethylhexyl) adipate mixtures were investigated with particular emphasis on how the charge size influenced the extension of the ignition boundary; and a series of dodecane-1,1-dineopentylethane mixtures were investigated with emphasis on the different types of ignition observed in passing from the region of hot flame ignition to the region of no ignition. The results of the cetane-di(2-ethylhexyl) adipate are shown graphically in figure 12. These curves are very instructive in helping one to understand the apparently confusing and contradictory results often appearing in the literature. A three dimensional ignition surface may be visualized by considering the charge size as the third

Figure 11

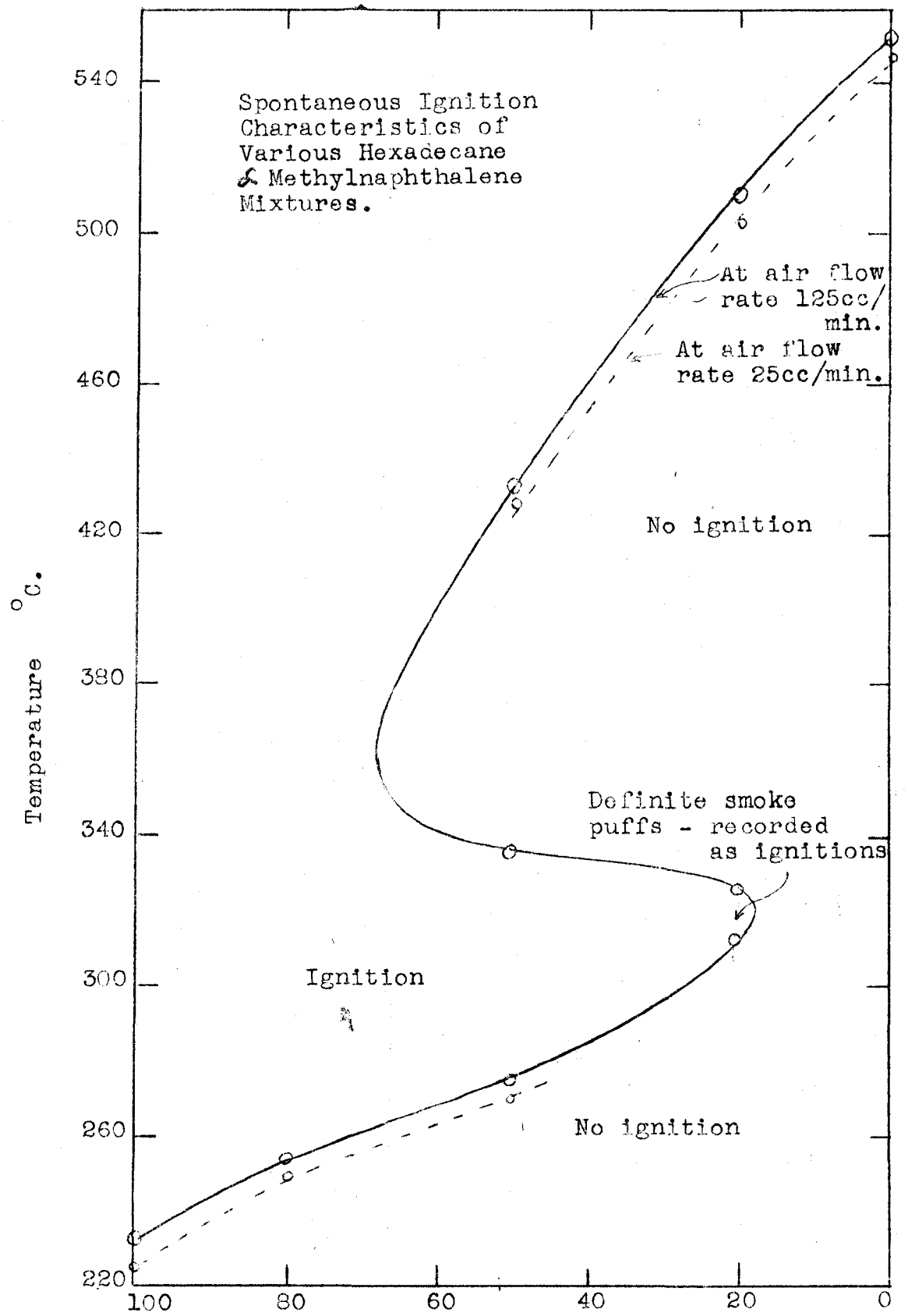
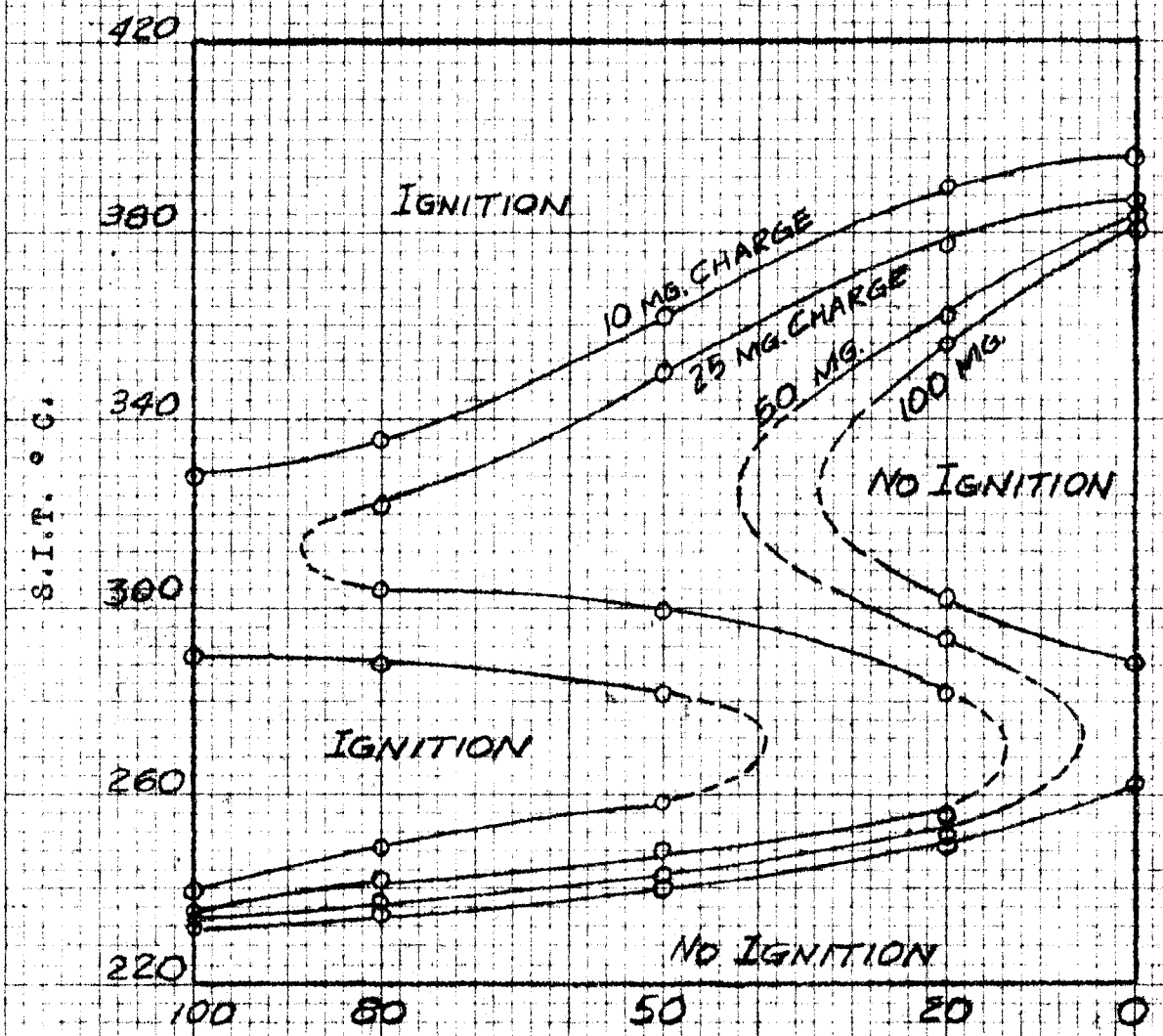


Figure 12

Spontaneous Ignition Characteristics of Various Cetane/di-(2-ethylhexyl) Adipate Mixtures at Four Different Charge Sizes.



Percent Cetane in Mixtures with di(2-ethylhexyl) adipate.

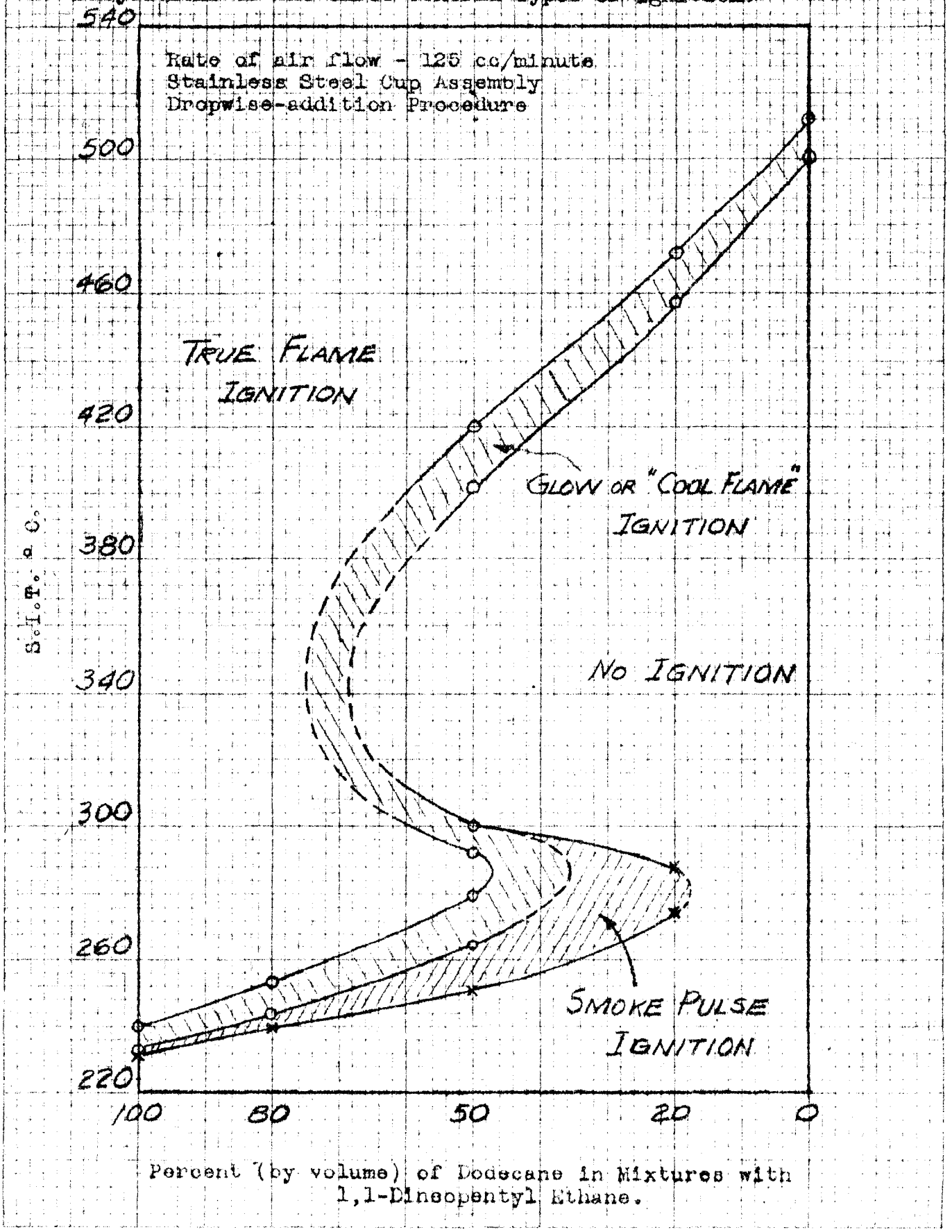
Rate of air flow - 125 cc/ min.
Dropwise-Addition Procedure

ordinate. This essentially gives a high temperature ignition "hill" and a low temperature ignition "hill" with a nonignition "valley" in between. Under some conditions the low temperature "hill" might be completely missed. This was the case with di(2-ethylhexyl) adipate. The ignition temperature reported for the compound was 395°C; our value was first considered to be 385°C. It was only by going to very large charge sizes that the ignition boundary was intersected and therefore a value of 265°C was obtained--120 degrees lower. The diesters were previously considered quite resistant to spontaneous ignition, but this development showed that there was still a potential low temperature fire hazard associated with their use as lubricants.

Figure 13 shows the spontaneous ignition characteristics of various dodecane-1,1-dineopentylethane mixtures. In moving left to right the first curve represents the maximum extension of the hot flame ignition boundary. Each point on the curve does not represent the same charge size as did the previous figure with cetane-adipate ester mixtures; this curve is the maximum extension for any charge size. The next curve represents the further extension of the ignition boundary by considering the blue glow or "cool flame" region, and the last curve is a still further extension of the low temperature ignition peninsula by considering the smoke pulse ignitions. A three dimensional figure may again be visualized with charge size as the third ordinate. However, from the data on this graph alone, the three dimensional figure could not be constructed because the ignition temperatures as a function of charge size is not indicated. If this data were available, the space figure could be constructed; figure 13, then, would represent the projection of the three ignition boundary surfaces onto the temperature-composition plane.

Figure 9 13

Spontaneous Ignition Characteristics of Various Dodecane-1,1-Dineopentyl Ethane Mixtures Showing the Boundary Projections of the Three General Types of Ignition.



Percent (by volume) of Dodecane in Mixtures with 1,1-Dineopentyl Ethane.

3. Spontaneous Ignition Temperatures of Various Types of Lubricants.

The data obtained on the various pure compounds discussed in the previous sections gave a good foundation for the investigation of the spontaneous ignition characteristics of lubricants--the more practical side of the picture in which NACA was interested. As the study of a variety of lubricants progressed it soon became apparent that volatility limitations imposed upon lubricants of high viscosity were obscuring the expected correlation between structure and spontaneous ignition. To overcome this limitation as much as possible a spray injector was constructed and the ignition temperatures of some of the same lubricants were determined under spray injection conditions for comparison with dropwise addition. Acknowledgement is made to Mr. Donald E. Swarts for the actual spray ignition data in the following tables and graphs. With the spray injection modification, correlation of structure with spontaneous ignition was extended over a much wider viscosity range for these lubricants.

In some cases an open cup spontaneous ignition temperature was determined for comparison with the normal closed cup result. Some of these open cup values were lower than the closed cup values. This suggested that if higher fuel/air ratios could be obtained the closed cup values should drop below the open cup values. Confirmation of this suggestion was obtained with the spray injection procedure. In general, however, consistent and meaningful results were not given by the open cup procedure.

(a) Paraffin Lubricants

The spontaneous ignition temperature of a series of conventional lubricating oils were determined by both the dropwise addition and spray injection procedures. These results are shown in the following table and figure 14.

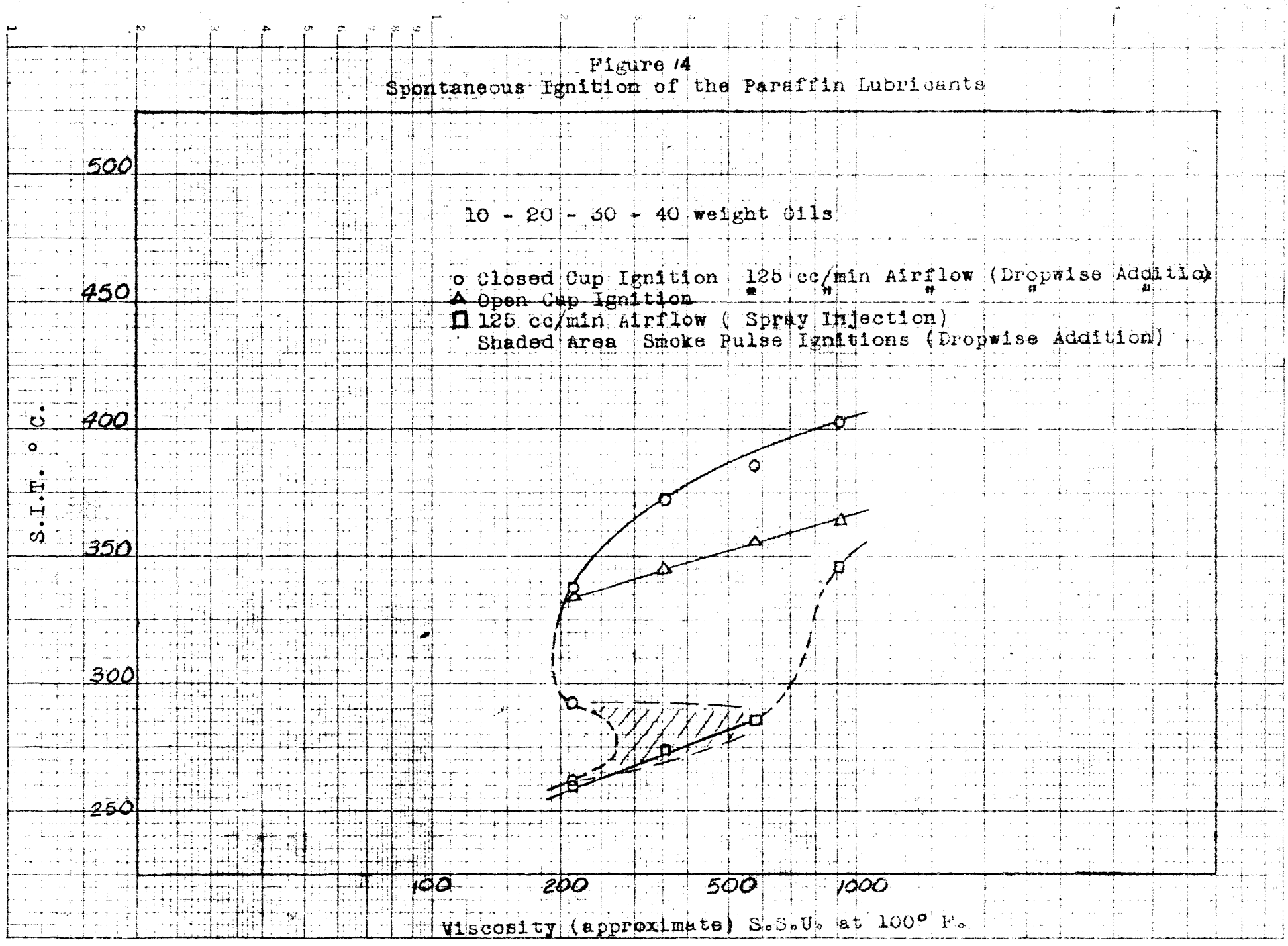
Spontaneous Ignition Temperatures of the Paraffin Lubricants

Lubricant	Spontaneous Ignition Temperature (°C)			Remarks
	Dropwise Addition		Spray Injection	
	Closed Cup Air Flow 125 cc/min	Open Cup Air Flow 125 cc/min	Air Flow 125 cc/min	
All State Motor Oil SAE 10	262	335	259	Heavy black tar-like residue
All State Motor Oil SAE 20	372	345	274	
All State Motor Oil SAE 30	385	355	286 (274)	
All State Motor Oil SAE 40	403	365	347	
Bardahl SAE 10	272			Very fine brown sand-like residue
Reciprocating Engine Oil 1120 ANO-8	395	375		Heavy black tar-like residue

This data shows quite strikingly how the ignition boundary can be greatly extended by the use of spray injection. Under the dropwise procedure only the SAE 10 oil ignited in the low temperature region with a nonignition zone in the intermediate temperature region. With spray injection the nonignition zone was completely eliminated and the SAE 10, 20 and 30 oils gave reasonable ignition temperature in the low temperature region. The spray injector could not satisfactorily handle the SAE 40 because of its high viscosity; nevertheless, a drop of 60° was effected for this oil. The EP additives responsible for "Bardahl's" unusual properties evidently did not markedly influence its ignition properties as an SAE 10 oil. An aircraft oil, 1120 ANO 8 (reciprocating engine) whose viscosity was greater than an SAE 40 oil gave ignition temperatures in the same region as the SAE 40 oil. All of these products left heavy, tar-like residues in the ignition cup.

The chemical structure considered to be chiefly responsible for the spontaneous ignition characteristics of these oils is the

Figure 14
Spontaneous Ignition of the Paraffin Lubricants



polymethylene chain containing a high percentage of secondary hydrogen atoms. The aromatic and naphthenic content is assumed to have only a minor influence on the ignition properties.

(b) Polyisobutylenes and Hydrogenated Polyisobutylenes.

The high ignition temperatures of isooctane, diisobutylene, and other highly branched paraffins suggested that an oil with a high degree of branching would have a high spontaneous ignition temperature. Accordingly a series of polyisobutylenes were synthesized and some were hydrogenated to the saturated derivatives.

The di- and tri-isobutylenes were prepared by the sulfuric acid dehydration and polymerization of t-butyl alcohol[32,33]; tetraisobutylene was prepared by the boron trifluoride-catalyzed dimerization of diisobutylene[34]. 1,1-Dineopentylethylene was obtained by the permanganate oxidation of triisobutylene which leaves only this isomer unchanged[35].

The higher polymers were prepared by the boron trifluoride catalyzed polymerization of isobutylene[34]. By simple vacuum distillation polyisobutylene samples of varying viscosities were obtained. Hydrogenation of these products over Raney nickel catalyst at about 180°C gave the saturated derivatives. A liquid copolymer of isobutylene and styrene (boron trifluoride catalyst) was also prepared. The spontaneous ignition characteristics of these products are summarized in table II and figure 15; other properties are listed in table III.

The ignition temperatures of all these materials show a remarkable resistance to spontaneous ignition when compared with all of the other lubricants tested. It is significant that spray injection did not lower the ignition temperatures obtained by the dropwise procedure. This is in marked contrast to the results obtained for the other lubricants where spray injection effected a considerable lowering of ignition

Table II

Spontaneous Ignition Temperatures of Various Polyisobutylenes and Their Hydrogenated Derivatives

Compound	Unsaturated S.I.T., °C. Dropwise Addition 125 cc/min Airflow	Dropwise Addition Zero Airflow	Spray Injection 125 cc/min Airflow	Compound	Saturated S.I.T., °C. Dropwise Addition 125 cc/min Airflow	Dropwise Addition Zero Airflow
Diisobutylene	470	435		Isooctane	518	502
1,1-Dineopentyl Ethylene	455	425		1,1-Dineopentyl Ethane	500	486
Triisobutylene	413	408	413	Isododecane	500	485
Tetraisobutylene	415	402		Isohexadecane	484	460
Mixture 1 pt. Di 5 pts. Tri 4 pts. Tetra	436	392				
Higher Polyisobutylenes						
Original Reaction Product	390	348				
After Precipitation of High Molecular Wt. Polyisobutylene with Acetone	392	364				
Polyisobutylene Distillate						
(1) <45°C/2 mm	392	355				
(2) 70-90/2	400	370	398			
(3) 110-114/2	403	366		(3) Hydrogenated	465	428
(4) 160-200/2	403	380		(4) Hydrogenated	434	410
(5) Residue	412	400		(5) Hydrogenated	431	408
Styrene-Isobutylene Copolymer	376	335				

Figure 15

Spontaneous Ignition Temperatures of the Polyisobutylenes and their Hydrogenated Derivatives

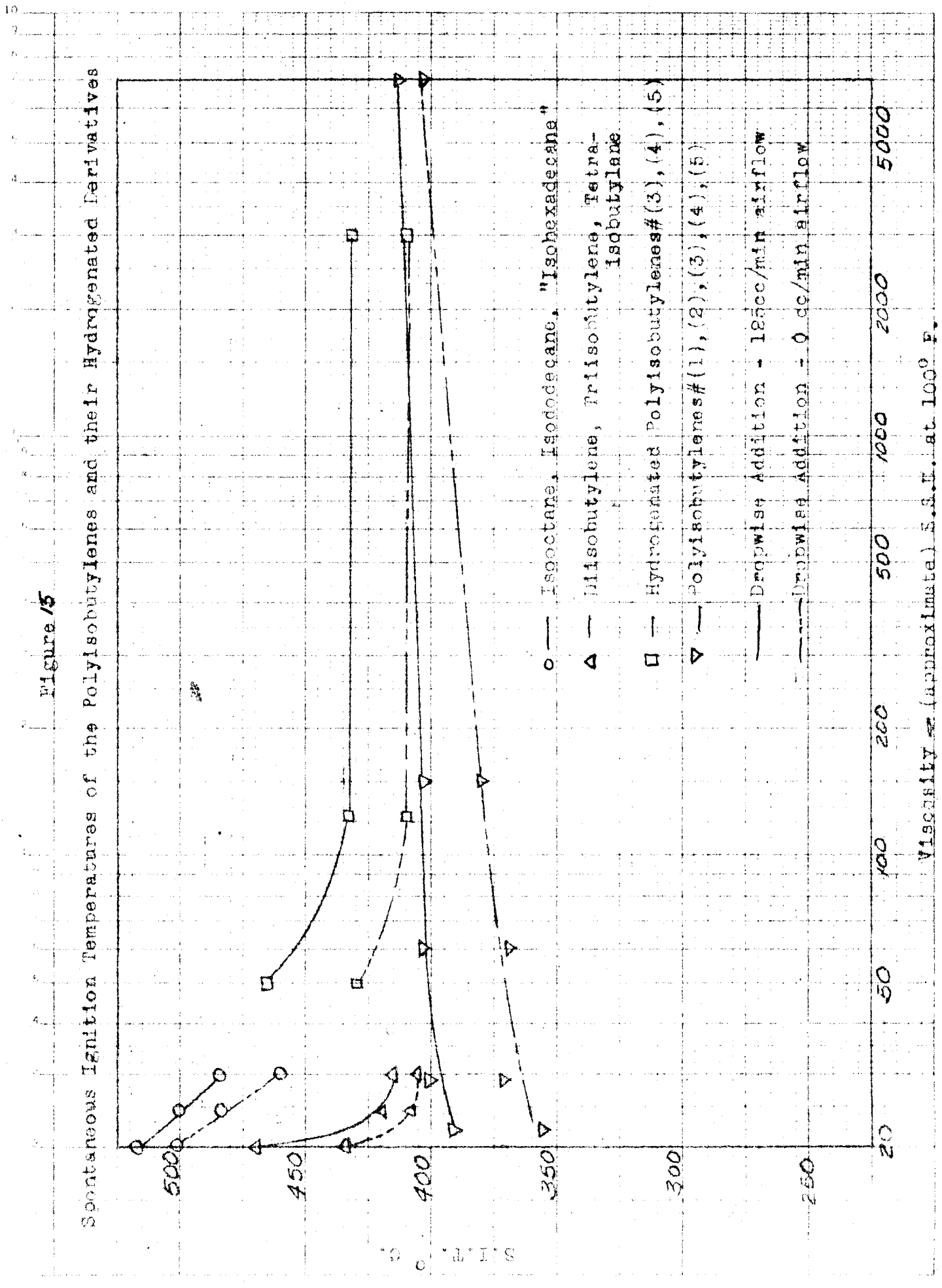


Table III

The Polyisobutylenes and Their Hydrogenated Derivatives-
Refractive Index, Boiling Point, and Viscosity Data

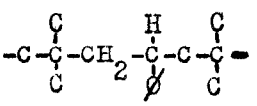
Compound	n_D^{25}	b.p. °/mm	Approx. Visc. SSU - 100° F
Diisobutylene	1.4073	101.5/740	
Isooctane	1.3890	98.5/740	
1,1 Dineopentyl Ethylene	1.4271	177-178/740	
1,1 Dineopentyl Ethane	1.4169	177-177.5/740	
Triisobutylene	1,4282	176-178/740	
Isododecane	1.4170	177-178.5/740	
Tetraisobutylene	1.4475	152-153.5/58	30
"Isohexadecane"	1.4370	118-119/15	28
Polyisobutylene Distillates			
(1)	1.4327	<45/2	22
(2)	1.4507	70-90/2	29
(3)	1.4612	110-114/2	50
(4)	1.4712	160-200/1-2	135
(5)	1.4894	>200/1-2	7000
(3) Hydrogenated	1.4524		50
(4) Hydrogenated	1.4638		125
(5) Hydrogenated	1.4840		3000
Styrene-Isobutylene Copolymer			370

temperature. In following the pattern set by the simple branched paraffins and olefins (page 32) the ignition temperatures of the hydrogenated polyisobutylenes were some 30 to 60 degrees higher than the corresponding polyisobutylenes.

Previously polyisobutylenes have not been considered desirable as synthetic lubricants, the undesireable properties being poor lubricity and poor thermal stability. However, in view of their superior resistance to spontaneous ignition, it seems that a re-evaluation of their properties would be in order. Extreme pressure additives could give the desired lubricity and, if not too great, thermal losses could be replaced. Another remarkable property of the polyisobutylenes is their clean burning characteristics. Under all the conditions explored in this investigation the polyisobutylene left substantially no residue; this is in marked contrast to other lubricants such as the paraffinic oils which leave a heavy lacquer-like residue.

In view of the results shown in figures 13 and 19 blending with other lubricants and use of anti-oxidant additives such as di-p-tolylamine show further promise for polyisobutylenes as special lubricants.

The copolymer of styrene and isobutylene gave an ignition temperature lower than that of a polyisobutylene of comparable viscosity. This at first seemed contrary to what would be expected for the incorporation of a phenyl group into the polymer; however, along with each phenyl group comes a methylene group and a tertiary hydrogen.



Comparison of this structure with cumene would indicate that the molecule is quite susceptible to peroxidation at the position of this tertiary hydrogen.

(c) Polypropylenes.

The exceptionally high spontaneous ignition temperatures of the polyisobutylenes prompted the evaluation of the polypropylene structure which would show an intermediate degree of branching between the polymethylene and polyisobutylene structures. The polypropylenes were prepared by dehydration and polymerization of isopropanol with a BF_3-H_3PO_4 catalyst. The following table shows a portion of the data collected by Mr. Swarts for these compounds.

	Spontaneous Ignition Temperature (°C)		
	Dropwise Addition		Spray Injection
Polypropylene	Air Flow 125 cc/min	Air Flow 0 cc/min	Air Flow 125 cc/min
Trimer	298	290	
Tetramer	288	284	
Hydrogenated Tetramer	385 (266)		
Pentamer	274 (266)	266 (254)	
Hydrogenated Pentamer	273 (228)	248 (220)	272 (230)

Values in parenthesis indicate lower limit of smoke pulse ignition.

These values with one exception are in the low temperature range of ignition. The reason for the low ignition temperatures in spite of the considerable degree of branching must be due to the tertiary hydrogen atoms that accompany the branching.

(d) Polyethylenes.

Three German polyethylene oils were obtained through the courtesy of Dr. W. A. Zisman of the Naval Research Laboratory. These oils were synthesized using an $AlCl_3$ catalyst for the polymerization of ethylene. According to Whitmore's carbonium ion mechanism for polymerization a certain degree of methyl branching would be expected for these oils. This was confirmed by Murphy and Sanders[36] in their examination of these oils. Their results indicated that the structure was best represented by a methylene chain with occasional methyl branching, containing

one double bond per molecule and free from aromatic and naphthenic groups. Therefore, not a great deal of difference is to be expected between these and the n-paraffin oils of comparable viscosity. For these compounds a heavy tar-like residue remained after ignition. The spontaneous ignition results are shown in the following table and figure 16.

Lubricant	Spontaneous Ignition Temperature (°C) Dropwise Addition	
	Closed Cup Air flow 125 cc/min	Open Cup Air flow 125 cc/min
German Oil V-120	245	
German Oil SS 903	388	390
German Oil SS 906	420	

(e) Polyethers

In view of the importance of the polyethers as synthetic lubricants, a large number of these have been tested; these included both the "Ucons" (Carbine and Carbon Chemicals Corporation) and the "Polyglycols" (Dow Chemical Company). The results are given in tables IV and V and figures 17 and 18.

The polyethers, in a rather general way concerning spontaneous ignition characteristics, are similar to the paraffin oils. With dropwise addition procedure the spontaneous ignition temperatures increase with increasing viscosity and molecular weight, and the ignition temperatures of oils in the intermediate viscosity range dropped considerably by using spray injection. The actual values of the ignition temperature are higher for the polyethers of viscosity comparable with that of paraffin oils, but the general shape of the ignition curves is the same.

A marked advantage of the polyethers over the paraffin oils is their small ignition residue. Those igniting in the low temperature range left a relatively slight lacquer-like deposit; those in the intermediate range left a dark residue which gradually disappeared; those igniting at

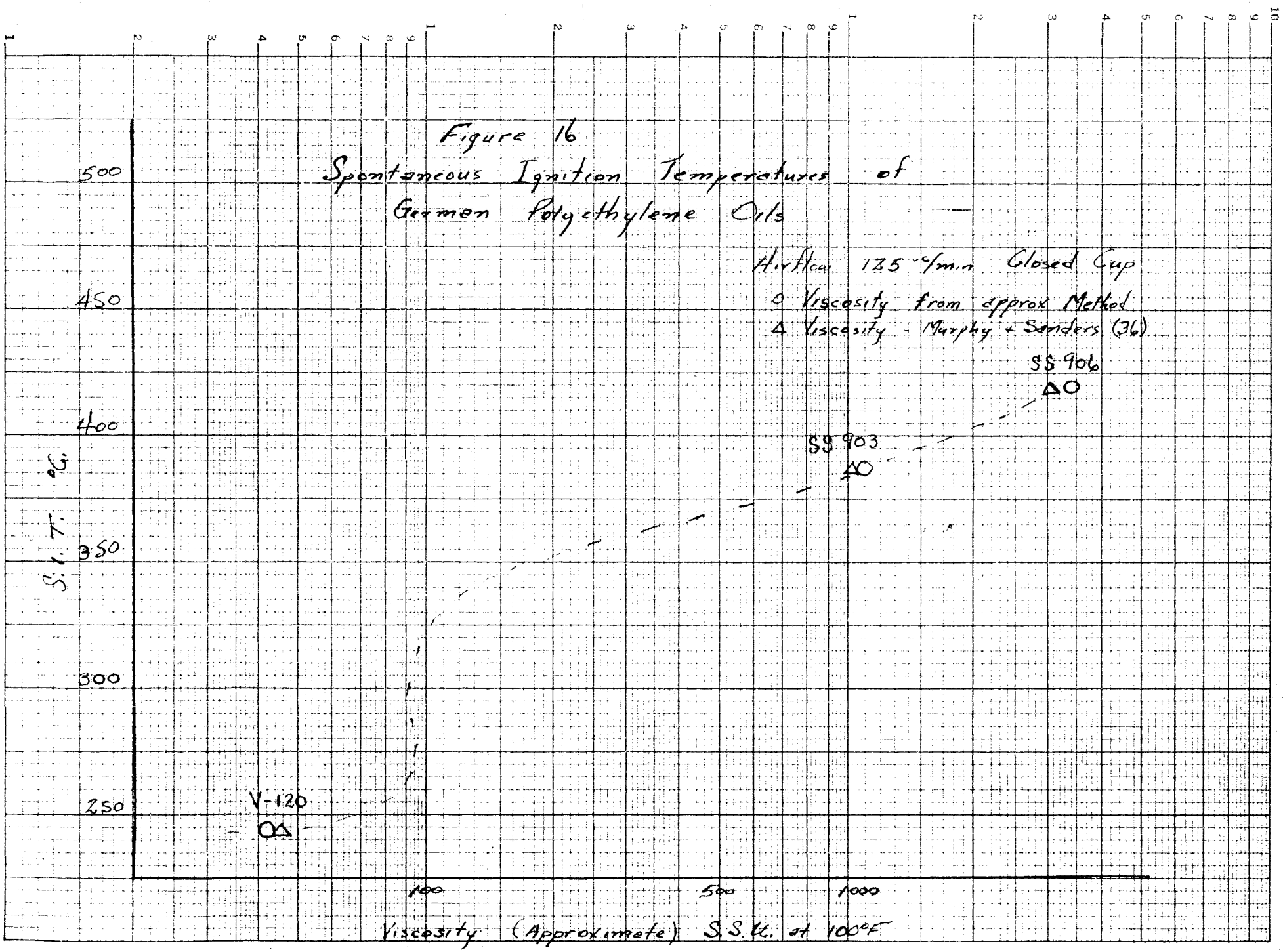


Table ~~VII~~ IV

Spontaneous Ignition Temperatures of the "Ucons"

Lubricant	S.I.T., °C. Dropwise Addition Closed Cup 125 cc/min Airflow	Dropwise Addition Open Cup 125 cc/min Airflow	Spray Injection 125 cc/min Airflow	Remarks
LB 1800 X	412	355		No residue at 400° C but at 350-375° a dark residue forms which slowly oxidizes away.
LB 1715	405	350	397	
LB 400 X	397	352		
LB 385	380	355	330	
LB 170 X	375	355		
LB 135	350	333		
LB 70 X	240	*	216	Lacquer-like residue
LB 65	280	*	210	
50 HB 5100	412	364		Residue at lower temperatures is black and lacquer-like
50 HB 280 X	400	355		
50 HB 260	376	358	321	
50 HB 100	350	348	253	
50 HB 55	255	*	235	
75 H 1400	410	~375		
75 H 480	396	376		
DLB EHD 190 B	374	340		Lacquer-like residue
DLB 50 BX	325	*		
"818"	382	>378		Residue oxidizes away
DLB 50 B	330			
DLB 100 B	352			

* Much higher values in open cup than in closed cup - no definite value determined.

Table ~~VIII~~ V

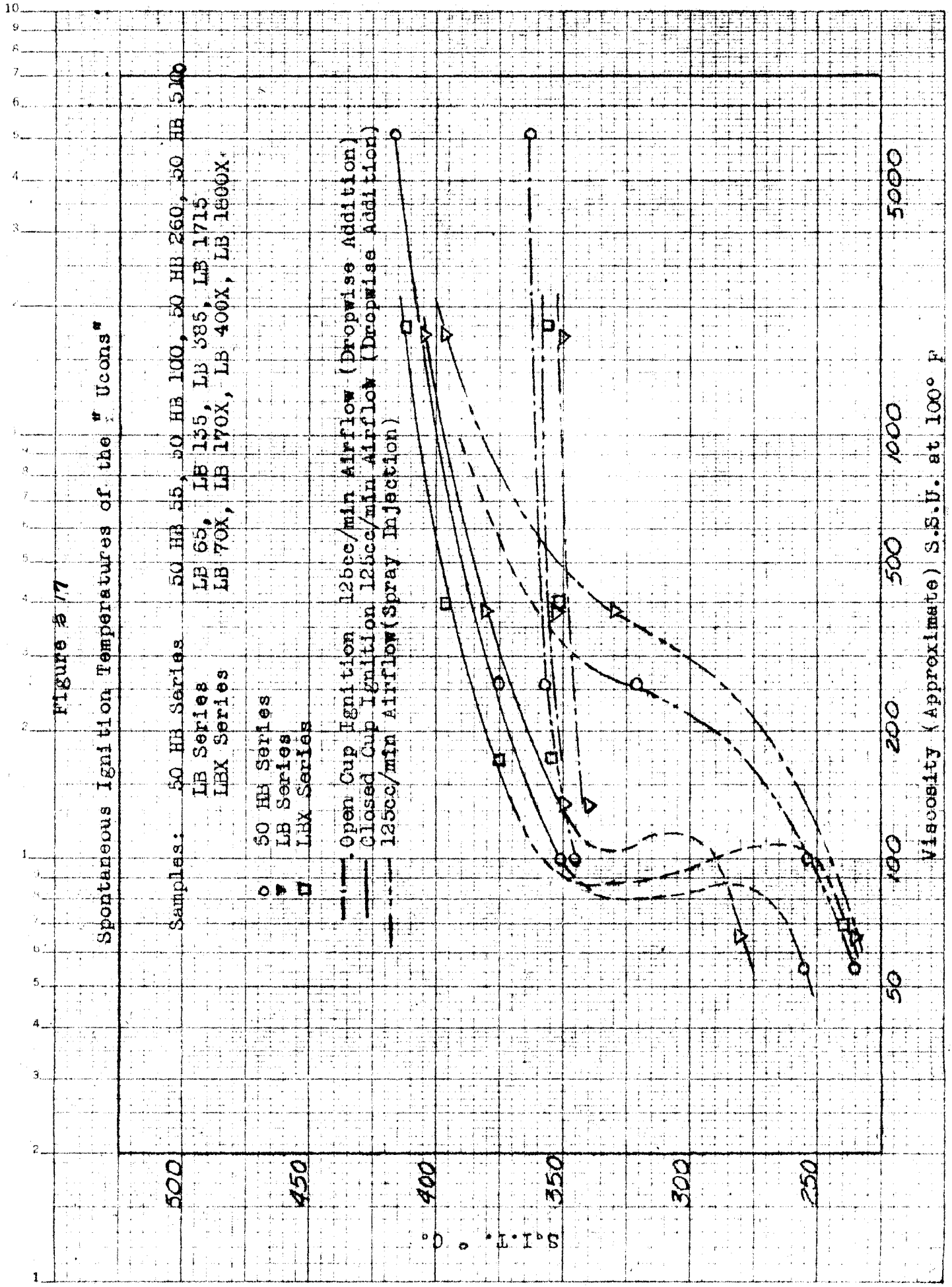
Spontaneous Ignition Temperatures of "Polyglycols" (1)

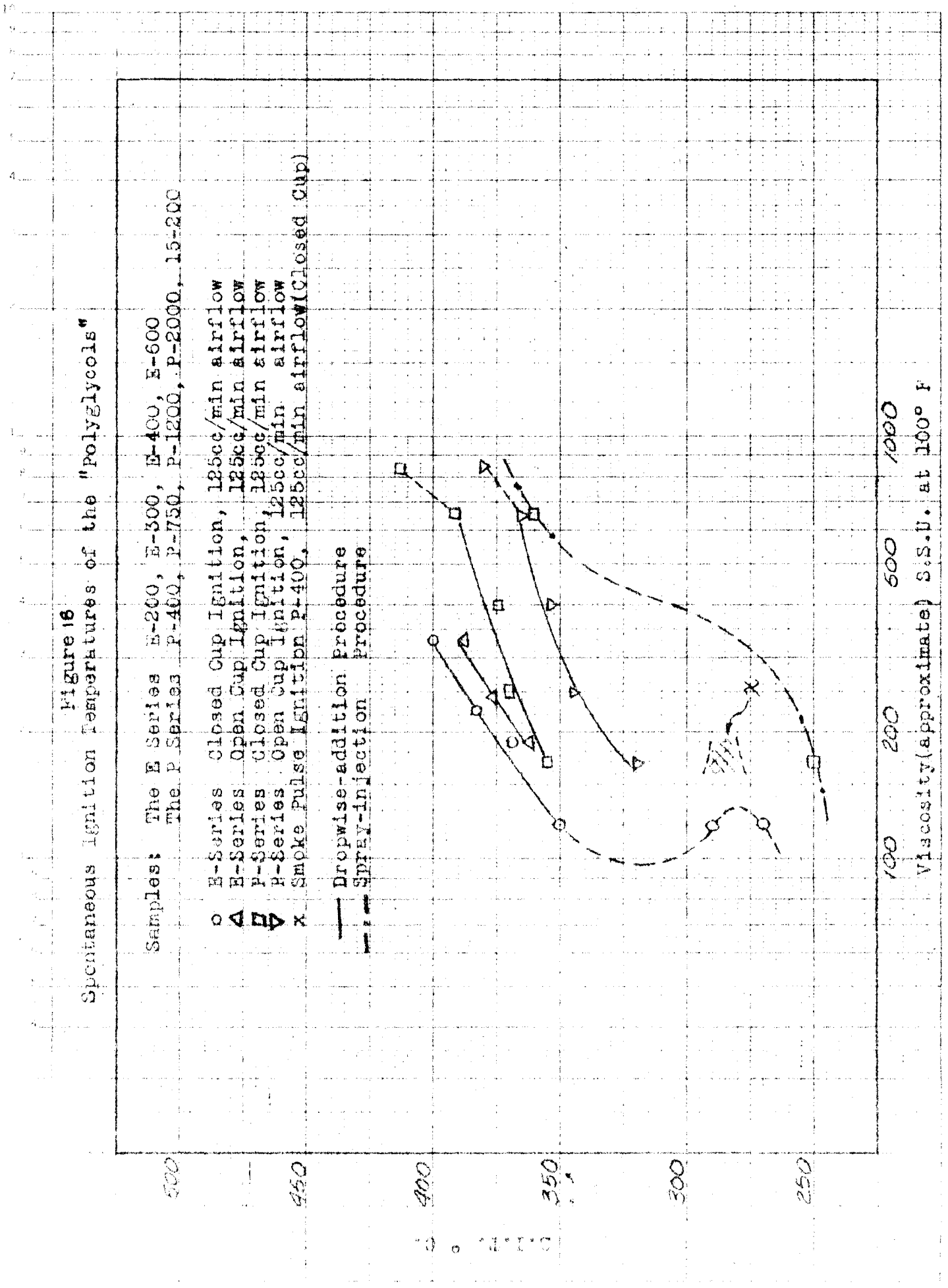
Lubricant(2)	S.I.T., °C.		
	Dropwise Addition		Spray Injection
	Closed Cup 125 cc/min Airflow	Open Cup 125 cc/min Airflow	125 cc/min Airflow
15-200	414	406	
P-2000	392	378	360
P-1200	375	352	
P-750	370	345	
P-400	355	318	250
E-600	400	400	
E-400	384	384	
E-300	368	365	
E-200	350 (270)(3)	-	

(1) Ignition residues similar to those for "Ucons", Table VII.

(2) P series - Polypropylene Glycols
E series - Polyethylene Glycols
Numbers indicate average molecular weight.
Sample 15-200 is a Polyglycol "Derivative"

(3) Below 350° a zone of non-ignition was observed; a small zone of low temperature ignition then was found in the range from 270-280° C.





high temperatures burned cleanly. This is the result of the ignition temperature itself, rather than of any structural differences in the three product ranges.

The polyethers are polymers of ethylene oxide, propylene oxide, or a combination of the two. The polymer ends may or may not be "stoppered" with ether or ester groups.

A sample of tetra-penta-propylene-glycol-normal-butyl-ether-acetate gave an ignition temperature of 326°C at 125 cc/minute air flow.

(f) Diesters.

The diesters are among the most promising of the synthetic lubricants. In fact, di(2-ethylhexyl)adipate has been made available in commercial quantities. Therefore, it was of interest to evaluate their spontaneous ignition characteristics. These characteristics have been adequately discussed in previous sections (page 35).

Although the diesters have much to recommend them as synthetic lubricants[29] they can no longer be considered free from low temperature ignition as previously assumed.

(g) A Jet Engine Lubricant.

A sample of a jet engine lubricant was obtained from the Cleveland NACA Laboratory. This oil had a low viscosity and yet gave a spontaneous ignition temperature of 320°C at 125 cc/minute air flow which is considerably higher than the ignition temperatures of the paraffin oils and polyethers of comparable viscosity. The structure of this oil was not given us so an interpretation of its spontaneous ignition behavior cannot be advanced.

(h) Summary

Table VI on page 65 summarizes the spontaneous ignition data obtained

on the various lubricants examined. The fundamental structural units have been included for correlation with this ignition data.

The polyisobutylenes possess the highest ignition temperatures and show the greatest degree of branching. The polypropylenes show an intermediate degree of branching but much lower ignition temperature than would be expected on the basis of the branching concept alone. Therefore, it is obvious that branching alone is not sufficient to produce high ignition temperature. The critical factor for high ignition temperatures appears to be the reduction of secondary and tertiary hydrogens to a minimum. A completely methylated carbon chain would give a structure with all primary hydrogens. Such a structure is apparently ruled out on practical grounds because synthesis of such a polymeric structure has not been realized due to the steric strain involved. Therefore, it seems that the polyisobutylene structure is the closest approach to a practical structure of minimum number of secondary and tertiary hydrogen atoms and maximum number of primary hydrogen atoms. This gives added support to Boord's postulate[37] that the relative oxidation rates of hydrocarbons may be correlated with the reactivities of their hydrogen atoms, the order of reactivity being 3° 2° 1°.

Full significance as to the effect on ignition properties of ether and ester groupings in a lubricant molecule cannot be given at this time; however, the relative numbers of primary, secondary, and tertiary hydrogen atoms is considered still to be the dominating factor.

Some additional speculation may be warranted regarding the nature of the ignition residue deposited by these various lubricants as related to their possible intermediate oxidation products. The polyisobutylenes would be expected to yield mainly acetone and formaldehyde[38]. All except the polyisobutylenes would be expected to yield other aldehyde

Table ~~III~~ VI

Spontaneous Ignition Temperatures of Various Lubricants

Lubricant	Approx. Primary C-H Bonds, %	Ignition Residue	Range of Spontaneous Ignition Temps., ° C. (Viscosity Range: 100-300 SSU at 100°F) Dropwise	Spray
Paraffin and Naphthene Mixture $\{ CH_2 \}_n$	10	Heavy Lacquer	ca 320	< 270
Polyethylene $\{ CH_2\text{-}CH_2 \}_x \left\{ \begin{matrix} H \\ C \\ CH_3 \end{matrix} \right\}_y$	30	Heavy Lacquer	ca 320	< 270
Polypropylene $\{ C - \underset{C}{C} \}_n$	50	Heavy Lacquer	ca 320	< 270
Polyisobutylene $\{ C - \overset{C}{\underset{C}{C}} \}_n$	80	None	> 400	> 400
Polyethylene Glycol $\{ C - C - O \}_n$	0	Lacquer Burns Away	ca 350	< 290
Polypropylene Glycol $\{ C - \underset{C}{C} \}_n$	50	Lacquer Burns Away	ca 350	< 290
Diesters Di - (2-Ethyl Hexyl)Adipate Di - (1-Ethyl Propyl) Sebacate	30	Lacquer	ca 350	< 290 (< 100 SSU)

intermediates in addition to formaldehyde; all except the polyisobutylenes deposit lacquer-like residues. These lacquers from the polyethers should possess higher oxygen contents and more α-positions reactive to further attack; this situation may help to explain the readiness with which these residues disappear.

4. Effect of Additives on Spontaneous Ignition Temperatures.

The use of additives is an attractive possibility for modification of conventional lubricants to impart desireable ignition resistant properties. Accordingly a number of different avenues of the effect of additives on spontaneous ignition were investigated.

(a) n-Dodecane with Various Additives.

Approximately 65 chemical compounds were tested at concentrations of 5 mole percent for their effects on the spontaneous ignition temperature of n-dodecane; these results are summarized in table VII. The greatest rise in ignition temperature was achieved with tetraethyl lead. Of the more usual inhibitors of free radical reactions, three secondary amines were most effective in raising the ignition temperature. These were ethyl-o-toluidine, diphenyl-amine and N-methylaniline. Di-tert-butyl peroxide gave the only major drop in ignition temperature; this mixture behaved in much the same way as did dihexyl ether, that is, low ignition temperatures and very short induction periods.

The effectiveness of the secondary amines with methylation in the para position suggested the use of di-p-tolyl amine. This amine was synthesized by heating an equimolar mixture of p-toluidine and p-toluidine hydrochloride. Di-p-tolylamine was more effective than the other amines listed above actually raising the "hot flame" ignition temperature of dodecane to 320°C.

(b) The Effect of Additives on the S-shaped Ignition Curve of Dodecane-Dineopentylethane Mixtures.

The manner in which the ignition boundary of dodecane-dineopentylethane mixtures is pushed back by di-p-tolylamine, tetraethyl lead, and dilaurylselenide is shown in figures 19, 20, and 21.

TABLE # VII

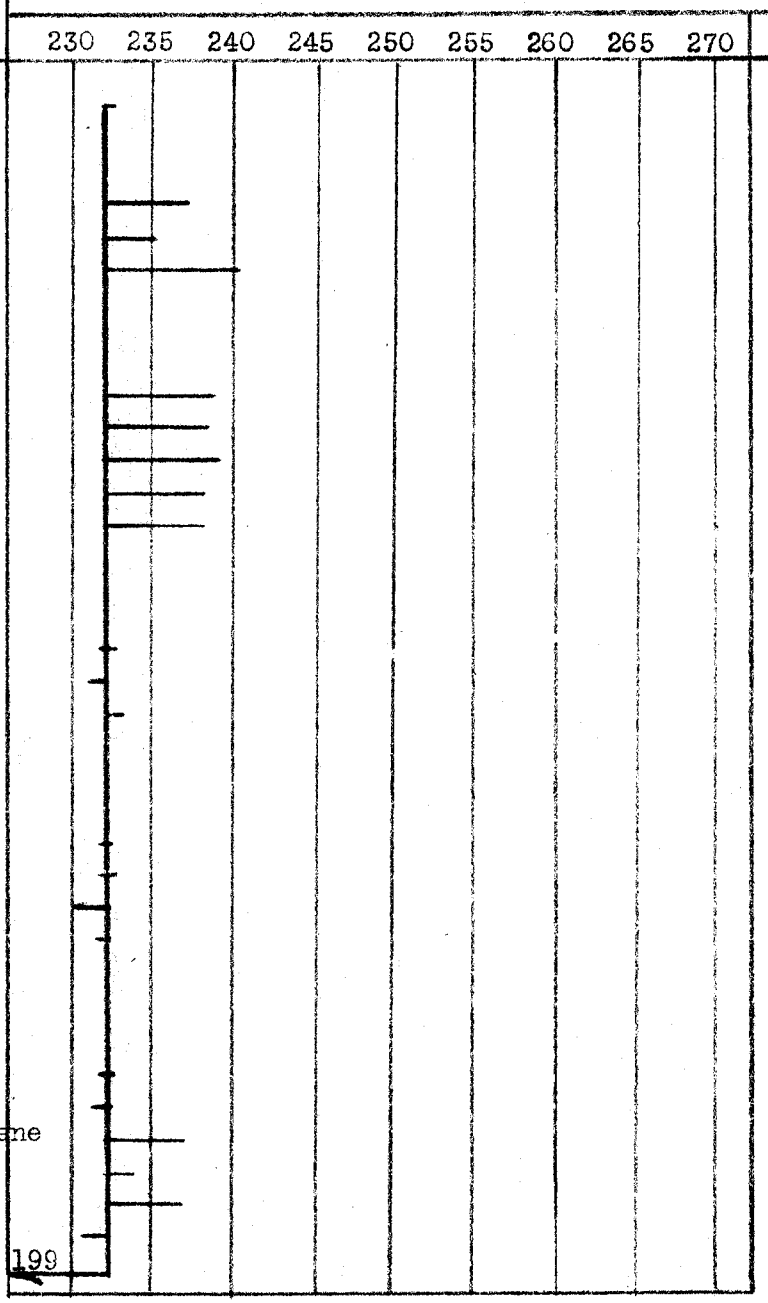
S.I.T. of Dodecane Containing Various Additives (5 mole %)

Additive	Spontaneous Ignition Temperature (125 cc air/min)
	230 235 240 245 250 255 260 265 270
None	232
Amines	
Aniline	243
o-Toluidine	255
p-Toluidine	259
2-Amino-1,3-dimethyl benzene	265
2-Amino-1,4-dimethyl benzene	266
5-Amino-1,3-dimethyl benzene	265
4-Amino-1,3-dimethyl benzene	267
N-Methyl aniline	268
Ethyl o-toluidine	271
Diphenyl amine	272
o-Chloroaniline	237
m-Chloroaniline	239
p-Chloroaniline	245
N,N-Dimethyl aniline	232
Triethanol amine[1]	234
Diethanol amine[1]	233
Mono ethanol amine[1]	234
Pyridine	233
o-Nitro aniline	235
m-Nitro aniline	234
p-Nitro aniline	231
Diethyl amine	248
Benzyl amine	238
Triethyl amine	234
Phenols	
Phenol[1]	239
Resorcinol[1]	235
Hydroquinone[1]	245
Guaicol	244
Hydrocarbons	
Benzene	232
Toluene	232
o-Xylene	233
m-Xylene	234
p-Xylene	234
Mesitylene	234
1,2,3 Trimethylbenzene	234
1,2,4 Trimethylbenzene	238
Triethyl benzene	236
Hexamethyl benzene	246
Hexaethyl benzene	239
Naphthalene	236
α Methyl Naphthalene	238
Biphenyl	231

[1] These addit ives were not completely miscible with Dodecane.

Table VII (Cont'd)

Additive	Spontaneous Ignition Temperature (125 cc air/min.)
	230 235 240 245 250 255 260 265 270
None	232
Alcohols	
Isopropanol	237
Benzyl Alcohol	235
Decanol	240
Naphthenates[2]	
Cobalt Naphthenate	239
Calcium Naphthenate	238
Iron Naphthenate	239
Manganese Naphthenate	238
Lead Naphthenate	238
Carbonyl Compounds	
Acetophenone	232
Benzaldehyde	231
Cyclohexanone	233
Halogen Compounds	
Bromobenzene	232
Chlorobenzene	232
Carbon tetrachloride	230
1,1,2-Trichloroethane	232
Miscellaneous	
Ethylbenzoate	232
Nitrobenzene	231
a-Methyl,o-trifluoromethyls tyrene	237
Isopropyl ether	234
Isoamyl nitrite	237
Cumene hydroperoxide	230
t-Butyl peroxide	199



Tetraethyl lead	Air Flow Rate 125 cc/min	25 cc/min	0 cc/min
5 mole %	580	434	420
1 mole %	525	436	420

The majority of the additives listed here were obtained from readily available sources and further pruified by simple distillation or recrystallization.

2. 5% of Solution of Naphthenate by weight in Dodecane

Figure 10

The Change in Spontaneous Ignition Characteristics of Dodecane-1,1-Dineopentyl Ethane Mixtures when 5 Mole Percent Di-p-Tolyl Amine is Added to These Mixtures.

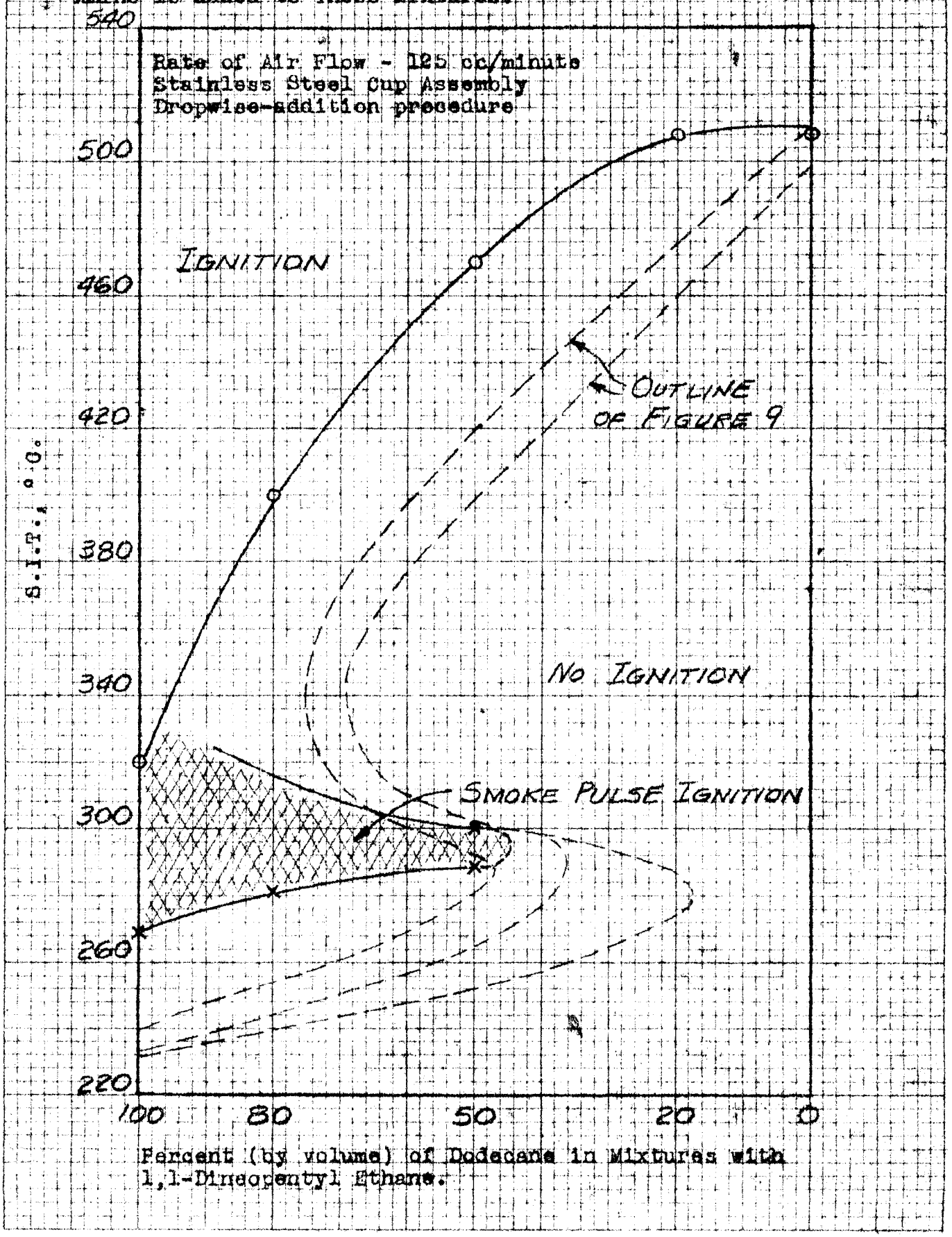


Figure 20

Influence of 1% mole Tetraethyl Lead on Spontaneous Ignition Characteristics of Dodecane-1,1-Dineopentyl Ethane Mixtures (Dropwise Addition Procedure

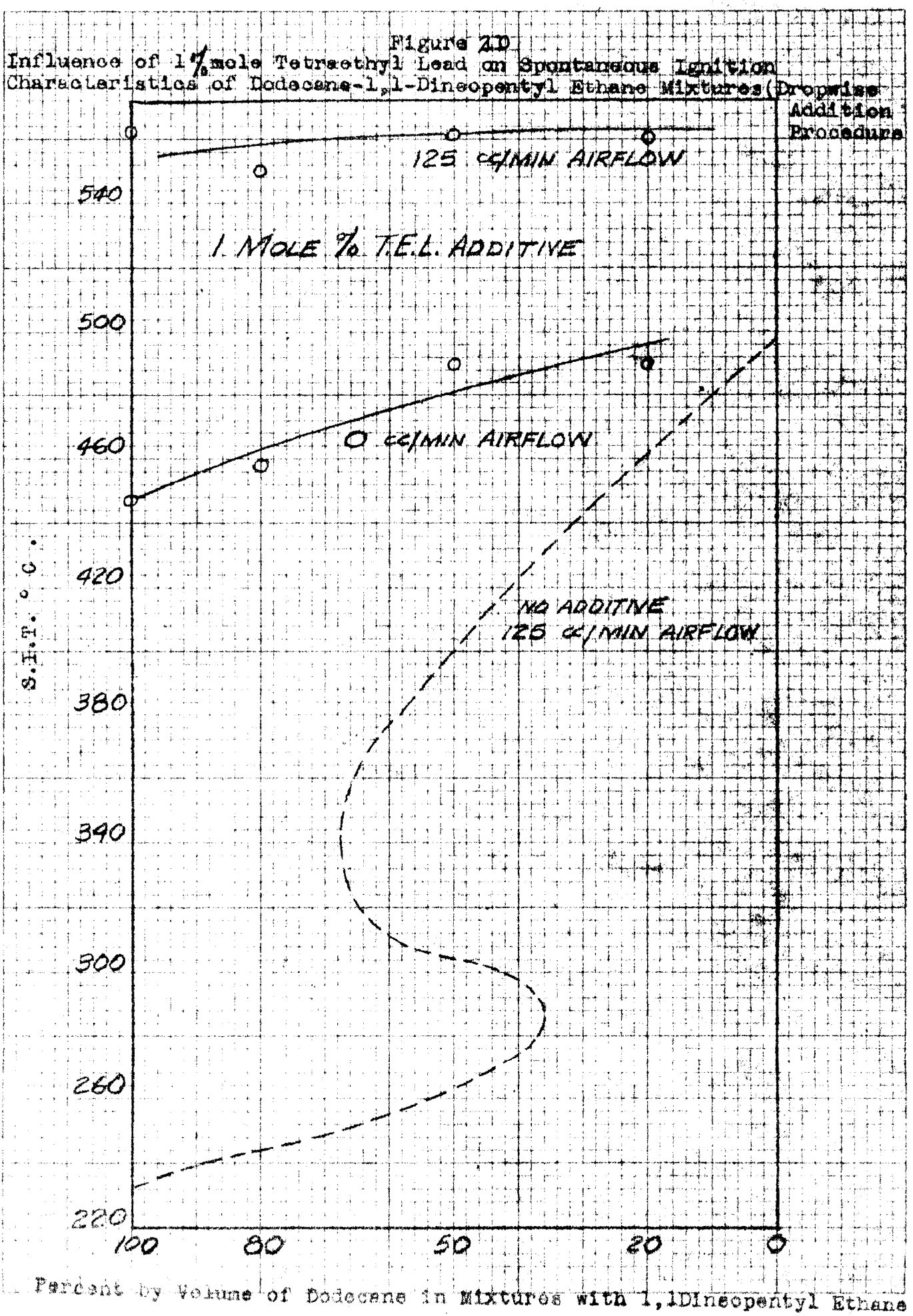
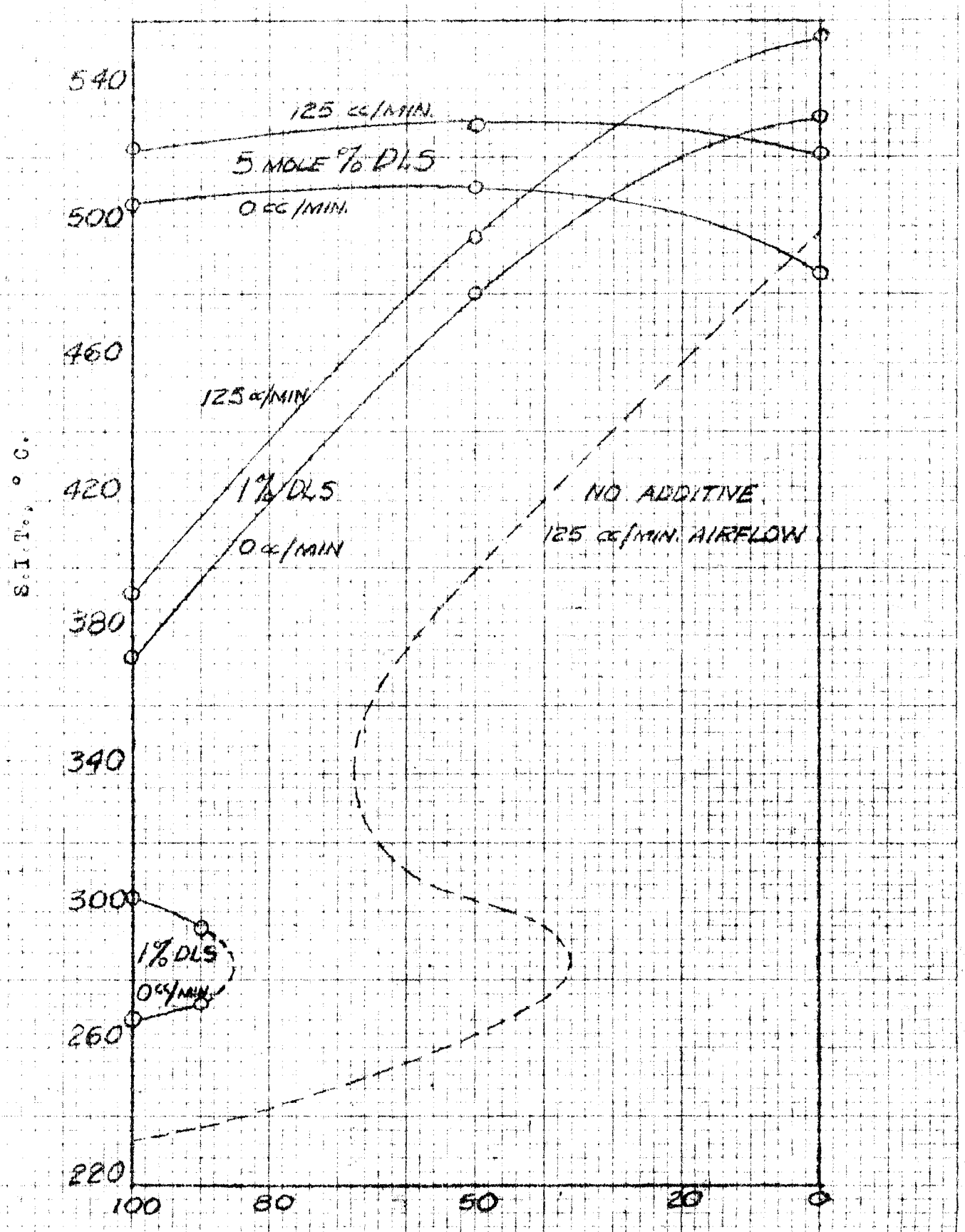


Figure # 21

Influence of 1 mole and 5 mole Dilauryl Selenide (DLS) on the Spontaneous Ignition Characteristics of Dodecane-1,1-Dineopentyl Ethane Mixtures. (Dropwise-Addition Procedure)



Di-p-tolyl amine seems to have eliminated any glow or cool flame ignition region. This is significant because compounds capable of inhibiting chain reactions in the cool flame region are considered the most powerful antiknocks. Another significant feature with lubricant blending implications is that whereas 5 mole percent di-p-tolyl amine raises the minimum flame ignition temperature 80° for dodecane and 8° for 1,1-dineopentyl ethane, the rise is 190° for a 50-50 mixture of the two paraffins.

Tetraethyl lead produces somewhat of a leveling action on the ignition curve similar to its action upon the knock ratings of various fuels. There is a considerable difference between the curves at the 125 cc/minute and 0 cc/minute air flow rates; this parallels the different knock ratings obtained under different test conditions.

A sample of dilaurylselinide was obtained through the courtesy of Dr. W. A. Zisman of the Naval Research Laboratory. The behavior of the compound is somewhat similar to that of tetraethyl lead with the exception of a slight ignition zone in the low temperature range. Also at 5 mole percent concentration the behavior was quite unusual, the spontaneous ignition temperature of dodecane being raised above that of dineopentylethylene.

(c) Influence of Halogenated Compounds on Spontaneous Ignition of Dodecane and Dineopentylethane.

In view of a recent literature review[39] on the effectiveness of halogenated compounds as fire-extinguishing agents, it was suggested that consideration be given them in the procedure employed here. The results obtained are shown in the following table.

Influence of Halogenated Compounds on Spontaneous Ignition Temperature of Dodecane and 1,1-Dineopentyl Ethane *

Additive 5% Mole	Spontaneous Ignition Temperature (°C) In Dodecane	In 1,1-Dineopentylethane
None	232	498
Ethylene dibromide	234	468
Iodine	260	488
Phosphoryl Chloride	233	490
Methylene bromide	234	460

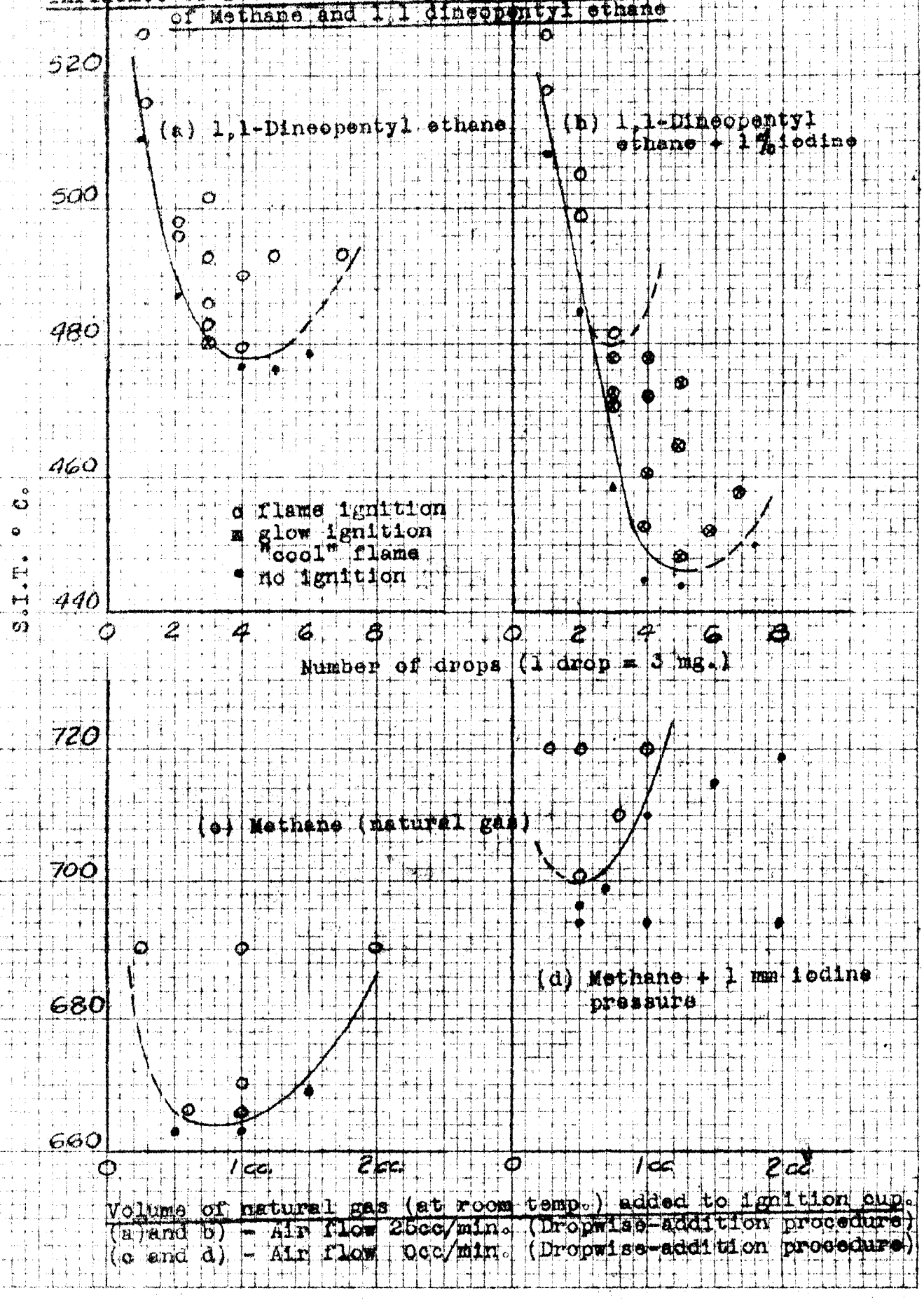
* Air flow rate - 125 cc/min; dropwise addition procedure.

These data indicate that halogenated compounds cannot serve as effective inhibitors of spontaneous ignition in spite of the fire extinguishing properties. Conversely, antiknock compounds have little value as fire extinguishing agents and often are of a highly inflammable nature.

A more detailed study was made of the influence of iodine vapor on the ignition of methane and 1,1-dineopentylethane; the results are shown in figure 22. Iodine inhibits the ignition of methane but promotes a cool flame ignition with dineopentylethane.

Figure # 22

Influence of Iodine on the Spontaneous Ignition Characteristics of Methane and 1,1 dineopentyl ethane



(a) and b) - Air flow 25cc/min. (Dropwise-addition procedure)
(c and d) - Air flow 0cc/min. (Dropwise-addition procedure)

5. Effect of Metal Surface on Spontaneous Ignition Temperatures

A variety of metals are used in aircraft construction. Accordingly it was obvious that some effort should be made in determining the role of the metal surfaces in influencing the spontaneous ignition of fuels and lubricants.

A series of eight metals were obtained from the Cleveland NACA Laboratory. Ignition cup assemblies similar to the one described on page 9 were constructed from the following metals: stainless steel, copper, aluminum, black iron, brass, inconel, and an aluminum alloy (designation 24-S). A sample of magnesium metal was also obtained but only a base plate was constructed from this metal.

While a high degree of quantitative precision was not obtained throughout the whole range of ignition temperatures investigated it does seem that significant generalizations could be made concerning the effect of metals in the low temperature ignition region, in the high temperature region, and in an intermediate temperature region.

Table VIII shows the results obtained for a series of n-paraffins, α-olefins, alcohols, and ethers, all of which ignite in the low temperature region. The various metals show substantially no effect. For any one compound the difference between the high-low values for the series of metals was never more than 6°C. Also it seems that the degree of oxidation of the metal surface (table IX) has little effect on the ignition temperature of compounds in this low temperature region.

With compounds igniting in the high temperature region the catalytic effect of the metal surface becomes pronounced. This is shown in tables IX and X. In table IX a number of compounds were ignited in the stainless steel cup with the cup subjected to varying

Table VIII

Effect of Metals on Ignition of Compounds of Low S.I.T. Values

Metal	Compound Ignited							
	Tetradecane	Dodecane	Octadecane	Dodecene	Octadecene	Decanol	Dodecanol	Dioctyl Ether
Stainless Steel	232	232	235	257	251	291	283	207
Copper	233	230	240	261	255	288	278	206
Aluminum	230	235	235	256	251	289	280	-----
Black Iron	233	235	237	257	252	294	284	208
Brass	234	234	241	255	253	289	278	208
Inconel	230	235	236	256	251	292	281	207
Aluminum Alloy (24-S)	231	232	237	256	251	289	280	208
Magnesium	233	---	---	257	252	---	---	---
Difference between high and low values	4	5	6	6	4	6	6	2

degrees of surface oxidation. In the case of p-xylene a difference of more than 50°C was observed between the bright metal cup and the cup heavily oxidized. This fact proves troublesome in determining reproducible ignition temperatures for materials which ignite at high temperatures; the metal cup must be cleaned frequently to prevent the gradual rise in ignition temperature due to the rather rapid oxidation of the metal surface at these temperatures.

Table IX

Effect of Condition of Metal Surface on Spontaneous Ignition Temperature of Hydrocarbons

Compound	Condition of stainless-steel surface	Spontaneous ignition temperature (°C) at Air flow 125 cc/min	Air flow 25 cc/min
a-Methylnaphthalene	Oxidized	579	
	Bright metal	553	547
p-Xylene	Heavily oxidized[1]	697	
		708	704
		710	708
	Bright metal	657	650
m-Xylene	Heavily oxidized		700
	Bright metal	652	645
Toluene	Slightly oxidized	644	640
	Bright metal	635	630
Cetane	High temperature; oxidized cup	234	232
	Low temperature; oxidized cup	232	225
	Bright metal	235	232

[1]Data given for three successive runs.

Table X shows the effect of six metals on the spontaneous ignition temperature of a highly branched paraffin, 1,1-dineopentylethane. The range of values were 44° at the 125 cc/minute air flow rate and 65° at the zero air flow rate. It is perhaps significant that the ignition temperature increased with the extent of surface oxidation. The reason might be that the increase in surface area intensifies the chain-breaking

action of the walls and higher temperatures are needed to overcome the action by providing more chain initiators.

Table X

Effect of Metals at High Temperatures on the Spontaneous Ignition of 1,1-Dineopentylethane

Metal	Spontaneous Ignition Temperature (°C) Air flow 125 cc/min	Air flow 0 cc/min	Final Condition of Metal Surface
Copper	540	540	Heavy oxide coating (flakes)
Black Iron	538	507	Dark oxide coating
Brass	510	494	Tarnished
Aluminum Alloy	503	485	Dark grey surface
Inconel	502	482	Slightly tarnished
Stainless Steel*	496	475	Slightly tarnished

*These values were determined immediately after the cup had been cleaned with fine emery cloth. The slightly higher values in table II, page 52, were determined after a few preliminary runs, which seem to bring the surface of the cup to a condition more favorable for reproducible results.

In the following table spontaneous ignition temperatures for 4-isopropylheptane in four different metal cups are listed. The differences observed here probably result from shifting of the nonignition zones. Accordingly some compounds in the critical intermediate temperature range may have even wider differences because one metal may not permit low temperature ignition while another will.

Metal	Spontaneous Ignition Temperature (°C) Air flow 125 cc/min
Inconel	257
Copper	256
Stainless Steel	288
Aluminum Alloy	281

Therefore, although no consistent trend was observed with the individual metals throughout the whole range of investigation, it seems that the following generalizations warrant consideration:

(a) Compounds having long polymethylene chains ignite via the low temperature mechanism and are influenced only slightly by differences in the metal surface.

(b) Compounds of an aromatic or highly branched paraffinic nature ignite via the high temperature mechanism and are markedly influenced by the condition of the metal surface, especially the extent of surface oxidation of the metals.

(c) Compounds such as some moderately branched paraffins, having borderline ability to ignite by the low temperature mechanism are probably influenced by metals to the extent that the metal is able to shift the nonignition zone and the sensitive low temperature ignition peninsula.

6. The Slow Vapor Phase Oxidation of Organic Compounds as a Route to the Initial Reaction Processes Leading to Spontaneous Ignition

This section of the report will describe a few exploratory experiments on what we believe to be a new and promising approach to the study of the reaction processes leading to spontaneous ignition. Basically this approach is to partially oxidize a selected organic compound by passing the compound and oxygen through a hot tube, immediately cooling and condensing the vapor and then analyzing the reaction mixture. This approach has been used before as recorded in the literature; however, in these investigations the contact times were of the order of many seconds and the reaction tube diameters of the order of a few centimeters. The results obtained in these investigations have shown a large number of components to be present and no definite mechanism of the reaction could be substantiated from the data obtained. The essential differences in the procedure used here have been contact times of the order of tenths and hundredths of a second and reaction tube diameters of the order of one or two millimeters. Under these conditions the amount of oxidative conversion will be small but this should give only the intermediates associated with the initial reaction processes. The quantitative characterization of these initial intermediates should permit a better evaluation of the mechanisms proposed for such reactions.

Table XI shows the results on a series of runs with a stoichiometric isooctane-oxygen mixture at various temperatures and contact times. The numbers on the following sketch indicate the position at which analyses were made; these numbers correspond with those in table XI.

Table XI

Isooctane Oxidation:

Reaction Products in Millimoles Based on One Mole Isooctane Passing Through the Reactor

Temperature	Contact Time - Seconds (estimate)	Olefin (Figure 2)			Peroxide (Figure 2)					Carbonyl (Figure 2)				Acid	Ratio,
		3	6	Total	1-2	3	4-5	6	Total	3	6	7	Total	Total	Olefin: Peroxide: Carbonyl
550	.5-.7	13.7	1.5	15.2	3.0	1.2	.4	.15	4.8	1.13	.23	.19	1.55	.30	10:3.2:1
550	.3-.4	4.3	.7	5.0	1.3	.7	-	-	2.0	1.51	.11	-	1.62 (?)	.30	10:4:3.2 (?)
550	.2-.3	2.9	.5	3.4	.8	.5	-	-	1.3	.15	.07	-	.22	.15	10:3.8:0.6
450	.55-.75	4.0	.31	4.3	.30	.59	.06	.18	1.13	1.06	.22	.19	1.47	<.15	10:2.6:3.4
450	.35-.45	1.7	.06	1.8	.20	.35	0	.02	.57	.39	.20	-	.59	<.15	10:3.2:3.4

On the walls of the first two traps a solid ice-like substance collects. This fraction contains an appreciable peroxide and carbonyl concentration. The bulk solution in the first two traps contain olefins, carbonyl compounds, an additional peroxide concentration and the unreacted isooctane. Acids in very small concentration may be present.

The amount of reaction decreases with a decrease in the contact time and/or a decrease in temperature. The ratio of olefin:peroxide seems to be rather constant over the range of contact times and temperatures investigated. The olefin:carbonyl ratio decreases considerably for the shortest contact time.

A more detailed analysis was then made of the reaction occuring at a temperature of 550°C and a contact time of .23 seconds. The six-tube reactor was used and approximately 150 mls. of isooctane were passed through the reactor. The general group analysis gave the following data (millimoles per mole of isooctane passing through the reactor):

H_2O_2	5.79
Other Peroxides	1.77
Olefin	9.35
Carbonyl	5.13
Acid	----

The olefin contains at least two components. As the temperature of the reaction mixture rose from -70°C to room temperature a volatile fraction was collected. Water was added to this fraction to wash out any carbonyl compounds. The vapor remaining was passed into a trap containing bromine. In this fashion a small amount of a bromine derivative was obtained. Two samples of pure isobutylene were brominated: (1) with a water solution of Br_2; (2) with pure Br_2. Refractive indices

were then taken on these three samples:

Dibromides	n_D^{27}
Isobutylene	
(1) with bromine water	1.5158
(2) with pure bromine	1.5157
Sample	1.5154

Therefore, it is concluded that the olefin fraction contains some isobutylene.

The reaction mixture was fractionated, and it was observed that the fraction coming over at the boiling point of isooctane contained a definite olefin concentration with the bromine titration. Dry hydrogen bromide from a bromine-tetralin generator was passed into the remaining portion of this fraction. The isooctane was removed by a simple vacuum distillation leaving a small amount of a bromo derivative. This derivative was compared with a derivative obtained in a similar fashion from a known diisobutylene-isooctane mixture. The refractive index of the standard was 1.4550 and for the sample 1.4565. The conclusion made on the basis of this data is that one or more C_8 olefins are present in the reaction mixture, and this C_8 olefin fraction may contain the components of diisobutylene.

The analysis of the peroxides by first the titanium sulfate-colorimetric method and second the potassium iodide-acetic acid method show a difference in results. Because titanium sulfate reagent is specific for H_2O_2 the difference must be due to an alkyl peroxide or hydro peroxide. Per-acids are ruled out because no appreciable acid concentration is observed. Further evidence of an alkyl peroxide was obtained by vacuum distilling another reaction mixture holding the distilling pot at room temperature. All the volatile material, the bulk of which was isooctane, was removed leaving a small amount of material which showed a high peroxide concentration.

Conclusive evidence for the presence of formaldehyde was obtained by the reaction of formaldehyde with methone to give a white crystalline precipitate, m.p. 186°C; m.p. (literature) 189°C. The presence of acetone is suggested on the basis of the following data obtained in the chromatographic separation of the 2,4-dinitrophenylhydrazones obtained from an earlier experiment run at a temperature of 600°C

Fraction	Weight mg.	Melting point °C
1	.5	162 - 175
2	1.6	170 - 185
3	.2	
4	4.8	109 - 116
5	16.2	119 - 122

Melting point of acetone derivative - 124°

Small amounts of other carbonyl compound may be present also, because a number of bands are observed moving down the chromatographic column.

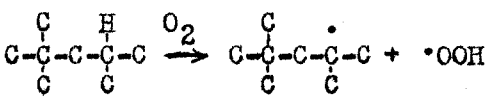
Another run was made at a much shorter contact time to determine which of the components observed previously would diminish in relative amount. The temperature was 550° and the contact time .04 second. General group analysis gave (millimoles per mole isooctane passing through the reactor):

H_2O_2	.31
Other peroxides	.05
Olefin	.76
Carbonyl	---
Acid	---

The carbonyl fraction is the one that has decreased in relative amount to the extent that no carbonyl compounds were observed in the analysis.

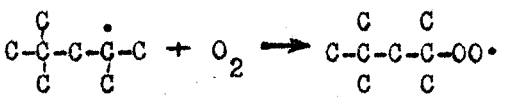
It will now be interesting to see how these observations fit in with the current theories of vapor phase oxidation.

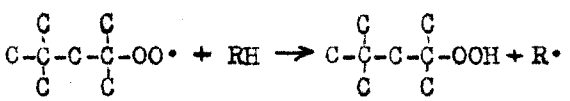
Isooctane was selected as the compound for this exploratory study, since the presence of a single tertiary hydrogen atom should make for more selective, and accordingly, less complex reaction mixtures. There is a general agreement that the initiation of the reaction involves the loss of this hydrogen atom, presumably with the formation of the •OOH radical [40, 41].



The resultant alkyl radical may then undergo one of several reactions:

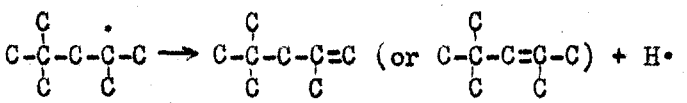
(1) Formation of a hydroperoxide (original mechanism of Walsh[40])





(2) Addition of oxygen and decomposition of the peroxide radical[42,43]

(3) Loss of a hydrogen atom to yield an olefin[42,44,45]



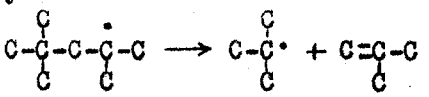
This last reaction possibly has received considerable support recently. Garner and Petty[45] report that olefins were obtained from the oxidation of isooctane, heptane and methylcyclohexane. Kooijman[46] obtained propylene in the oxidation of propane.

The following table is suggestive of the influence the reaction condition has on the tendency toward olefin and peroxide formation.

Compound Oxidized	Reference	Contact Time (Seconds)	Maximum Olefin Yield	Total Peroxide Yield	H_2O_2 Yield
Heptane	Garner and Petty (45)	9 - 13	27%	~ .0001%	—
Propane	Kooijman (46)	4	83%	15%	9%
Isooctane	Page 83	.23	~ 60%	> 70%	> 60%
	Page 85	.04	~ 94%	> 50%	> 40%

By using the very small contact time the reaction products were limited to olefins and peroxides.

Therefore, this data (at small contact times) lends support to reactions (1) and (3) listed on the previous page as the important initial reactions taking place with isooctane. However, these two alone do not account for the presence of isobutylene. On the basis of certain depolymerization reactions previously discussed by Taylor[47] a depolymerization of the initial radical may be postulated to account for the formation of isobutylene.



In conclusion it may be said that this approach shows definite promise in advancing the understanding of the reaction processes leading to spontaneous ignition. The chief criticism is recognized to be whether or not the information obtained under conditions of high surface:volume ratio (e.g. reaction tube of very small diameter) can be extended to the more practical situations involving reaction vessels of smaller surface:volume ratio.

The high yield of hydrogen peroxide reported here is an apparently new development in the field of vapor phase oxidation and may have important industrial significance.

VI. Summary

The overall objective of this investigation has been the development of information which would permit the formulation of lubricants of reduced spontaneous flammability for use in aircraft. The more specific aims have been: (a) the determination of the spontaneous ignition characteristics of a series of pure compounds; (b) the extension of the determination to a variety of commercial and synthetic lubricants; (c) the observation of the effect of the metal surface and various additives on the spontaneous ignition characteristics of representative compounds and lubricants; (d) the correlation of the spontaneous ignition data with antiknock ratings; and (e) the characterization of some of the intermediates in the slow oxidation of hydrocarbons to obtain some rather exploratory information about the reaction processes leading to spontaneous ignition.

Accordingly the following results have been obtained:

1. Spontaneous ignition temperatures have been determined for some sixty organic compounds including normal and branched paraffins, olefins, aromatic hydrocarbons, ethers, alcohols, and esters. The length of the uninterrupted carbon chain is the most important single factor in determining the general location of the ignition temperatures for these compounds; i.e. compounds with long uninterrupted carbon chains have low ignition temperatures while highly branched compounds have high ignition temperatures. Aromatic hydrocarbons have very high ignition temperatures.

2. Correlation between spontaneous ignition temperature and antiknock rating has been observed. Compounds with high octane numbers (low cetane numbers) have high ignition temperatures. There is a close correlation between critical compression ratios and spontaneous ignition

temperatures of aromatic hydrocarbons. A particularly important factor in the ignition of paraffins is the relative number of primary, secondary, and tertiary hydrogen atoms in the molecule.

3. The determination of one "spontaneous ignition temperature" for a compound is often inadequate. This seems to result from a sensitive nonignition zone for compounds with polymethylene chains. A more complete understanding is obtained in some of these cases by plotting the data in the form of three dimensional ignition boundary surfaces.

4. Of the actual lubricants tested the polyisobutylenes have been the only ones with consistently high spontaneous ignition temperatures. In the low viscosity range the paraffin oils, polyethylene oils, polyglycols, polypropylene oils, and diesters have low ignition temperatures; even in an intermediate viscosity range these same oils have low ignition temperatures if spray injection is used. In the high viscosity range all of the lubricants have high ignition temperatures due to low volatility. Therefore, in the low viscosity range and in the intermediate viscosity range using spray injection, good correlation between structure and ignition temperature is obtained for these lubricants.

5. Ignition cups of eight different metals have shown the metal surface to be of almost no effect on the ignition temperatures of compounds igniting in the low temperature range (below 300°C) and of considerable effect on compounds in the high temperature range (above 400°C). In the high temperature range the effect seemed to parallel the extent of the surface oxidation of the cup--the greater the surface oxidation the higher the ignition temperature.

6. Of the additives tested the most effective in raising the ignition temperature of a normal paraffin are tetraethyl lead and dilauryl selenide. Di-p-tolyl amine, although not as effective as

these organometallic compounds, did raise the ignition temperature of dodecane considerably; its advantage over these organometallics would be greater stability in hot oils.

7. In some experiments on the slow oxidation of isooctane, the following materials were observed in the reaction mixture: hydrogen peroxide, alkyl peroxides, isobutylene, other olefins, formaldehyde, acetone, and other carbonyl compounds. By using a contact time of a few hundredths of a second the only reaction products were olefins and peroxides. The major portion of the peroxide fraction was hydrogen peroxide. This high yield of hydrogen peroxide under these conditions is apparently a new development in the field of vapor phase oxidation of hydrocarbons.

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