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HIGH TEMPERATURE HYDRAULIC FLUIDS

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FOREWORD

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ABSTRACT

An extensive literature search and thermal stability screening of available chemicals were conducted as a basis for planning a research program for the development of a high-temperature (700°F) hydraulic fluid. Esters of organic and inorganic acids offer the best possibilities from the standpoint of ease of synthesis, fluidity and viscosity. Phenolic esters have better thermal stability but poorer hydrolytic and viscosity properties than esters of aliphatic alcohols. Research effort therefore should be directed toward the improvement of the thermal stability of the aliphatic esters and toward the improvement of the viscosity and hydrolytic stability of the aromatic esters. Suggestions for a research program have been made and the thermal stability screening test data are reported for 42 compounds.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

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I. INTRODUCTION

As research progresses in the development of ultra high speed and high altitude aircraft there is an urgent need that suitable hydraulic fluids be developed to meet the stringent operational requirements of these machines at extremes of temperature and speed.

The severe nature of these demands makes it imperative that certain hydraulic fluids possess a high thermal stability, a low pour point, a small temperature coefficient of viscosity, a low vapor pressure and a satisfactory lubricity.

Specifications to characterize the hydraulic fluid with which we are concerned in this report are that it must possess a viscosity not greater than 2500 centistokes (cs) at 0°F (maximum 30°F) and after exposure at 700°F for 10 hrs at 3,000 psi shear it shall have a viscosity of not less than 1.5 centistokes. The vapor pressure at 700°F shall be below 100 mm (maximum 600 mm) of mercury and the autogenous ignition temperature shall not be below 750°F. It must be noncorrosive and have satisfactory lubrication and wear properties as measured by suitable specified tests.

Although there has been a wealth of research in the field of hydraulic fluids, it has been quite limited in the temperature range of 700°F. It is quite apparent that the most important obstacle to progress in this development, where "tailored" synthetic organic chemical molecules are involved, is thermal instability.

As a preliminary to a possible longer range research program for the development of a hydraulic fluid stable at 700°F this four months research project had as its primary objective the gathering of data and information through a literature survey of the available pertinent literature and the concomitant laboratory screening of chemicals, with a view to determining the present state of the knowledge and for use as a guide in the judicious direction of future research. Toward this end the project was divided into two parts, literature survey and physical testing.

The literature logically falls into two classes, that available through Armed Services Technical Information Agency Documents Service Center (ASTIA) and chemical literature through chemical publications. It was anticipated that ASTIA literature would serve more for orientation purposes and information on what has been studied under limited conditions rather than for pertinent information about thermal stabilities of chemicals in the range of 700°F.

The task of searching the chemical literature completely through even one class of chemical compounds is enormous, and the usefulness of such a complete search seems questionable. We, therefore, chose to search for sufficient data on vapor pressure, thermal stability and viscosity in each class of compounds to permit an intelligent choice of the most promising classes and to furnish a guide for the design of specific promising compounds in the selected classes. The following classes were searched: hydrocarbons, ethers, esters, ketones, sulfones, nitrogen compounds, phosphorus compounds, boron compounds, silicon compounds and organo compounds of the higher elements of Groups III, IV and V.

As the search progressed the lack of systematic data on the stability of compounds between 350°-400°C became apparent. In an attempt to correlate the data which are available, likely modes of decomposition for the various classes of compounds were considered qualitatively from a theoretical viewpoint. This approach helped to bring out the best lines of attack for improving thermal stability.

In this report three properties were initially considered for screening, namely, thermal stability, viscosity and vapor pressure at temperatures up to 700°F. Thermal stability is regarded as the most important property in this initial investigation, because in any class this property should be less easily modified by additives and structural changes than other properties. Assuming thermal stability, chemical modifications may be made if need be to improve other desirable properties.

Accordingly, screening tests to measure thermal stability, viscosity and vapor pressure were set up as described in the body of the report. Numerous available chemicals were subjected to the thermal stability test in order to obtain some first hand information as to the thermal stability properties of certain functional groups.

II. LITERATURE SURVEY

Hydrocarbons

Thermal Stability. While there has been no systematic investigation on the thermal stability of paraffins at 370°C, there is voluminous literature considering the cracking of paraffins both theoretically and experimentally. Thermodynamic data show that the temperature for the zero free energy value of splitting decomposition for ethane is 313°C, decane 295°C and *n*-eicosane 192°C and that decomposition into the elements is probable in the range of 400°-500°C (216). Observed temperatures of initial decomposition, however, are higher; *n*-butane begins to decompose at 400°C, *n*-hexane at 343°C (75), docosane shows no sign of decomposition at 280°C (162) and n-octacosane begins to decompose at 298°C (see section on vapor pressure measurements). The rate of decomposition at these temperatures must be slow, however, for several high molecular weight paraffins have been distilled in this range: tetratriacontane, 336°C/15 mm, pentatriacontane 380°C/50 mm (70). Hexadecane showed no decomposition during a short exposure at 390°C (96), while n-octane showed no cracking at 450°C and only 4% decomposition on passage through a hot tube at 480°-500°C (125). Several fractions of midcontinent oil had sufficient thermal stability to permit determination of their viscosities at 370°C (184). Hydrocarbon polymers showed varying thermal stability; ethylene polymer was unchanged in 2 hours above 300°C, propylene polymer was unchanged in two hours at 200°-300°C and butylene polymer was changed in 24 hours at 150°C (153).

The thermodynamic prediction of decreased stability with increasing molecular weight is in accord with observation; while methane undergoes no change at 480°C in 6 days and pyrolyses slowly at 650°-700°C (36), ethane begins to dissociate at 550°C (273). After one hour at 425°C n-decane is 18% decomposed and dotriacontane is 77% decomposed (216). The rate of cracking for homologous normal paraffins at 500°C is given by the equation:

$$k(\mathrm{sec}^{-1}) = (n-1)(1.57n-3.9)10^{-5} \quad 4 \leq n \leq 16$$

where n is the number of carbon atoms in the chain (42). In general, branched chain molecules appear to be slightly less stable than their straight chain isomers, and after 1 hour at 425°C n-decane undergoes 18% decomposition versus 30% for bi-isoamyl (216).

It is apparent from these data that as a class paraffinic hydrocarbons are on the borderline for meeting the requirements of stability at 700°F for 10 hours. As an aid to designing a hydrocarbon of the highest possible stability several generalities relating to the decomposition of hydrocarbons are considered below.

As a first approximation to the stability of a given C-C bond the bond dissociation energy of the bond may be used, because in a simple homolytic fission of a bond into two radicals the bond dissociation energy is equal to the energy of activation (247). In the absence of data showing the bond dissociation energy for a bond with particular substituents, it is possible to estimate the stability of the bond relative to other bonds of a similar type by the effectiveness of the substituent in stabilizing the fragments which would result from fission of the bond. Besides resonance stabilization by conjugation or hyperconjugation, stabilization from the relief of steric strain in going from a tetrahedral to a planar configuration should be considered.

In addition, the effect of symmetry in increasing thermal stability should be noted. Quantum theory indicates that the more symmetrical a molecule the more difficult it will be to transfer energy from one mode of vibration to another. This will have the effect of making it more difficult for a molecule to build up bond rupturing concentrations of energy in a given vibrational mode.

Substituents on a C-C bond, which weaken it by stabilizing the fission fragments, may, on the other hand, tend to increase the overall thermal stability of the molecule by increasing the symmetry. The following reported order of thermal stability for low molecular weight hydrocarbons illustrates these opposing influences: isobutane > butane > neopentane > n-pentane > isopentane (75). In larger aliphatic chains any increases in stability because of symmetry effects are probably small, but in more compact molecules such as rings or cage compounds these effects may become important.

The estimation of the thermal stability of a hydrocarbon structure is further complicated because of the possibility of decomposition by a free radical chain reaction. This provides a path for decomposition involving much less energy than direct fission, because energy used in bond breaking is furnished in part by bond formation. The cracking of hydrocarbons is believed to proceed by a free radical chain reaction, and the complex mixture resulting from the decomposition of hexadecane at 500°C (262) has been satisfactorily accounted for by the theory of Rice (149) which is here summarized.

Small alkyl radicals accumulate to a steady state concentration. These radicals remove hydrogen atoms from paraffin molecules leaving a large radical which rapidly decomposes, ultimately regenerating a small radical (ethyl or methyl) which continues the chain. At 500°C the relative rates of removal of hydrogen are primary 1, secondary 3.66, tertiary 13.4; the total rate of removal of hydrogen is proportional to the number of each type times the relative rates. The radicals formed by removal of hydrogen atoms always rupture at a C-C bond that is removed by one carbon atom from the hydrogen deficient carbon; no C-H bonds are made or broken when rupture occurs, and the products are always an olefin and a smaller radical. When alternative beta bonds are available, the relative rates of cracking are determined by the resonance stabilizations of the radicals that crack off.

The large radicals although too short lived to be converted to paraffin are sufficiently long lived to undergo isomerization prior to rupture. The radical position can only shift by a coiling mechanism to a carbon atom separated by three or more carbon atoms from the original position. Branched chain radicals are not formed from straight chains by these isomerizations. The radicals are assumed to isomerize to equilibrium before cracking further; the relative orders of stability being primary 1, secondary 13.4 and tertiary 47.7.

This theory is for the initial cracking only and does not take account of the further decomposition of the first products of cracking. Nevertheless, the predicted reaction mixture for the partial cracking of hexadecane at 500°C and atmospheric pressure agrees well with the mixture actually obtained.

The direct fission theory of Burk (47) suggests that cracking occurs by direct fission of a paraffin into a smaller paraffin and an olefin. This theory appears to be untenable because it predicts only two moles of products per mole cracked and a mixture of olefins and paraffins for all carbon number two or more below that of the paraffin cracked (262). However, no paraffins above propane are observed in the cracking of hexadecane and 378 moles of product are formed for 100 moles cracked. Direct fission may, however, account for the initiation of the chain reaction proposed by Rice.

Since it appears certain that paraffins decompose mainly by a free radical chain reaction, it is probable that the thermal stability of paraffins could be increased by a free radical inhibitor, if one suitable for use at 700°F could be found.

Cyclic paraffins have greater thermal stability than the straight chains. In cracking, for example, the long side chains of the naphthenes crack long before the ring breaks down (216), which, in general, requires a temperature in the neighborhood of 600°C. Cyclopentane is 35% decomposed after 10 min at 674°C and cyclohexane is 43% decomposed after 0.7 min at 622°C (90). At 350°C cyclohexane undergoes no change in 3 days (231) and tetralin does not pyrolyze until 490°C (141). Several complex cycloparaffins which have been distilled near 370°C are tricyclohexylmethane, 340°-5°C (275), perhydrochrysene, 359°-60°C (241), and piceneperhydride, 360°C, (155).

Aromatic compounds are the most stable of hydrocarbons, but there is a considerable variation in stability among aromatic nuclei. Below 500°C benzene is unaffected and the lowest temperature for diphenyl formation is 650°C (166). Biphenyl at 500°C for 60 hours gave only 1% coke (251) while anthracene at 475°C for 3.5 hours was completely transformed to coke (217). The relative rates of coke formation for naphthalene, phenanthrene and anthracene are 1:78:10,800 (250). Examples of other aromatic compounds whose thermal stability is indicated by a high boiling point are chrysene, bp 448°C, 2,2'-binaphthyl, bp 452°C, and picene, bp 518°-520°C (76).

The thermal stability of alkyl aromatic compounds depends on the stability of the paraffinic moiety of the molecule. Paraffin and paraffinic side chains of cyclic hydrocarbons having the same number of carbon atoms decompose at approximately equal rates. For example, at 440°C for 1 hour n-octadecane gave 85% liquid decomposition products and phenyl n-octadecane gave 91% liquid decomposition products (216). Thermal stabilities of several alkylated aromatics listed in Table I also illustrate this point (239). The instability of the cyclopentane derivatives was ascribed to the ease of elimination of cyclopentene. A cyclohexyl radical might impart improved stability.

Table 1

DECOMPOSITION POINT OF SELECTED HYDROCARBONS

Compound	Decomposition Temperature	Calculated BP
1-Octylnaphthalene	>332°C	332°C
2-Octyl-5,6,7,8-tetralin	>322	322
Trioctylnaphthalene	352	389
Cyclopentylacenaphthene	<210	359
Dicylopentylacenaphthene	<240	452
Tribenzylnaphthalene	<302	510

In view of the stability of methane it is not surprising that methylated benzenes are as stable as benzene itself and at 630°C o-xylene and toluene formed less gas than benzene (198). Methylated naphthalenes are less stable than methylated benzenes and are partially dealkylated at 450°-475°C. β-Methyl naphthalene is more stable than the α-isomer (252).

In this review of the thermal stability of hydrocarbons olefinic and acetylenic compounds have not been considered, because they would tend to polymerize at high temperatures, undergo cleavage at the carbon atom β to the site of unsaturation and be more subject to oxidation.

Viscosity. In the development of a high temperature hydraulic fluid the viscosity characteristics were judged to be the next most important property after thermal stability. Although there has been a great amount of work devoted to correlation of structure and viscosity characteristics, there exists at present only a body of rules of varying generality to serve as guides in the design of a hydraulic fluid.

Zisman has summarized the following useful guides. First, to obtain an organic liquid with a small temperature coefficient of viscosity, the molecule should not contain chemical groups having strong associating tendencies, and it should have a linear or rodlike molecular structure possessing the greatest possible flexibility through free rotations about the chemical bonds. Second, if the viscosity (at 100°F for example) is to be low for a high boiling liquid, the molecule should have no side chains. Third, the most reliable and effective way to synthesize into a liquid the property of having a very low freezing point is to attach a minimum number of short side chains to the principal chain of the molecule in such a way as to create the maximum possible hindrance to close interlocking or alignment of neighboring molecules. (Branch chains near the center of the principal chain are more effective than those near the end of the chain in reducing the freezing point.) Fourth, the most satisfactory way to obtain a low viscosity liquid of high boiling point is to introduce into the molecule one or more nonhydrocarbon, non-associating groups such as the ester group. Fifth, other things being equal, the greater the molar coefficient of thermal expansion of a liquid, the greater the temperature coefficient of viscosity. This is simply one way to allow for the effects of large differences in the internal cohesive forces in the liquids (277).

Empirical rules correlating specific structural features of hydrocarbons with viscosity have been published from time to time (162, 172, 222), but the most reliable seem to be those of Project 42 of the American Petroleum Institute at Pennsylvania State College (220, 221, 222, 223, 224). The examples cited to illustrate these rules refer to Table 2.

1) Viscosity is increased and ASTM slope decreased by increasing molecular weight, basic molecular structure remaining constant (cf, Compounds 1,2,3,4,5,6,7). Aromatics and naphthenes containing one cyclic group per molecule exhibit greater viscosity increase and ASTM slope decrease for a given increase in molecular weight than do the corresponding isoparaffins (cf, Compounds 18,11; 34,32; 33,31; 53,48). For a series of trialkyl methanes ranging from C_{20} to C_{50} the rate of increase of the ASTM slope decreases with increasing molecular weight; the ASTM slope appears to approach a limit of 0.60 at C_{50}.

2) Increased branching of a molecule causes an increase in 100°F viscosity and an increase of the ASTM slope (cf, Compounds 4,10; 6,16). The n-paraffins exhibit the best viscosity-temperature characteristics. Roughly the ASTM slope value of a given hydrocarbon is equal to the slope of the n-paraffin containing the same number of carbon atoms as the longest straight chain of the hydrocarbon in question (cf,

Table 2

PHYSICAL PROPERTIES OF REPRESENTATIVE HYDROCARBONS

	Compound	BP Lit. °C	Calc NBP(2) °C	Calc NBP(2) °F	MP °C	Viscosity cs 32°F	Viscosity cs 100°F	Viscosity cs 210°F	Viscosity cs 400°F	ASTM Slope 100°-210°F	Ref.
1	n-Dodecane	147/100	220	428	-9.5	2.98	1.50	0.749	0.356	0.86	219
2	n-Pentadecane	136/10	278	532	9.9	6.50(1)	2.59	1.12	0.483	0.82	219
3	n-Hexadecane	148/10	295	563	18.0	7.80(1)	3.07	1.26	0.531	0.81	219
4	n-Octadecane	174/10	326	619	27.8	12.6(1)	4.18	1.58	0.630	0.77	219
5	n-Eicosane	197/10	355	671	36.6	18.0(1)	5.54	1.94	0.738	0.73	219
6	n-Hexacosane	257/10	430	806	56.2		6.59/140°F	3.30	1.10	0.67	219
7	n-Octacosane	272/10	450	842	60.7	62.(1)	14.0(1)	3.82	1.23	0.64	219
7a	n-Hexatriacontane	331/10	524	975			29.2	6.407		0.61	219
8	n-Dodecene	144/100	216	421	-35.4	2.57	1.34	0.689		0.86	219
9	n-Pentadecene	134/10	275	527	-3.4	5.28	2.32		0.676/300°F	0.81	219
10	4,9-Di-n-propyl dodecane	151/10	295	563	-43.5	12.13	3.55/77°F	1.25		0.90	219
11	7-n-Hexyltridecane	171/10	322	612	28.3	15.61	4.55	1.51	0.562	0.86	219
12	10-n-Amyl eicosane				-8.7		14.13/77°F	2.57		0.76	162
13	10-n-Heptyleicosane				15.2		16.7/77°F	2.92		0.73	162
14	10-n-Nonyleicosane				12.2		19.71	3.21		0.72	162
15	4-n-Propylheptadecane	186/10	340	644	46.0	17.9(1)	4.95	1.67	0.67	0.80	219
16	11-n-Decylheneicosane	282/10	460	860	9.0	78.5(1)	15.12	3.67	1.12	0.71	219
17	13-n-Dodecylhexacosane	272/1	530	986	13.7	15.0(1)	25.68	5.56	1.511	0.64	219
18	9-n-Octylheptadecane	232/10	400	752	-13.8	37.9	8.93	2.49	0.826	0.76	219
19	Cyclopentane	49.2	49.2		-94.3	.746	.436/122°F			1.04	219
20	Cyclohexane	80.8	80.8		5.86	1.36/59°F	1.06/86°F			1.21	70
21	cis-Decalin	125/100	194	381	-43.3	6.11	2.62	1.10		0.84	70
22	trans-Decalin	117/100	184	363	-30.4	3.64	1.811	0.861		0.84	219
23	Bicyclopentyl	120/100	188	370		2.26	1.32	0.719		0.78	219
24	1,3-Dicyclopentyl-cyclopentane	146/10	290	554		7.67	3.32	1.43		0.71	219

Table 2 (Cont'd)

	Compound	BP Lit. °C	Calc °C	NBP °F	MP °C	Viscosity cs 32°F	Viscosity cs 100°F	Viscosity cs 210°F	Viscosity cs 400°F	ASTM Slope 100°-210°F	Ref.
25	Perhydrofluorene	117/10	253	487		12.82/68°F	4.52	1.66		0.76	219
26	Perhydrochrysene	196/10	353	667		76.79/68°F	26.4	4.081		0.83	219
27	1,2,3,4,5,6,7,8,13,14,15,16-Dodecahydrochrysene	216/10	380	716		14.24	495.5	8.185		1.15	219
28	1-Cyclohexyldecane	152/10	297	567	-1.7	12.36	4.21	1.56		0.78	219
29	Tricyclopentylmethane	140/10	283	541	22.	25.9	6.105	1.855		0.81	219
30	Tricyclohexylmethane	191/10	347	657	55.4		52.9/140°F	8.21	1.22	1.08	219
31	7-Cyclopentylmethyltridecane	173/10	325	617		21.13	5.48	1.698	0.613	0.85	219
32	7-Cyclohexyltridecane	176/10	329	624		36.10	7.413	1.96	0.653	0.87	219
33	9(3-Cyclopentylpropyl) heptadecane	241/10	413	775	-20.6	54.6	11.53	2.91	0.915	0.76	219
34	9(2-Cyclohexylethyl) heptadecane	240/10	411	772	Glass	83.04	14.72	3.29	0.962	0.77	219
35	Tri(3-cyclopentylpropyl) methane	252/10	422	792	-23.7	196.	25.7	4.63	1.21	0.75	219
36	Tri(2-cyclohexylethyl) ethane	255/10	429	804	41.2		170(1)	10.10	1.60	0.85	219
37	1-Cyclopentyl-heneicosane	264/10	439	822	45.2		7.88/140°F	3.80	0.992	0.65	219
38	1-Cyclohexyleicosane	265/10	440	824	47.9		8.90/140°F	4.13	1.26	0.67	219
39	9-Cyclohexyleicosane	250/10	420	788	Glass	95.02	16.19	3.52	1.024	0.76	219
40	Benzene	80	80	176	5.51	0.794/59°F	0.646/86°F			1.1	70
41	Diphenyl	255	255	491	69.2		1.21/176°F	0.922/212°F			70
42	o-Terphenyl	330-50	350	662	55.		29.7/130°F	2.70/250°F		1.1	175
43	Naphthalene	218	218	424	80.27		0.99/176°F	0.782/212°F		1.0	70
44	Toluene					0.678/68°F	0.565/104°F	0.459/140°F		1.03	72
45	1-Methylnaphthalene	168/100	243	469	-31.	5.94	2.22	0.919		0.94	219

Table 2 (Cont'd)

	Compound	BP Lit. °C	Calc °C	NBP °F	MP °C	Viscosity cs 32°F	Viscosity cs 100°F	Viscosity cs 210°F	Viscosity cs 400°F	ASTM Slope 100°-210°F	Ref.
46	2-Methylnaphthalene	166/100	241	466	34.3		1.74	0.782		0.94	219
47	1-Phenyldecane	154/10	300	572	-14.4	7.90	3.02	1.237		0.80	219
48	7-Phenyltridecane	173/10	325	617	-28.2	26.16	5.92	0.939	0.596	0.90	219
49	1-Phenyleicosane	265/10	438	820	42.3		11.5(1)	3.33		0.66	219
50	9-Phenyleicosane	247/10	416	781	17.9		13.9	3.20	0.968	0.77	219
51	Tri-(2-phenylethyl)methane	267/10	440	824	-25°F	454	25.7	3.82		0.86	219
52	1,4-Di-n-decylbenzene	263/10	437	819		53(1)	12.2	3.35		0.68	219
53	9-(2-Phenylethyl)heptadecane	240/10	411	772	-26.7	43.5	9.38	2.53		0.78	219
54	Trioctadecylbenzene				47		49.6/129°F	14.56/212°F		0.54	70
55	1-α-Naphthylpentadecane	267/10	440	824	41.6		9.46/140°F	3.95		0.75	219
56	Mid Continent Oil, The Texas Co.					1748	120.6	12.37	7.49/250°F		184
	Specification AN-0-8 Grade 1065					4.60/300°F 1.366/500°F 0.66/700°F	3.11/350°F 1.113/550°F	2.259/400°F 0.923/600°F	1.728/450°F 0.780/650°F		

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(1) Extrapolated value.

(2) NBP = boiling point at 760 mm Hg.

Compounds 1,10; 5,11,12,13).

3) Cyclization results in large increases in 100°F viscosity (cf, Compounds 11,31,32,48). In order of increasing ability to raise the 100°F viscosity the various naphthene groups are, cyclopentyl, cyclohexyl, perhydrophenanthrene, perhydroanthracene, 4-methylcyclohexyl, α-decalyl. The viscosity is decreased by the hydrogenation of fused 6-membered rings systems and increased by hydrogenation of non-fused 6-membered rings. The viscosity increase per additional ring is greater the more rings per molecule. Cyclization to phenyl and cyclohexyl groups results in a large increase in the ASTM slope and the increase per additional ring becomes greater the more rings per molecule (cf Compounds 18,36,34,51,53). The ASTM slope is affected only slightly by increase in the number of cyclopentyl type rings per molecule (cf Compounds 34,33,18). (This interesting observation may be rationalized as follows: cyclization to a phenyl group increases intermolecular attractive forces resulting in an increase in slope; cyclization to a cyclohexyl group increases the cross section of the molecule resulting in an increase in slope; cyclization to cyclopentyl causes little increase in cross section since the cyclopentyl group is coplanar and no increase in intermolecular attractive forces so that the slope is unchanged).

4) The 212°F viscosity tends to increase as a cyclic group is shifted from the center toward the end of a 20 carbon straight chain (cf Compounds 49,51; 38,39). For phenyl and cyclohexyl derivatives the ASTM slope decreases greatly as the ring approaches the end of the straight chain.

5) Olefinic unsaturation is generally accompanied by a decrease in viscosity and a decrease in slope (cf compounds 1,8; 2,9).

6) Pure hydrocarbons and hydrocarbon mixtures having the same average "type" composition and basic molecular symmetry have remarkably similar physical properties. The maximum deviation in viscosity and viscosity index for naphthenic-paraffinic mixtures is 6% and for aromatic mixtures is 17%.

7) Viscosity changes of as much as 10 times may result from seemingly minor structural changes which affect molecular rigidity and ability for close packing of the molecules (cf Compounds 3,29,30; 26,27). A molecule with free rotation will have a lower viscosity and ASTM slope than a more rigid isomer, because rotation may permit conformations having a smaller cross section than the rigid isomer and leads to a looser molecular packing. Structures which permit close packing

increase the intermolecular attractive forces which leads to the prediction that a closely packed structure will have a higher isothermal viscosity and ASTM slope than a less closely packed isomer.

Several interesting compounds which are exceptions to the above generalizations are compared with *n*-paraffins of the same number of carbon atoms in Table 3 (219). It will be noted that compounds 1 and 2 in Table 2 are of a rigid compact structure and yet have better slopes than the corresponding *n*-paraffin. This may be ascribed to a spherical shape which reduces molecular packing. Compound 7 has only two C-C bonds with free rotation and yet has a much better slope than the corresponding *n*-paraffin.

Table 3

HYDROCARBONS WITH ANOMALOUS VISCOSITY PROPERTIES

	Compound	100°F Viscosity,cp	ASTM Slope 100°-200°F
1.	Perhydrofluoroanthene	9.34	0.78
2.	Perhydropyrene	12.15	0.78
3.	n-Hexadecane	2.34	0.81
4.	1,3-Dicyclopentyl-2-dodecylcyclopentane	25.9	0.76
5.	n-Hexacosane	9.12	0.67
6.	Tricyclopentylmethane	5.64	0.81
7.	1,3-Dicyclopentylcyclopentane	2.98	0.71
8.	*n*-Pentadecane	1.96	0.82

In Table 2 the viscosity characteristics and other physical properties of a number of representative hydrocarbons are listed. The ASTM curves of several (Compounds 42,7,16,52,25,24,56) are plotted for illustrative purposes in Fig. 1. It is apparent that none of the compounds has a slope as good as that of 0.50 required by the specification. Actually, this slope is probably too high as it does not take account of the fact that the viscosity-temperature curve becomes convex at temperatures above 500°F (184) as illustrated by curve M Fig. 1.

The viscosity-volatility properties of hydrocarbons have not been considered, because a hydrocarbon of the required viscosity will probably be of sufficiently high molecular weight to have a vapor pressure less than 100 mm at 370°C. For example, hexatriacontane (Compound 7a, Table 2) has a 100°F viscosity of 29 cs as compared to that of 100 cs for the specified fluid and has a vapor pressure less than 100 mm at 370°C.

Conclusions. The foregoing discussion suggests that since no hydrocarbon with an ASTM slope as low as that required is known, it is unlikely that a hydrocarbon suitable for use without additives will be found. It is probable, however, that a hydrocarbon thermally stable *in the absence of air* at 370°C can be prepared. The problem then becomes one of finding first, the best balance between the thermal stability of the cyclic structure and the relatively good viscosity properties of long chain paraffins; and second, of attaining the desired liquid range by making minor alterations in the structure or by mixing several similar compounds.

The data indicate that at 370°C a long chain paraffin will be on the borderline of stability. Exact data on the variation of stability with chain length at 370°C **are unavailable**. Such information is essential for the design not only of hydrocarbons but of other compounds in which a long chain is incorporated.

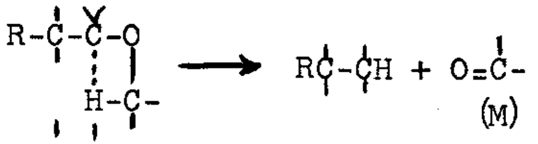
The most promising cyclic group, from the point of view of structure, is cyclopentyl which combines good thermal stability with good viscosity properties. From the synthetic point of view, however, an aromatic ring (or its hydrogenated naphthene) would be easier to prepare. Two novel approaches to a hydrocarbon hydraulic fluid are suggested by the leads in the API report that rigid spheroid-like molecules and 1,3-dicyclopentyl-cyclopentane have good viscosity properties.

Directions for the preparation of several types of hydrocarbons which might be of interest as high temperature fluids have been given by L. I. Smith (236).

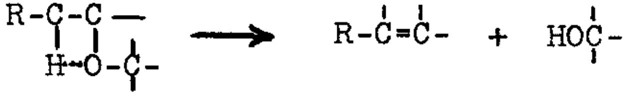
Ethers

Thermal Stability. In ethers or esters the relative bond dissociation energies indicate that decomposition by a simple fission would be more likely to occur at a C-C bond (83 kcal) than at a C-O bond (90 kcal). There is, however, a decomposition path of lower energy which favors cleavage at the C-O bond. This mode of decomposition proceeds through a "four centric" transition state (11,229) and predicts two sets of products.

A



B



The energy of activation is much less by this path than by direct fission, because the energy required to break the C-O bond is furnished by the energy released in formation of the C=O or H-O bonds. Comparison of the energy changes using Pauling's values for bond energies (196), shows that route A is favored over route B by 20 kcal when M is formaldehyde to 30 kcal when M is a ketone. This suggests that methyl ethers should be more stable than n-aliphatic ethers, and that secondary alcohols should form the least stable and tertiary alcohols the most stable of aliphatic ethers. Attempts to improve the stability of ethers by blocking both routes A and B by replacing the hydrogens by alkyl groups would probably fail because the α-C-C bonds would be weakened by excessive steric crowding. The stability of ethers should be improved by replacement of all α and β hydrogen atoms by fluorine.

In mixed aryl-aliphatic ethers route A is blocked, but the tendency to route B should be considerably increased because of the greater resonance stabilization of phenol over aliphatic alcohols. Thus, there should be little increase in stability on replacement of an alkyl group in a dialkyl ether by an aryl group when route B is still open. If route B were blocked as by the replacement of the β-hydrogen atoms by alkyl groups, then an ether of good thermal stability should result.

Diaryl ethers should have good thermal stability. There is no obvious low energy decomposition path such as A or B and the energy of activation for decomposition should approach the bond dissociation energy of the C-O bond.

In agreement with the above discussion pyrolysis of most aliphatic ethers yields aldehydes or ketones and saturated hydrocarbons. Decomposition occurs materially below 370°C. Methyl ethyl ether on heating in a silica bulb at 400°C and 77 to 449 mm initial pressure shows as a result of decomposition a 50% increase in pressure in 11-17 minutes which represents approximately 25% decomposition (104). Dimethyl ether when heated in a silica bulb at 504°C and an initial pressure between 91 and 312 mm is decomposed 25% in 11-20 minutes (121). Dibenzyl ether decomposes rapidly at its boiling point (295°C) and slowly at 210°-215°C. The decomposition products are toluene and benzaldehyde (152). Pyrolysis of ethers of the type $(C_6H_5)_3$ COR yields either aldehydes or ketones depending on the R grouping. Decomposition temperatures for such ethers are shown in the following decreasing order in which R is methyl (262°C), ethyl (241°C), n-butyl (238°C), isoamyl, β-phenylethyl (236°C), n-propyl (230°C, isobutyl, benzyl, isopropyl and sec-butyl. The temperature of decomposition is markedly lowered by catalysts (191).

The initial decomposition of some polyethylene glycols is shown in Table 4. The ease of decomposition of diethylene glycol dimethyl ether was unexpected (94).

Table 4

DECOMPOSITION OF POLYETHYLENE GLYCOL

Compound	Temp. of initial decomp. °C	Rate of decomp.mm change of press./min.
Ethylene glycol	164.9	1.30
Diethylene glycol	164.5	0.30
Triethylene glycol	206.5	0.38
Tetraethylene glycol	237.9	0.89
Tetraethylene glycol mono chlorohydrin	139.6	0.09
Diethylene glycol dimethyl ether	60.0	0.22

Diphenylmethyl sulfide decomposes rapidly at 267°C while dibenzyl ether can be distilled at 267°C (226). Dibenzyl sulfide decomposes when heated above 185°C (20).

Mixed aromatic-aliphatic ethers appear to undergo pyrolysis at somewhat more elevated temperature than do aliphatic ethers and the products of decomposition are phenols and unsaturated hydrocarbons. Anisole undergoes pyrolysis at 380°-400°C into phenol and ethylene (167). The ethyl ether of thymol pyrolyses into thymol and ethylene at 360°-400°C but to only a small degree at 320°-330°C. Phenyl isobutyl ether decomposes at 380°-400°C into butylene and phenol (9). Secondarybutyl and isobutyl phenyl ethers do not rearrange on heating 10 hrs at reflux (196°C). At 193°C in a few hours tertiarybutyl phenyl ether isomerizes completely to p-tertiarybutyl phenol (237). Benzyl phenyl ether when heated for some time at 250°C rearranges into phenol and benzyl phenol (14). Other mixed ethers have been reported to show decomposition or slight decomposition at the following indicated temperatures: 2-biphenyl isopropyl ether, 315°-317°C (40); biphenyl benzyl ether, 324°C (40); 1,3-diphenoxypropane, 340°C (15); isoamyl α-naphthyl ether, 317°C/742 mm (21), and isoamyl β-naphthyl ether, 323°C/759 mm (22). Although all the mixed ethers cited decomposed below 370°C, there is a good theoretical probability that mixed ethers in which the aliphatic moiety contains no β-hydrogen will not pyrolyze below 370°C in short periods of time.

The aromatic ethers are remarkably more thermally stable than are the aliphatic or mixed aromatic-aliphatic ethers. The initial decomposition temperature of diphenyl ether is 440°C (243). Diphenyl ether, when heated for 8-1/3 hours in its own atmosphere at constant pressure in contact with a molten alloy ("Cerrobend") of bismuth, lead, tin and cadmium, decomposes approximately 3% at 455°C, 8% at 479°C and 22% at 495°C; in 100 hours it is decomposed 0.0084% at 343°C, 0.078% at 371°C, 0.59% at 399°C and 1.49% at 413°C (10) If the diphenyl ether is passed through a red hot glass tube, it decomposes into diphenylene oxide, benzene and phenol (109). β,β'-Dinaphthyl ether decomposes at 380°C and the α,α'-dinaphthyl ether will distill undecomposed (21,22).

Viscosity. The following excerpt from an article by Murphy and Zisman (186) is a good discussion of the viscosity characteristics of aliphatic ethers. The di-n-alkyl ethers because of their structural similarity to the n-alkanes would be expected to differ only slightly in viscometric properties, the differences decreasing as the alkyl groups increase in length. For purposes of this discussion, the hydrocarbon analogous to the ether is considered formed by replacing the ether oxygen with a methylene group. The viscosities and slopes of some di-n-alkyl ethers are given in Table 5 where they are compared with the analogous alkanes. It is seen that the ethers are less viscous and have larger slopes than the analogous hydrocarbons. This is not unreasonable, as the addition of an ether oxygen causes an increase in chain length comparable to that of a methylene group, but its cross-sectional area is less. As the ether oxygen is smaller in diameter and has no side chains attached, there is even more freedom of rotation about the bond between the ether oxygen and the adjacent carbon atoms than about the aliphatic carbon-carbon bonds.

Table 5

VISCOMETRIC CHARACTERISTICS OF DI-n-ALKYL ETHERS AND n-ALKANES

Identification	Viscosity, cs 100°F	Viscosity, cs 210°F	A.S.T.M. Slope
Di-n-butyl ether	0.735	0.430	0.964
n-Nonane	0.807	0.465	0.925
Di-n-amyl ether	1.089	0.580	0.897
n-Undecane	1.229	0.645	0.868
Di-n-heptyl ether	2.22	0.992	0.856
n-Pentadecane	2.58	1.119	0.814
Di-n-octyl ether	3.06	1.089	0.790
Di-n-octyl thioether	3.84	1.500	0.768
n-Heptadecane	3.59	1.417	0.787
Di-n-decyl ether	5.26	1.862	0.737
Di-n-decyl thioether	6.67	2.237	0.703
n-Heneicosane	5.90 (1)	2.10 (1)	0.734
Di-n-dodecyl ether	8.18	2.58	0.699
n-Pentacosane	10.4 (1)	3.0 (1)	0.680

(1) Extrapolated

As the slopes of n-alkanes vary inversely as the viscosity at a reference temperature, the ethers would be expected to have larger slopes than the analogous hydrocarbons, for they are less viscous. When the slopes of the ethers are plotted against the viscosity at 100°F, the two ethers of lower molecular weight, di-n-butyl and di-n-amyl ether, are above the plot for the n-alkanes, while all the higher molecular weight ethers are below this line. The di-n-alkyl ethers have lower freezing and boiling points and higher densities than the analogous hydrocarbons. Even greater reduction in freezing points would be expected of the unsymmetrical ethers, though they would probably be slightly more viscous than their symmetrical isomers. A further reduction in freezing points (or pour points) can be obtained by suitably placed side chains, though this would be obtained at the expense of the good viscometric properties.

A variety of polyglycol ethers have been studied. These may be considered as condensation polymers of ethylene and isopropylene glycol. The polymers containing two unreacted terminal hydroxy groups are associated liquids and their viscometric properties are abnormal, especially at extreme temperature. Those which are chain-stoppered at one end with an alkyl group behave more normally. The polyisopropylene glycols have greater slopes than do the copolymers containing both isopropylene and ethylene oxide units. This is in accord with the generalizations as to the effect of the number of branched chains on viscosity and slope or viscosity index. Both types of polymers have larger slopes than the comparable n-alkanes but have much lower pour points.

The polyethers which are chain-stoppered at both ends have lower ASTM slopes than the n-alkanes of the same viscosity. In these condensation polymers of isopropylene glycol the effect of the ether linkages more than counteracts the adverse action of the methyl branches on the slope.

The thioethers are more viscous than the analogous hydrocarbons and have smaller slopes. When the slopes are plotted against their 100°F viscosities it is seen that they are smaller than those of the alkanes of the same viscosity. Their boiling points are higher than the analogous n-alkanes and their freezing points are much lower. These changes in properties would be expected because of the larger diameter of the sulfur atom, resulting in an unsymmetrical long-chain molecule with a larger cross section (186).

Perfluoro straight chain ethers have lower viscosities and temperature coefficients of viscosity than fluoro hydrocarbons of the same molecular weight. This was explained on the basis of freer rotation about the carbon-oxygen bond than about a carbon-carbon bond which gives more flexibility to the ether molecule and requires less energy of activation (41).

Viscosity data on aromatic ethers are scarce. Although the mixed ethers shown in Table 6 are not considered stable at 700°F, they are included for possible future comparative use (35).

Fig. 2 compares the viscosity of di-n-dodecyl ether, diphenyl ether, and α-naphthyl cetyl ether. Of these three ethers di-n-dodecyl ether has much the best 100°-210°F ASTM slope (0.70). Diphenyl ether has a slope of 1.076 and a melting point of 26.8°C. Alkylation should materially decrease this slope and lower the melting point.

Spontaneous ignition temperatures are given for some ethers (88) and a second article reports on the comparative ease of oxidation of ethers in the gaseous state (74).

Table 7 contains some literature references to a few typical ethers and indicates the reported boiling point and/or melting points. It is apparent that the unsubstituted aromatic ethers are reasonably high melting solids. Well chosen substitution offers a possibility of lowering the melting point.

Conclusions. The theoretical and literature data indicate that aliphatic ethers and mixed aliphatic aromatic ethers other than the neopentyl aryl type will be unstable at 370°C. The diaryl ethers should be stable at this temperature. The stability of substituted diaryl ethers needs experimental verification although certain alkylated or halogenated aryl ethers should be thermally stable at 370°C and possibly substitution will effect a lowering of the melting point. The effect of alkyl chain length on thermal stability remains to be determined.

Esters of Carboxylic Acids

Thermal Stability. The formation of olefins by the pyrolysis of esters having a β-hydrogen atom has long been a method for the preparation of olefins (193). The observations that the pyrolysis of 3,3-dimethyl-2-butyl acetate gives only 3,3-dimethyl-1-butene (60) and that 2,2-dimethyl-3-pentyl acetate gave only 2,2-dimethyl-3-pentene (270) show that the pyrolysis does not proceed by a free radical or ionic mechanism. Recent work (1,6) demonstrating that the elimination of the acid proceeds preferentially cis points to a decomposition path involving an intramolecular cyclic transition state. It is generally assumed that a quasi - six-membered ring is involved. This transition state will be stabilized by

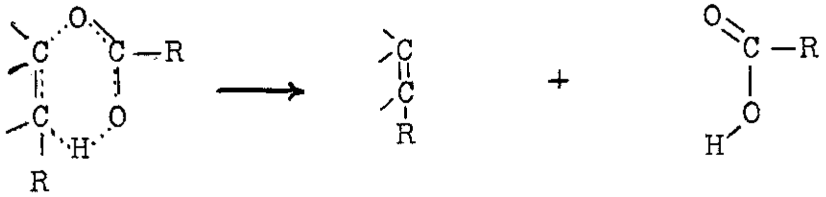


Table 6

VISCOSITIES OF SOME AROMATIC ALIPHATIC ETHERS AND DIPHENYL ETHER

Compounds	MP°C	Viscosity cs						ASTM Slope	Ref.
		122°F	176°F	266°F	356°F	464°F	572°F	100°-210°F	
Phenyl cetyl thioether	49	6.73	3.69	1.859	1.166	0.762	-		35
Phenyl nonyl thioether	12.9	-	1.757	1.014	0.678	0.471	-		35
α-Naphthyl cetyl ether	43.9 BP 255/3 mm	15.9	6.70	2.709	1.523	0.938	0.642	0.75	35
β-Naphthyl cetyl ether	60.5 BP 278/3 mm	-	7.10	2.833	1.585	0.974	0.692		35
Hydroquinone bisdodecyl ether	74.3 BP 280/3 mm	-	6.34	3.31	1.874	1.165	0.794		35
		68°F	104°F	140°F	176°F				
Diphenyl ether	26.8 BP 257.9/760 mm	3.966	2.459	1.706	1.272			1.076	72

Table 7

PHYSICAL PROPERTIES OF TYPICAL ETHERS

Compound	Lit. BP °C/mm Hg	Lit. MP °C	Calc NBP °C	Calc NBP °F	Ref.
Didodecyldiphenyl oxide	255-300/20	Liq.	460	860	33
Tetraamyldiphenyl oxide	285-299/3	41.5	530	986	173
Diamyldiphenyl oxide	211-215/6	Liq.	398	748	173
Ac-(2-xenoxy)tetrahydronaphthalenes	200-229/4.5	Liq.	420	788	182
Ac-(4-tertiary butyl-phenoxy)-tetrahydronaphthalene	190-197/4	Liq.	385	725	182
Ac-(4-chlorophenoxy)tetrahydronaphthalenes	185-200/4	Liq.	390	734	182
Trichlorobenzyl phenyl ether	194-195/7	-	363	685	123
2-Phenyl-4-acetylphenyl benzyl ether	180-182/3	-	375	707	12
Cetyldiphenyl ether	205-220/2	-	440	824	206a
Caprylchlorodiphenyl ether	170-205/2	-	415	779	206a
Dicapryldiphenyl ether	195-225/2	-	445	833	206a
p-Benzyldiphenyl ether	-	41-2			258
1,2-Diphenoxyethane	-	97-98			Beil. VI 647
1-Ethoxy-3-phenoxypropane	328-330/760		330	626	Beil. VI 647
1,3-Diphenoxypropane	338/762	61	338	640	Beil. VI 647
1,5-Diphenoxypentane		48-49			Beil. VI 647
2,2'-Dimethyldiphenyl ether	272-278		278	532	Beil. VI 353
Phenyl α-naphthyl ether	350/753	55	350	662	Beil. VI 642
Phenyl β-naphthyl ether	335/753	93	335	635	Beil. VI 642
1,3-Di-(o-cresoxy)propane	341-343	oil	343	649	Beil. VI 354
Phenyl m-tolyl ether	274/738	oil	274	525	Beil. VI 377
p-Tolyl dodecyl ether		23.5			114
o-Tolyl dodecyl ether	oil				114
Phenyl cetyl ether	-	42			114

Table 7 (Cont'd)

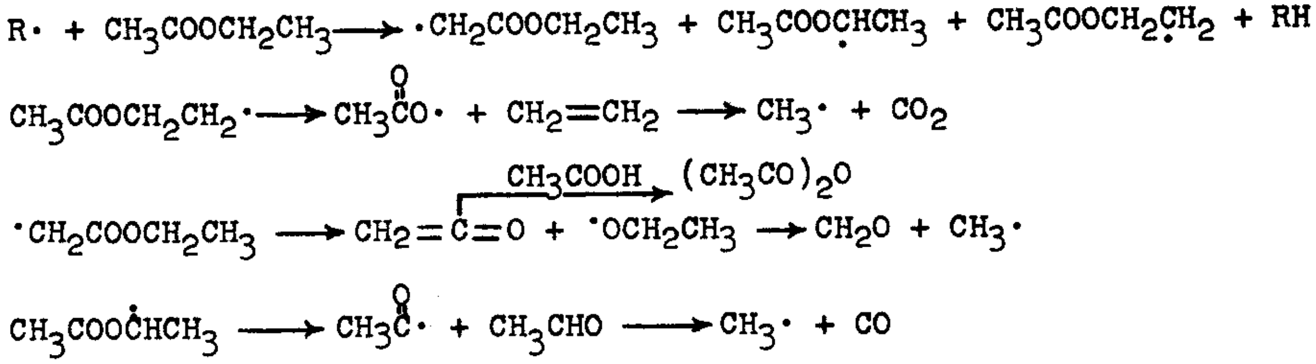
Compound	Lit. BP °C/mm Hg	Lit. MP °C	Calc NBP °C	Calc NBP °F	Ref.
β,β'-Dinaphthyl ether	380 dec.	105	380	716	Beil. VI 642
α,α'-Dinaphthyl ether	Distills	110			Beil. VI 607
p,p'-Diphenoxybiphenyl		111			150
p,p'-Diphenoxy-p-terphenyl		153			150
4-tert-Amyl diphenyl ether	190-200/23		332	630	227
Isoamyl α-naphthyl ether	317/742 dec.		318	604	Beil. VI 607
Bis(p-phenylphenoxy)methane		180			173
Bis(o-cyclohexylphenoxy)-methane		96			173
m-Tolyl p-anisyl ether	141-143/2		335	635	260
Di(p-Cyclohexylphenyl)ether		86			37
4-4'-Dibenzyldiphenyl ether	260-70/4 mm		482	900	227
Diphenyl ether		26.9			-

hydrogen bonding between a β-hydrogen atom of the alcohol moiety and the carbonyl oxygen and by substituents on the α or β carbon atoms which can resonate with the incipient carbon-carbon double bond. Since weaker acids form the stronger hydrogen bonds, it would be expected that with the same alcohol the weakest acids should form the least thermally stable esters. This conclusion is the reverse of the prediction that would be made assuming the decomposition proceeded by direct fission of the alkyl carbon-oxygen bond. In this case the weakest acid would have the least tendency to be eliminated and should form the most stable esters.

There is no evidence excluding the possibility of a "four-centric" transition state similar to that postulated for ethers. In decomposition by this path the entropy should be lower than for decomposition by the six-membered ring, but the energy of activation should be higher because presumably a hydrogen bond to a carbonyl oxygen is stronger than one to an ether oxygen.

Both modes of decomposition could be prevented by replacing the β-hydrogen atom with alkyl groups or possibly fluorine atoms. Another approach would be to inhibit formation of the carbon-carbon double bond by placing either the α or β carbon atoms of the alcohol at the bridgehead of a cage compound. The thermal stability of an ester should be considerably improved by application of one of these two devices.

Decomposition via a cyclic transition state is not the only route followed by esters with β-hydrogen atoms. Careful analysis of the products of the thermal decomposition of ethyl acetate at 550°C showed the following yields: 82% acetic acid, 83% ethylene, 9% acetaldehyde, 6% formaldehyde, 5% acetic anhydride, 8% methane, 4% hydrogen, 1% CO and a trace of ketone. Similarly, isopropyl acetate at 430°-460°C gave, in addition to acetic acid and propylene, 3% acetone, 4% acetaldehyde, 12% CO and traces of isobutyraldehyde, CO and methane. A free radical mechanism was proposed to account for the products other than the acid and olefin (127).



$$R\cdot + CH_3COOCH_2CH_3 \longrightarrow \cdot CH_2COOCH_2CH_3 + CH_3COO\dot{C}HCH_3 + CH_3COOCH_2\dot{C}H_2 + RH$$

$$CH_3COOCH_2CH_2\cdot \longrightarrow CH_3\overset{O}{\overset{\|}{C}}O\cdot + CH_2{=}CH_2 \longrightarrow CH_3\cdot + CO_2$$

$$\cdot CH_2COOCH_2CH_3 \longrightarrow CH_2{=}C{=}O + \cdot OCH_2CH_3 \longrightarrow CH_2O + CH_3\cdot \qquad CH_2{=}C{=}O \xrightarrow{CH_3COOH} (CH_3CO)_2O$$

$$CH_3COO\dot{C}HCH_3 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}\cdot + CH_3CHO \longrightarrow CH_3\cdot + CO$$

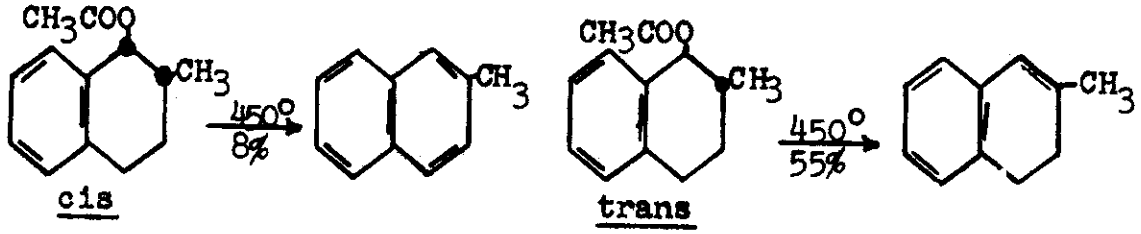
In general the pyrolysis of esters is carried out by passing the ester rapidly through a hot tube at 400° - 500°C. The initial decomposition temperature, however, is considerably lower, and 2-ethylhexyl adipate begins to decompose at 280°C (162). Although ethyl acetate is unchanged after 10 hrs at 290°C (80), t-amyl acetate undergoes 4% decomposition into acetic acid and amylene at 155°C in 20 hrs (165). Ethyl stearate decomposes slowly in a sealed tube at 300°C into stearic acid and ethylene (54), and ethyl formate starts to decompose at 300°C giving hydrogen, CO_2, CO and ethylene (79).

Esters having no β-hydrogen atoms have a higher stability than those that do. While most β-hydrogen esters begin to decompose near 330°C, methyl benzoate undergoes no pyrolysis in 8 hrs at 400°C (80), but at this temperature it has been shown that a rearrangement, as given in the following equation, occurs.

$$C_6H_5\overset{O}{\overset{\|}{C}}-O^{18}-CH_3 \longrightarrow C_6H_5\overset{O^{18}}{\overset{\|}{C}}OCH_3$$

The amount of rearrangement after 3 hrs at 360°C is 5% and after 3 hrs at 400° - 405°C is 66% (272). This high thermal stability is related to the acid as well as the alcohol parts of the ester, because methyl phenylacetate at 360°C yields toluene and methanol along with CO_2, CO and methane (80). Benzyl benzoate after 2 hrs at 340° - 350°C was 50% decomposed yielding toluene, benzaldehyde, benzoic acid and tar (126).

Esters in which cis-elimination of an acid is blocked are much more stable than esters in which this decomposition path is open. On passage through a hot tube at 450°C, cis-2-methyl-1-tetralyl acetate underwent only 8% pyrolysis giving 2-methylnaphthalene while the trans isomer underwent 55% pyrolysis giving 2-methyl-3,4-dihydronaphthalene (1).



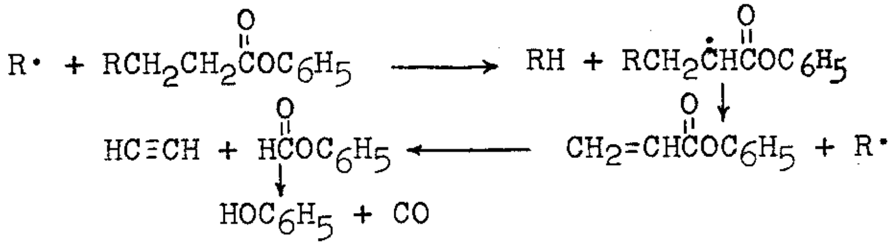
Phenyl esters do not seem to be much more stable than esters having β-hydrogen atoms. While diphenyl succinate distills undecomposed at 330°C (267), it is decomposed by slow heating, forming, among other products, CO_2 and dibenzyl (3). Several examples of the thermal decomposition of other phenyl esters decomposing near 300°C on heating in a sealed tube for several hours are given in Table 8.

Table 8

THERMAL DECOMPOSITION OF PHENYL ESTERS

Ester	Temp. °C	Products	Ref.
Phenyl margarinate	328	margarenic acid, phenol, tetradecane	234
Phenyl palmitate	290-315	phenol, tridecane, others	233
Phenyl stearate	280-315	stearic acid, formic acid, pentadecane, phenol, acetylene, CO_2	233
Phenyl oleate	290-300	phenol, others	232
Phenyl erucate	290-300	phenol, product of mp 21	232

Most of the results for decomposition of esters without β-hydrogen atoms can be explained by free radical mechanisms. The decomposition of phenyl esters, for example, is postulated to proceed in the following way (126).



$$\begin{tikzcd}
R\cdot + RCH_2CH_2\overset{O}{\overset{\|}{C}}OC_6H_5 \arrow[r] & RH + RCH_2\dot{C}H\overset{O}{\overset{\|}{C}}OC_6H_5 \arrow[d] \\
HC\equiv CH + H\overset{O}{\overset{\|}{C}}OC_6H_5 \arrow[d] & CH_2{=}CH\overset{O}{\overset{\|}{C}}OC_6H_5 + R\cdot \arrow[l] \\
HOC_6H_5 + CO &
\end{tikzcd}$$

The preceding discussions have eliminated from considerations as high temperature fluids all esters containing β-hydrogen atoms, phenyl esters of aliphatic acids and benzyl esters of aromatic acids. There remains to be considered ortho esters, esters of t-alkylcarbinols and 2,2-difluoroalkanols and esters of carbonic and aromatic acids with alcohols having no β-hydrogen atoms.

It might be expected that if hydrogen bonding of a β-hydrogen atom to the carbonyl group in an ester is an important factor in decomposition by a quasi - six-membered ring, then ortho esters, which have no carbonyl group, should have good thermal stability. Unfortunately, this is not borne out by experiment. Staudinger showed that vacuum distillation (12 mm) of triethyl orthophenylacetate gave phenylketene acetal while distillation at 760 mm gave, in addition, ethyl phenylacetate (244). A series of alkyl orthoacetates pyrolyzed at 200°C in twenty hours by elimination of an alcohol according to the following equations (163):

$$\begin{array}{lll} RCH_2C(OR)_3 & \longrightarrow & RCH{=}C(OR)_2 + HOR \\ & & \downarrow \\ & & RCH_2COOR + CH_2{=}CHR'. \end{array}$$

Ortho esters can also decompose by elimination of an ether molecule. Ethyl orthobenzoate was 60% decomposed at 220°-225°C after 6 hours to ethyl benzoate and ethyl ether, and phenyl dialkyl orthoacetates pyrolyze by elimination of an alkyl aryl ether. These data show ortho esters are not thermally stable enough for use as a high temperature hydraulic fluid.

Carbonates might be expected to have exceptional thermal stability since the acid moiety cannot decompose into a ketene, and, in fact, carbonates of glycols have been used as heat transfer media (187). While methyl carbonate decomposes above 500°C and benzyl carbonate above 350°C, benzhydryl carbonate decomposes at 260°C (38). Methyl carbonate is 28% decomposed after passage through a hot tube at 500°C and diethyl carbonate is 66% decomposed (211). Phenyl carbonate is more stable than alkyl carbonates and is not completely decomposed by passage through a tube at 640°-670°C (211).

Examples of thermal instability have now been cited from all classes of esters except methyl, benzyl and *t*-alkylcarbinyl esters of aliphatic acids and phenyl and *t*-alkylcarbinyl esters of aromatic and carbonic acids. Polybasic aliphatic esters have been assumed to be about as stable as the monobasic analogs, and there were insufficient data to compare stabilities of polybasic aromatic acids.

Viscosity. The viscosities and slopes of monoesters are nearly the same as the analogous alkanes up to a chain length of 37; above this the esters appear to have lower slopes. For esters of the same chain length the esters of lower viscosity are the ones with the ester group in the center of the chain (186). For chain type dibasic acid esters an increase in the size of the dibasic acid while holding the chain length constant improves the ASTM slope at 100°F. Branched chain alcohols give lower melting esters than straight chains but have larger ASTM slopes (199). Phthalate esters are more viscous and have larger slope than aliphatic diesters of approximately the same chain length (186). Hydrogenation of the phthalates lowers the 100°C viscosity, decreases the ASTM slope except for the orthophthalates, does not decrease the boiling point and tends to lower the melting point (199). Tri-and tetraesters are more viscous and have higher slopes than diesters of corresponding chain length (186). The replacement of a carbon atom by an oxygen in an ester having several ester groups per molecule generally increases the ASTM slope while decreasing the 100°F viscosity (4). Since ethers are less viscous than alkanes, and esters have nearly the same viscosity as alkanes, it appears that the CO group is responsible for the higher viscosity of esters. Examples of some of these relations may be seen by reference to Table 9; compounds 33 and 42 in Table 9 are plotted for illustrative purposes in Fig. 2.

Hydrolysis. One of the important disadvantages of esters as hydraulic fluids is their susceptibility to hydrolysis. The structures of the acid and alcohol moieties of esters affect the ease of hydrolysis by both steric and electronic influences. In general, steric factors are more important in changing the rate of hydrolysis than polar effects in those hydrolyses which proceed by a bimolecular mechanism.

Substituents on the alcohol have a greater effect in retarding alkaline hydrolysis of an ester than substituents on the acid. For example, while the ratio of the rate of alkaline hydrolysis in 85% alcohol at 25°C of ethyl acetate to that of ethyl trimethyl acetate is about 260, the ratio of the rate of alkaline hydrolysis in 56% by weight aqueous acetone at 25°C of methyl benzoate to that of t-butyl benzoate is about 680. It also appears that substituents six atoms removed in the chain from the carbonyl oxygen are more effective in retarding hydrolysis than those five carbons removed (188).

Several mechanisms for hydrolysis have been postulated (130). Alkaline hydrolysis proceeds with few exceptions by a bimolecular mechanism involving acyl-oxygen fission. This mechanism can be retarded by increasing the size of substituents. In neutral or weakly basic solution a unimolecular mechanism involving alkyl-oxygen fission has been observed. The tendency toward this mechanism corresponds to the stabilities of the resulting carbonium ions and is of importance only in the cases of esters of such alcohols as t-butanol and triphenyl carbinol.

A similar situation exists in acid hydrolysis. Most esters are hydrolyzed by a bimolecular mechanism involving acyl-oxygen fission, but those in which the alcohol radical can form a stable carbonium ion may proceed by a unimolecular mechanism involving alkyl-oxygen fission.

These considerations suggest that while substituents on the α carbon of the alcohol moiety would be most effective in retarding hydrolysis by the bimolecular mechanism, too many

Table 9

PHYSICAL PROPERTIES OF SELECTED ESTERS

	Compound	BP Lit. °C	Calc BP °C	Calc BP °F	MP °C	Viscosity cs -40°F	Viscosity cs 100°F	Viscosity cs 210°F	ASTM Slope 100°-210°F	Ref.
1	Ethyl heptanoate	70/8	192	378			1.15		-	186
2	n-Nonyl acetate	210	210	410			1.42		0.98	186; Beil., II, 135
3	*n*-Amyl caproate	227	227	441			1.57		0.862	186; Beil., II, 323
4	*n*-Decyl acetate	92/1.5	265	507			2.24		0.849	186
5	Methyl laurate	136/10	273	523			2.50		0.826	186; Beil., II (2), 319
6	n-Heptyl heptanoate	273	273	523			2.53		0.815	186
7	Ethyl myristate	326	326	619	10-12		3.65		0.769	186; Beil., II (2), 326
8	n-Decyl caproate	104/1.5	281	538			3.44		0.795	186
9	*n*-Amyl laurate						4.06		0.763	186
10	Ethyl stearate	182/2	377	711	30-31		6.40		0.718	186; Beil., II (2), 352
11	n-Octadecyl acetate	208/9	364	687	29-31		7.61		0.749	186; Beil., II (2), 147
12	*n*-Decyl laurate				22		7.34		0.710	186
13	*n*-Amyl stearate				30		8.37		0.692	186
14	*n*-Decyl stearate				38		13.9		0.650	186
15	*n*-Octadecyl laurate				44		17.5(1)		0.654	186
16	Melissyl acetate	313/8	503	937	73		29(1)		0.609	186; Beil., II (2), 147
17	n-Octadecyl stearate				62		27(1)		0.613	186
18	*n*-Amyl melissate				70		43(1)		0.581	186
19	Melissyl caproate				68		53(1)		0.485	186
20	n-Decyl melissate				69		42(1)		0.560	186
21	Melissyl laurate				70		45(1)		0.554	186
22	Melissyl stearate				77		57(1)		0.524	186
23	n-Octadecyl melissate				77		65(1)		0.519	186
24	Melissyl melissate				91		109(1)		0.509	186
25	Di-*sec*-amyl succinate				-45	281	3.65		0.93	199
26	Dicapryl succinate				-20	965	7.55		0.81	199
27	Di-2-ethylhexyl succinate				-70	1,059	7.00	2.10	0.82	199

Table 9 (Cont'd)

	Compound	BP Lit. °C	Calc BP °C	Calc BP °F	MP °C	Viscosity cs -40°F	Viscosity cs 100°F	Viscosity cs 210°F	ASTM Slope 100°-210°F	Ref.
27a	Di-2-ethylhexyl adipate				<-80	798	8.11	2.35	0.77	199
28	Di-sec-amyl adipate					246	4.48		0.83	199
29	Dicapryl azelate				-10	1.350	11.22	3.01	0.73	199
30	Di-2-ethylhexyl azelate					1,164	11.10	3.01	0.72	199
31	Diamyl sebacate				30		7.34	2.38	0.69	199
32	Diheptyl sebacate				60		11.3	3.25	0.66	199
33	Di-2-ethylhexyl sebacate				-55	1,400	12.3	3.28	0.71	199
34	Diisononyl sebacate						18.9	4.6	0.64	199
35	Di-n-butyl phthalate	197/10	349	660			9.13	2.24	0.85	199
36	Di-n-butyl isophthalate				-10		11.1	2.51	0.85	199
37	Di-n-butyl terephthalate	180/4	355	671	60		9.86	2.43	0.81	199, Beil., IX, 375
38	Di-2-ethylhexyl phthalate	247/10	413	775			29.7	4.26	0.83	199
39	Di-2-ethylhexyl hexahydrophthalate	232/10	394	741			20.0	3.51	0.83	199
40	Di-2-ethylhexyl isophthalate	256/10	420	788	<-65		35.2	4.80	0.82	199
41	Di-2-ethylhexyl hexahydroisophthalate	245/10	410	770			17.4	3.57	0.76	199
42	Di-2-ethylhexyl terephthalate	257/10	422	792	-65		33.9	4.97	0.79	199
43	Di-2-ethylhexyl hexahydroterephthalate						18.7	3.81	0.75	199
44	Trimethylolethane tricaproate						11.5	2.92	0.764	186
45	Pentaerythritol tetracaproate						23.4	4.71	0.716	186
46	Tri-(2-ethylhexyl) tricarballylate						24.5	4.20	0.788	186
47	Benzyl benzoate	323	323	613	21	$7.43^{77°}$	$3.00^{140°}$	1.56	0.88	31
48	Ethyl benzoate	212	212	414	-34.6		1.95	$1.17^{122°}$	-	31

(1) Extrapolated value.

substituents would favor hydrolysis by the unimolecular mechanism. Substituents on the β carbon would also decrease the rate of hydrolysis and should not increase the tendency toward hydrolysis by the unimolecular mechanism. Substituents on the acid moiety of aliphatic esters, while less effective in retarding hydrolysis than those on the alcohol, should not influence greatly the mechanism of hydrolysis.

Conclusions. The advantages of esters for application as a hydraulic fluid are ease of preparation, good viscosity properties and a wide liquid range. The chief disadvantage for the particular application of this contract, where hydrolytic and oxidative stability may be relatively unimportant, is lack of thermal stability. All esters which have been used as hydraulic fluids or subjected to thermal stability tests have been susceptible to decomposition by elimination of a stable molecule. It is therefore possible that an ester designed to inhibit all obvious modes of decomposition would have the requisite thermal stability for a high temperature hydraulic fluid. Such esters might be made from the following alcohols and acids: t-alkyl carbinols, 7-norbornanols (or other alcohol with α or β hydrogen atoms at the bridgehead of a cage compound), 2,2-difluoroalkanols, tere- and isophthalic acids, carbonic acid and dibasic aliphatic acids.

Ketones

Thermal Stability. Pyrogenic decomposition of acetone yields methane and ketene; of diethyl ketone yields ketene, methyl ketene, ethane and ethylene; of acetophenone yields dypnone, $C_6H_5COCH=C(CH_3)(C_6H_5)$, 1,3,5-triphenylbenzene and α,β'-diphenylfuran (125). The last compound is in disagreement with the results of reference (132).

Acetone decomposes in 2 hrs at 400°C in a chrome-vanadium steel autoclave (119). No catalysts have been found for ketene production but some metals catalyze the decomposition of acetone. At 270°C over nickel, acetone is rapidly decomposed into methane, carbon monoxide, hydrogen and carbon; below 400°C copper has no effect on ketones; iron at 600°C catalyzes the decomposition of acetone (or ketene) into carbon and hydrogen (125). At 350°-400°C the decomposition of acetone is via dehydration (125). Decomposition of acetone by heat is not through acetylacetone but exclusively into simpler compounds (129).

Pinacolin, $(CH_3)_3C\text{-}COCH_3$, is remarkably stable. On passing through a Pyrex combustion tube at 3 cc/min no significant decomposition took place at 605°C and 665°C; at 1 cc/min and 705°C decomposition was nearly complete but only 1.5 to 2.0% of ketene was produced (129).

Acetophenone on heating at 270°-300°C decomposed into triphenylbenzene, 3,4-diphenylfuran and a resin (132); on heating in a sealed glass tube at 330°C for 10 hrs it was 70% decomposed into dypnone, triphenylbenzene and a solid melting at 109°C; it was 80% decomposed after refluxing for 16 days at 200°C to produce dypnone, 1,3,5-triphenylbenzene and α,β'-diphenylfuran (78). p-Methoxyacetophenone has a decomposition temperature of 360°C (125). p-Methoxyisobutyrophenone is 20% decomposed in 18 hrs at 360°-380°C. This is a higher decomposition temperature than for the corresponding hydrocarbon (125). Dibenzyl ketone yielded carbon monoxide, toluene and carbon on heating in a tube for 14 hrs at 200°-360°C (78).

Methyl β-tetralyl ketone showed little change on passing through a tinned iron tube at a rate of 10 g/30 min and a temperature of 600°-620°C; at 680°-700°C approximately a 30% yield of pure methyl β-naphthyl ketone was produced with some naphthalene (39).

Benzophenone is much more stable to heat than the aliphatic or mixed aliphatic aromatic ketones. On heating for 2 hrs at 400°C in a chrome-vanadium steel autoclave it showed no decomposition (119); on heating to 430°C it remained intact, but was completely decomposed at 500°-550°C (132). 2,5-Dimethylbenzophenone on refluxing (303°C) several days was converted into methylanthracene (77). Substituted benzophenones such as p,p'-dimethylaminobenzophenone and o,o'-dihydroxybenzophenone distill without decomposition at 360° and 330°C respectively (125). Among the decomposition products of benzophenone are benzene and benzaldehyde (125).

Although the 3,4'-dimethyl-, 4,4'-dimethyl- and 4,4'-ditertiary-butylbenzophenones are solids, alkylation in numerous other instances (Table 10) lowers the melting point.

Viscosity. No viscosity data were found on any benzophenones. The viscosities of four ketones are shown in Table 11. In Fig. 2 are plotted the viscosities of palmitone and palmitophenone. Although these two ketones are solids at room temperature (Table 11), their viscosities are extrapolated to zero and the 100°-210°F ASTM slopes were determined for uniformity in making comparisons. They have respective ASTM slopes of 0.64 and 0.73.

Conclusions. Aliphatic ketones unsubstituted on the α carbons are unstable at 370°C. Mixed aliphatic aromatic ketones also without substitution on the α carbon, such as acetophenone, appear to be unstable at 370°C. Methyl β-tetralyl ketone may be an exception to this, as it is reported stable (39) at 600°-620°C. This datum is, however, for a very short sojourn at this high temperature; on longer exposure at a lower temperature the compound might show greater instability.

Table 10

PHYSICAL PROPERTIES OF SOME BENZOPHENONES

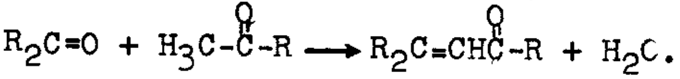
Compound	Lit. BP °C/mm Hg	Lit. MP °C	Calc NBP °C	Calc NBP °F	Ref.
Benzophenone	306/760	48	306	583	Beil. VII, 411
4,4'-Dichlorobenzophenone	353/757	145	353	667	Beil. VII, 420
3,4'-Dimethylbenzophenone	328/760	82	328	622	Beil. VII, 451
4,4'-Dimethylbenzophenone	333/725	95	337	638	Beil. VII, 452
4-Propylbenzophenone	344-346/716	oil	348	658	Beil. VII, 455
4-Isopropylbenzophenone	334-336	oil	334	633	Beil. VII, 456
4-Benzylbenzophenone	Calc 415	oil	415	779	Beil. VII, 524
4,4'-Diphenoxybenzophenone	-	147	-	-	69
4,4'-Dibenzoylbenzophenone	-	227	-	-	55
4,4'-Dicyclohexylbenzophenone	-	135	-	-	189
4-Methyl-2,5-diethylbenzophenone	330	-	330	626	83
4-Octylbenzophenone	251/12	-	420	788	210
4,4'-Ditertiarybutylbenzophenone	-	134	-	-	61
4-Cyclohexylbenzophenone	195-200/3	58-60	393	739	143
3-Phenylbenzophenone	264/25	79	405	761	115
o-(α-Phenylethyl)benzophenone	184/0.8	-	400	752	29
4-Phenylbenzophenone	-	106	-	-	158
4,4'-Dibenzoylbiphenyl	-	218	-	-	158
4,4'-Dimethylaminobenzophenone	360	-	360	680	
2,2'-Dihydroxybenzophenone	330-340	-	330	626	
p-sec-Butylbenzophenone	188/9	-	346	655	118
p-sec-Amylbenzophenone	188-90/5	-	365	689	118
p-sec-Octylbenzophenone	212-214/5	-	400	752	118
p-sec Dodecylbenzophenone	243-45/4	-	450	842	118
2,5-Di-sec-butylbenzophenone	155/3	-	335	635	118

Table 11

VISCOSITY OF KETONES

		Viscosity cs									ASTM Slope	
Compound	BP°C	59°F	86°F	118.6°F	176°F	194°F	266°F	356°F	464°F	572°F	100°-210°F	Ref.
Diamyl ketone	228	2.35	2.19									253
Acetophenone	202	1.95	1.48	1.13								253
	MP°C											
Palmitophenone	59.0				3.97		1.90	1.162	0.746	0.513	0.73	35
Palmitone	83.2					5.52	3.05	1.794	1.12	0.774	0.64	35

Thermal decomposition of aliphatic ketones without α carbon substitution, at temperatures below the optimum for ketene production, probably occurs by condensation at the α carbon with the elimination of water, i.e.



$$R_2C{=}O + H_3C\text{-}\overset{O}{\overset{\|}{C}}\text{-}R \longrightarrow R_2C{=}CH\overset{O}{\overset{\|}{C}}\text{-}R + H_2C.$$

Substitution of the α hydrogen should stabilize the aliphatic and aliphatic aromatic ketones. The degree of substitution required may also involve steric hindrance effects as exemplified by pinacolin which is stable at 605°C on passing through a hot tube.

Aryl ketones are stable at 370°C but substitution in the aromatic ring will be required to produce a liquid product.

Sulfones

Thermal Stability. The high thermal stability of sulfones is exemplified by a limited number of compounds which have been distilled. Diphenyl sulfone distills undecomposed at 370°C (17); di-*p*-tolyl sulfone distills at 404°C (19) and benzyl phenyl sulfone is reported to distill undecomposed (144). Diisobutyl sulfone (bp 265°C) and diisoamyl sulfone (bp 295°C) distill without decomposition, which indicates a relatively high thermal stability for the aliphatic sulfones (15a). Since decomposition of aliphatic sulfones is probably via the elimination of an olefin to yield a sulfinic acid, the absence of a β-hydrogen should also stabilize this molecule.

Sulfones, both aliphatic and aromatic, are predominantly crystalline compounds (Table 12). Symmetrical 1,2-dialkylsulfonyl ethers through hexadecyl have been prepared and all are crystalline compounds, melting between 136° and 190°C. Unsymmetrical sulfones, such as ethyl dodecyl sulfone (mp 75°C) and ethyl hexadecyl sulfone (mp 77°C), are reasonably high-melting solids (2). One series of aliphatic *o*-tolyl sulfones through at least hexyl are all oils, with the cetyl melting at 65°C (18). No liquid aromatic sulfone was uncovered.

Conclusion. Aromatic sulfones should possess adequate thermal stability, but without further information on the rheological properties, and in view of the strong tendency to crystallinity, research in this field at this stage does not appear very fruitful.

Table 12

REPRESENTATIVE PHYSICAL PROPERTIES OF SULFONES

Compound	Lit. BP °C/mm Hg	Lit. MP °C	Ref.
Diphenyl sulfone	370	125-126	Beil., VI, 300
2-Methyldiphenyl sulfone		80	Beil., VI, 371
2,2'-Dimethyldiphenyl sulfone		134-135	Beil., VI, 371
4,4'-Dimethyldiphenyl sulfone	404/714	158	Beil., VI, 419
4,4'-Diethyldiphenyl sulfone		102	Beil., VI, 475
2,5,2',5'-Tetramethyldiphenyl sulfone		Needles	Beil., VI, 498
4,4'-Diisopropyldiphenyl sulfone		109	Beil., VI, 506
Bis-(2,3,5,6-tetramethyl)phenyl sulfone		37	Beil., VI, 547
Bis(pentamethylphenyl)sulfone		98.5	Beil., VI, 551
α,β'-Dinaphthyl sulfone		122	Beil., VI, 559
Phenyl β-naphthyl sulfone		115-116	Beil., VI, 658
Phenyl α-naphthyl sulfone		99	Beil., VI, 622
β,β'-Dinaphthyl sulfone		177	Beil., VI, 659
Dibenzyl sulfone		150	Beil., VI, 456
p-Tolyl benzyl sulfone		144-145	Beil., VI, 455
Phenyl benzyl sulfone		148	Beil., VI, 455
Ethyl β-naphthyl sulfone		43	Beil., VI, 658
Propyl β-naphthyl sulfone		73	Beil., VI, 658
1,2-Bis(phenylsulfonyl)ethane		179-180	Beil., VI, 302
1,3-Bis(phenylsulfonyl)propane		125-126	Beil., VI, 303
1,3-Bis(phenylsulfonyl)2-methylpropane		oil	Beil., VI, 303
1,2-Bis(o-tolyl sulfonyl)ethane		94-95	Beil., VI, 371
1,2-Bis(o-tolyl sulfonyl)propane		oil	Beil., VI, 371
1,3-Bis(o-tolylsulfonyl)propane		oil	Beil., VI, 371

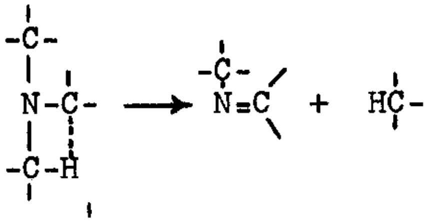
Table 12 (Cont'd)

Compound	Lit. BP °C/mm Hg	Lit. MP °C	Ref.
1,2-Bis(p-tolylsulfonyl)ethane		200-201	Beil., VI, 419
1,3-Bis(p-tolylsulfonyl)ethane		124-125	Beil., VI, 420
Propyl p-tolyl sulfone		53	Beil., VI, 417
Ethyl p-tolyl sulfone		55-56	Beil., VI, 417
1,3-Bis(ethylsulfonyl)propane		183	Beil., VI, 477
Diethyl sulfone	248	70	Beil., I, 346
Dibutyl sulfone		43	Beil., I, 371
Diisobutyl sulfone	265	17	Beil., I, 379
Diisoamyl sulfone	295	31	Beil., I, 406
Ethyl o-tolyl sulfone		oil	Beil., VI, 370
Butyl o-tolyl sulfone		oil	Beil., VI, 370
sec-Hexyl o-tolyl sulfone		oil	Beil., VI, 370

Nitrogen Compounds

Thermal Stability. By analogy with the modes of decomposition suggested for ethers, amines might be expected to decompose by one or both of the routes formulated below. In the

A)



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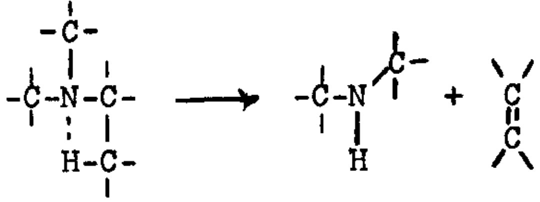
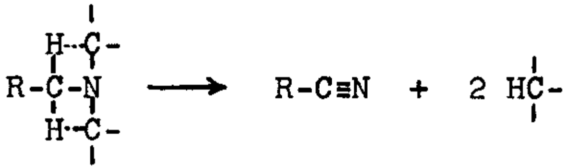


case of ethers, route A was favored over route B because the carbon-oxygen double bond had a much higher bond energy than the carbon-carbon double bond. In the case of amines, however, the carbon-nitrogen double bond and the carbon-carbon double bond have approximately the same bond energies ($C=C$, 100 kcal, $C=N$, 94 kcal) (196) so that the decomposition of amines would be expected to proceed by both routes. Nitriles could be formed by decomposition of the imine formed via route A or could result from a simultaneous decomposition of an amine into two molecules of a paraffin or hydrogen and one of a nitrile. Since the nitrile group has a much larger bond energy ($C\equiv N$, 144 kcal) (196) than an imine, the formation of nitriles in the decomposition of amines by one of the above routes is highly probable. If amines do decompose in the manner suggested above, then their thermostability would not be improved by replacing either the α or β hydrogen atoms by such substituents as alkyl groups or fluorine atoms.



The observed products from the thermal decomposition of amines are in line with the above speculations. Ethylamine pyrolyzed at 500°C over kaolin gives acetonitrile, ammonia, ethylene, nitrogen and hydrogen; the primary reaction course appeared to be decomposition into acetonitrile and hydrogen (259). Dimethylamine at 800°-1000°C gives hydrogen cyanide, methane and hydrogen (183) while trimethylamine gives hydrogen cyanide and methane almost exclusively. Dibenzylamine and tribenzylamine decompose on gradual distillation (maximum 300°C) with the formation of toluene, ammonia, dibenzyl and stilbene (44).

Aromatic amines are more stable than aliphatic, perhaps because nitriles cannot be formed so readily. Aniline when heated at 500°C forms only small amounts of diphenylamine, ammonia and resin (131); when passed at 300°C over finely divided nickel (215) or platinum on charcoal (276), it forms carbazole in good yield. *N*-Methylaniline was 97% recovered after being heated for 3 hrs at 330°-340°C, and *N*,*N*-dimethylaniline was 88% recovered after being heated for 12 hrs at 350°-360°C. Partial decomposition occurred but no primary amine was isolated (124). However, *N*,*N*-dimethylaniline when passed through a glowing tube gave chiefly benzonitrile along with benzene, carbazole, ammonia, hydrogen cyanide and other products (190). β-Naphthylamine after long heating in a sealed tube at 280°-300°C was only 3.5% decomposed into ammonia and β,β'-dinaphthylamine (28). *N*-o-Tolyl-β-naphthylamine boils undecomposed at 400°-405°C (25) and triphenylamine boils at 365°C (24). *N*-Methyl-*N*-cyclohexylaniline does not share the stability of other aromatic amines, but decomposes on distillation at atmospheric pressure (280°C) (23).

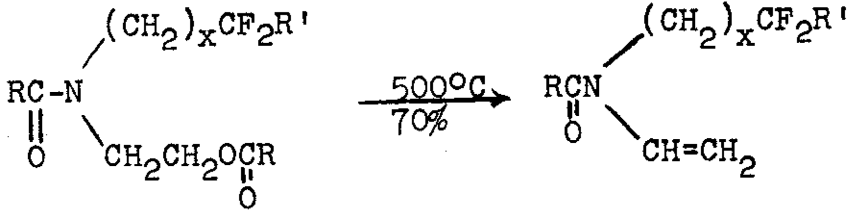
Mono- and diarylamines have a strong tendency to form carbazoles on passage through a glowing tube. Aniline gives carbazole along with diphenylamine (157), and *N*-phenyl-β-naphthylamine forms benzocarbazole (108).

The thermal stability of resonance-stabilized heterocyclic amines is similar to that of the aromatic hydrocarbons. Pyridine, for example, is obtained by passing nitrogen bases from petroleum distillate over a catalyst at 700°C (13). It is for the most part unchanged after eight hours at 490°C, only a small amount of α,α'-dipyridyl being formed (122), while at a bright red glow α,α'-, α,β'- and α,γ'-dipyridyl are formed (168). In the presence of $FeCl_3$ or $CuCl_2$ α,α'-dipyridyl forms at 300°C (116).

Amides can decompose in several ways. A primary amide on heating can dehydrate with the formation of a nitrile. Benzamide was converted in 90% yield to benzonitrile by passing benzamide vapors over alumina at 425°C (34). Primary amides of aliphatic acids give similar yields of nitriles when they are passed over sand at 425°C (34). A second type of decomposition which all classes of amides of aliphatic acids can undergo results in the formation of a ketene and an amine. Ketene was observed in the vapors resulting from distillation of acetamide through a quartz tube at 500°C (125). *N*-Acetylphthalimide and *N*-acetylcarbazole decomposed at the reflux temperature to diketene in 30 and 20% yields, respectively. *N*,*N*-Diphenylacetamide, however, was unchanged after 24 hours at 290°C or after passage through a tube at 500°-600°C (128). Triphenylacetamide is also very stable, and less than 1 cc of gas is produced from 0.2 g of the substance at 300°C (33). *N*-Caproyl-, *N*-isobutyryl- and *N*-diphenylacetylphthalimide yield ketenes on heating above 200°C (128).

Phthalimide begins to decompose at 350°C and at 480°C is almost quantitatively converted into benzonitrile (167), which is extremely stable towards heat. A chlorine substituent stabilizes phthalimides: 4-chlorophthalimide pyrolyzes only slowly to p-chlorobenzonitrile at 500°C and tetrachlorophthalimide is not decomposed rapidly even at 600°C (167).

That amides are more stable than esters is suggested by the fact that at 500°C an ester of a β-amidoethanol gave a N-vinylamide rather than a vinyl ester (59).



Viscosity. In general, the strong hydrogen bonding present in most amines, imines and amides is responsible for the high melting points and high ASTM slopes of those members of this series which have exposed functional groups. When the nitrogen is buried in the center of an aliphatic compound with suitably designed chain structures, the physical properties of the compound resemble those of equistructural esters and hydrocarbons (153). Amides, even when hydrogen bonding is eliminated by replacing all of the N-hydrogen atoms, however, still have higher melting points than aliphatic esters of the same chain length (186, 245).

Inspection of Table 13 shows that amines capable of forming hydrogen bonds have higher 100°F viscosities and ASTM slopes than the homomorphic hydrocarbons. Tertiary amines, in which hydrogen bonds cannot be formed, have lower ASTM slopes than the related hydrocarbons. The few examples in Table 13 suggest that aliphatic tertiary amines have lower 100°F viscosities and aromatic tertiary amines higher 100°F viscosities than the related hydrocarbons. This may be attributed to an increase in free rotation on replacing an aliphatic carbon atom by a nitrogen atom and by an increase in intermolecular attractive forces on replacing an aromatic carbon atom by a nitrogen atom. Tertiary amines containing 29-37 atoms in the chain have lower melting points than n-paraffins of the same chain length (245) and might, therefore, meet the requirements for the liquid range. The physical properties of a number of amines are given in Table 14.

Table 13

COMPARISON OF THE VISCOSITY PROPERTIES OF AMINES AND HYDROCARBONS

Compound	Viscosity cs	Temp. °F	ASTM Slope 100-210°F	Ref.
Di-n-butylamine	1.17	77	1.06	32
n-Nonane	0.92	77	0.91	70
Tributylamine	1.33	100	0.94	32
5-Butylnonane	1.54	100	0.98	219
Tri-n-amylamine	2.20	100	0.90	32
7-n-Hexyltridecane	4.55	100	0.86	219
7-n-Propyltridecane	2.69	100	0.90	219
Aniline	2.52	100	1.10	30
α-Picoline	0.70	100	0.98	89
Toluene	0.56	100	1.03	72
Isoquinoline	2.50	100	0.92	89
Naphthalene	1.90	100	1.01	70
N,N-Diethylaniline	1.65	100	0.99	91
Pentylbenzene	1.20	100	1.00	72

Amides, however, even when hydrogen bond formation is prevented by replacing all the N-hydrogen atoms, have higher melting points than aliphatic esters of the same chain length (245, 186) and appear to be unpromising with respect to the liquid range requirement. The melting points of a number of amides are given in Table 15.

Conclusions. Primary and secondary amines can be excluded from consideration on the grounds of poor viscosity because of association. Tertiary amines containing an aliphatic group appear to be too unstable for use at high temperatures, and little improvement in viscosity appears to result from replacement of a carbon by a nitrogen atom. Amines with one or more aromatic groups have a tendency to decompose to carbazoles at high temperatures.

Only heterocyclic amines, such as pyridines or quinolines, offer promise for application at high temperature. Because of their good thermal stability and the indication that their viscosity properties are better than aromatic hydrocarbons, heterocyclic amines should be considered. Possible types of compounds are alkylpyridines and alkylquinolines.

Table 14

PHYSICAL PROPERTIES OF REPRESENTATIVE AMINES

	Compound	BP °C/mm Lit.	MP °C	Viscosity cs 32°F	Viscosity cs 100°F	Viscosity cs 212°F	ASTM Slope 100°-210°F	Estm. 210°F Visc.	Ref.
1	Tri-n-amylamine	130/14		5.87	2.16/104°	0.933/212°	0.90	0.945	32, Beil., IV (2), 642
2	Tri-Isoamylamine	235		6.26	2.22/104°	0.933/212°	0.94	0.945	32, Beil., IV (2), 646
3	Tri-n-butylamine	216/760		2.82	1.29/104°	0.644/212°	0.94	0.650	32, Beil., IV (2), 157
4	Di-n-butylamine	159/749			0.734/138°	4.82/214°	1.06	0.492	91
5	Cyclohexylamine	132/745		2.83/59°	1.54/110°	0.70/215°	1.03	0.721	91
6	Benzylamine	184/755		1.81/72°	0.964/144°	0.64/214°	0.98	0.656	91
7	Aniline	184/760	-6.2	9.68/33°	2.17/113°	0.884/208°	1.10	0.885	30, Beil., XII (2), 46
8	n-Butylaniline	240/750			0.873/210°	0.506/320°	1.05/210-300°	0.873	91
9	N,N-Diethylaniline	216/755	-21.3	4.07/33°	1.55/104°	0.724/212°	0.99	0.734	91, 30, Beil., XII (2), 90
10	m-Toluidine	203/760	-31	8.61	2.25/104°	0.833/212°	1.09	0.842	32, Beil., XII (2), 464
11	N,N-Diethyl-m-toluidine	230/755			0.694/238°	0.594/275°	1.03	0.821	91
12	Piperidine	104/748		2.35/56°	0.907/148°		1.09/210-300°	0.606	91
13	o-Toluidine	200/760	-27.7	9.95	1.98/122°	0.891/212°	1.06	0.928	30, Beil., XII (2), 430
14	N-Ethylaniline	206		4.22	1.51/104°	0.675	1.07	0.680	30, Beil., XII (2), 90
15	Quinoline	237/760	-15.6	3.98/59°	2.76/86°		0.89	0.990	254, Beil., XX (2), 222
16	Isoquinoline	243/760	26.5	2.98/86°	1.67/140°	0.99/212°	0.92	0.990	89
17	α-Picoline	128	-70	0.861/68°	0.614/122°	0.470/176°	0.98	0.418	89
18	p-n-Octylamino-n-octylbenzene	234/14	11-13						120
19	N-Cetylaniline	266/23	41-43						120
20	N,N-Dicetylaniline	285/23							120
21	Triphenylamine	348	125						Beil., XII, 181
22	Diphenylamine	302	53						Beil., XII, 174
23	N-Ethyldiphenylamine	297							Beil., XII, 181
24	4,4',4"-Trimethyltriphenylamine	decomp.	117						Beil., XII, 907
25	N-o-Tolyl-β-naphthylamine	405	105						Beil., XII, 1277
26	N-Ethyl-β-naphthylamine	316	<-15						Beil., XII, 1274

Table 14 (Cont'd)

	Compound	BP °C/mm Lit.	MP °C	Viscosity cs			ASTM Slope 100°-210°F	Estm. 210°F Visc.	Ref.
				32°F	100°F	212°F			
27	3,5-Diisopropyl-2-isobutyl-pyridine	259/740	<-15						Beil., XX, 256
28	2-Phenylpyridine	270/740							Beil., XX, 424
29	2-(β-Phenylethyl)pyridine	290/766	-3						Beil., XX, 427
30	3-n-Amyl-2-n-hexylquinoline	355							Beil., XX, 423
31	N,N'-Diethyl-N,N'-diphenyl-ethylenediamine	223/16	75						Beil., XII, 282
32	N,N'-Dimethyl-N,N'-diphenyl-trimethylenediamine	246/21							Beil., XII, 283
33	n-Pentadecylamine	300	36						Beil., IV, 201
34	n-Heptadecylamine	340	49						Beil., IV, 202
35	N-Methyldidodecylamine	201/1.5	16						268
36	N-Methyldicetylamine	270/1	37						268
37	Carbazole	352	247						Beil., XX (2), 279
38	N-Ethylcarbazole	190/10	68						Beil., XX (2), 282

Amides, in general, appear to have better thermal stability than most esters but not enough to hold promise as a high temperature fluid. In addition, as the mode of decomposition of amides does not seem as clear-cut as for esters, it should prove more difficult to increase the stability of amides than of esters. Finally, the relatively high melting points of amides would make it difficult to attain the liquid range required for a hydraulic fluid.

Aromatic nitriles have good thermal stability and a wider liquid range than amides.

Table 15

MELTING POINTS OF SEVERAL AMIDES

	Compound	BP/760mm Calc °C	BP/760mm NBP °F	MP °C	Ref.
1.	Lauramide			15	245
2.	Stearamide			49	245
3.	Myristamide			103	245
4.	N-Methylmyristamide			79	245
5.	N-n-Dodecylstearamide			81-82	159
6.	N-n-Octadecylstearamide			94-95	159
7.	N,N-Dimethylheptamide	245	473	<-10	Beil.,IV,60
8.	N,N-Diethylheptamide	257	495	<-15	Beil.,IV,111
9.	N,N-Diisoamylvaleramide	275	527	--	Beil.,IV,184
10.	N,N-Dimethylmyristamide			32	245
11.	Acetanilide			112	245
12.	Hexanilide			92	245
13.	Octanilide			55	245
14.	Lauranilide			78	245
15.	Stearanilide			94	245
16.	Adipamide			224	159
17.	Sebacamide			208	159
18.	N,N'-Di-2-ethylhexyladipamide			64	159
19.	N,N'-Di-n-dodecyladipamide			149	159
20.	N,N'-Dihexadecyladipamide			145	159
21.	N,N'-Di-n-octadecyladipamide			144	159
22.	N,N'-Di-2-ethylhexylsebacamide			87	159
23.	N,N'-Di-n-dodecylsebacamide			144	159
24.	N,N'-Dihexadecylsebacamide			140	159
25.	N,N'-Di-n-octadecylsebacamide			139	159

Phosphorus Compounds

Thermal Stability. Only a small amount of published physical data on viscosity and thermal stability of phosphorus compounds were found, except in WADC reports. Statements about stabilities in general terms can be found in the chemical literature. Boiling points were considered a qualitative indication of stability. These data are shown in Table 16. Alkyl orthophosphates and mixed alkyl aryl orthophosphates with one or more hydrogen atoms on the β-carbon atoms of the alkyl groups are considered thermally unstable at 700°C (95,81). After 24 hrs at 150°C 2,2-dimethylpropyl diphenyl phosphate appears as stable as tritolyl phosphate (95). On distillation under 5 mm pressure in the absence of air tri-β-methylbutyl, tri-γ-methylbutyl and tri-n-hexyl orthophosphates decompose; the tri-n-amyl ester (bp 225°C/50 mm) shows distinct indications of decomposition on being distilled under 150 mm and, similarly, on distillation at 289°C/760 mm, tri-n-butyl phosphate shows decomposition (81).

Alkyl ditolyl phosphates are reported to be more heat-stable than the alkyl diphenyl phosphates (95). Thermal decomposition temperatures ranging between 626° and 741°F are given for three aryl phosphates with the most stable, namely, di-p-tolyl 1-naphthyl phosphate, decomposing at 741°F (248). Southwest Research has reported an additional large number of aromatic phosphates which are stable above 700°F (57). Nothing was found to indicate the thermal stabilities of alkyl -substituted aryl phosphates above tolyl.

Several literature statements indicate that phosphonic acids are among the most thermally stable derivatives of phosphorus, and the neutral esters of phosphonic acid appear to be more stable at high temperatures than the corresponding tertiary esters of phosphoric acid (148). The stability of the phosphonates is such that reactions may involve other parts of the molecule without affecting the phosphonate grouping (86). Dioctyl benzenephosphonate possesses a higher thermal stability than trioctyl phosphate (255). Data illustrating these differences in thermal stabilities between phosphates and phosphonates were not found.

Phosphines have good thermal stability (Table 16) but are toxic. Tri-n-octylphosphine, mp 30°C, bp 291°/5 mm, is unaffected when heated for an hour at 250°C. However, in the presence of air it is readily oxidized at ordinary temperature to the phosphine oxide, a white solid (133, 148). Cleavage of the constituent radicals of phosphine has not received much attention. Triphenylphosphine is transformed into benzene and phosphorus on heating in a hydrogen atmosphere only above 325°C; this is greater stability than that shown by the corresponding arsenic, bismuth or antimony compound (148).

Table 16

PHYSICAL PROPERTIES OF REPRESENTATIVE PHOSPHORUS COMPOUNDS

Compound	Lit. BP °C/mm Hg	Lit. MP °C	Calc NBP °C	Calc NBP °F	Ref.
Diphenyl 1-naphthyl phosphate	201-207/0.12	53.5	462	864	248
Diphenyl 2-naphthyl phosphate	203-207/0.14	64-65	471	880	248,185
Di-m-tolyl 1-naphthyl phosphate	213-214/0.10	-15	447	836	248
Di-p-tolyl 1-naphthyl phosphate	226-228/0.16	-12	473	883	248
Diphenyl 8-quinolyl phosphate	211-218/0.12	58-59	449	840	248
Tri-α-naphthyl phosphate		145			Beil., VI, 611
Tri-β-naphthyl phosphate		111			Beil., VI, 647
Triphenyl phosphate	245/11	45			Beil., VI, 179
0,0,0-Triphenyl thiophosphate	360/760	49			Beil., VI, 181
Triphenyl tetrathiophosphate		86			Beil., VI, 182
Tricresyl phosphate	420/760	<-35	420	788	174
Dibutyl 1-decanephosphonate	157/1.0		365	689	192
Dibutyl octadecanephosphonate	248-250/2		470	878	147
Diethyl 1-naphthylmethanephosphonate	205-206/5		380	716	146
Dioctyl benzenephosphonate	204-207/248		248	478	257
Diphenyl toluenephosphonate	>360			>680	170
Dipropyl cyclohexanephosphonate	123-5/0.6		325	617	110
Di-o-xenyl phenyl phosphite	308-327/9		490	914	179
Diphenyl o-chlorophenyl phosphite	238-246/6		420	788	179
Di-(p-tertiary-butylphenyl) phenyl phosphite	272-282/7		460	860	179,181
Ditolyl phenyl phosphite	225-238/9		390	734	179
Tri-(o-xenyl) phosphite	336-340/5	95	-	-	181
Tri-(p-tertiary-butylphenyl) phosphite	288-294/8	75-76	-	-	181

Table 16 (Cont'd)

Compound	Lit. BP °C/mm Hg	Lit. MP °C	Calc NBP °C	Calc NBP °F	Ref.
Tri-(o-cyclohexyl) phosphite	324-329/8		520	968	181
Tri-(p-tertiary octyl phenyl) phosphite	354-357/10		540	1004	181
Diphenyl o-xenyl phosphite	280-290/9		460	860	180
Di(o-chlorophenyl) carvacryl phosphite	265-270/10		430	806	180
Diphenyl p-tertiary-butylphenyl phosphite	240-253/7		415	779	180
Triisoamyl phosphite	265-270/760		265-270	509	135
Tri-β-oc [illegible] phite	162-164/2		350	662	97
Tri-p-tolyl phosphite	250-255/10		415	779	169
Di-2-octyl phosphite	138-140/2		320	608	148
Diphenyl phosphite	218-219/25		345	644	148
Tri-n-octylphosphine	291/50	30	410	770	133
Tri-p-tolylphosphine	-	146	-	·-	148
Tri-phenylphosphine	360/decomp.	79	-	-	148
Triamylphosphine	185.5/50	29	285	545	148
Trinonylphosphine	226.5-7.5/1		460	860	5
Tridecylphosphine	236.5-7.5/1.5		460	860	5
Trihexadecylphosphine	288-90/0.4	51	560	1040	5
Butyldiphenylphosphine oxide		89			178
Tributylphosphine oxide	300/760	needles		572	148
Triamylphosphine oxide		59			148
Triphenylphosphine oxide		153			148
Trihexylphosphine oxide	187-8/2		380	716	5
Trioctylphosphine oxide	225-7/2		430	806	5
Trihexylphosphine sulfide	188-8.5/2.5		370	698	5
Trioctylphosphine sulfide	224-6/0.5		470	878	5

Table 16 (Cont'd)

Compound	Lit. BP °C/mm Hg	Lit. MP °C	Calc NBP °C	Calc NBP °F	Ref.
Ethyl bis(*N*,*N*-pentamethyleneamido)phosphate	215-216/10	liq.	370	698	171
Ethyl di(diethylamido)phosphate	218-220/760	liq.	218	424	171
Tri(dipropylamido) phosphate	310-315/760	liq.	310	590	171
Ethyl di(dipropylamido)phosphate	164-166/20	liq.	285	545	171
Ethyl bis(*N*,*N*-pentamethyleneamido)thionophosphate	198-210/22	liq.	330	626	171
Phenyl bis(*N*,*N*-pentamethyleneamido)phosphate	215-16/10	liq.	370	698	148
Phenyl bis(dimethylamido) phosphate	158-160/0.5	liq.	375	707	148
Tetraethyl pyrophosphate	104-110/0.08		-	-	112
Tetra-*n*-propyl pyrophosphate	112-116/0.01				256
Tetra-*n*-butyl pyrophosphate	143-146/0.01		430	806	256

No liquid alkylphosphine oxides or sulfides were found (Table 16). The tri-n-amylphosphine oxide melts at 59°C (160). Higher aliphatic homologs may be liquid and, therefore, of interest as hydraulic fluids, However, if none are found to be liquid, they could still be of interest as anti-wear additives if they are soluble in hydraulic fluids. Phosphine oxides are hygroscopic.

Thermal decomposition of phosphoramides from primary amines takes place rapidly under vacuum at somewhat above 200°C (148). Mono-secondaryamidodiaryl esters of phosphoric acid may not possess the required thermal stability, as diphenyl diethylamidophosphate is reported to undergo decomposition on distillation in a vacuum (171). Distillation data (Table 16) on the disecondary-amidomonoesters indicate a high degree of stability (171). This class should not be completely overlooked.

Tetraethyl pyrophosphate (bp 104-110°C/0.08 mm) is reported to decompose at 208-213°C into ethylene and metaphosphoric acid (112). Water vapor at 175°C hydrolyzes the pyrophosphate instantly (112). The hydrolysis rates are much lower for the water-insoluble tetrabutyl pyrophosphates: 15% is hydrolyzed in five days in water emulsion (256). The tetraethyl compound is 17 times as toxic as the tetrabutyl (256). The hydrolytic stability of the alkyl pyrophosphates should improve with the proper choice of alkyl groups.

From the boiling point data (Table 16) the phosphites appear to have fairly high thermal stability. They are, however, oxidized slowly by air. The higher trialkyl phosphites are stable at 100°C in pure water (148). Triethyl phosphite decomposes at 250°C in a sealed tube (135). For use in a system where air can be reasonably excluded, the phosphites should not be rejected as possible hydraulic fluids.

Viscosity. The ASTM slopes of trinonyl phosphate, di-p-tolyl 1-naphthyl phosphate, tritolyl phosphate, dinonyl phosphite and diisoctyl benzenephosphonate are compared in Fig.3. The viscosities of these and a few other compounds are listed in Table 17.

It is interesting that the dialkyl benzenephosphonates and the triaryl phosphates are not materially different in ASTM slope (100°-210°F). The aromatic phosphates with a slope of 0.85 do not appear very promising as the major constituent of a hydraulic fluid with a specified slope of 0.50. The effect of alkylation on the viscosity of aromatic phosphates should be determined.

The alkyl phosphates, secondary phosphites and tetraalkyl thionopyrophosphates have better viscosity characteristics than the aromatic phosphates and dialkoxy aromatic phosphonates.

Table 17

VISCOSITIES OF SELECTED PHOSPHATES AND PHOSPHONATES

Compound	Lit. BP °C/mm Hg	Calc NBP °C	Calc NBP °F	Viscosity cs -65°F	Viscosity cs -40°F	Viscosity cs 0°F	Viscosity cs 100°F	Viscosity cs 210°F	Viscosity cs 700°F	ASTM Slope 100°-210°F	Ref.
Specifications		>371.1	>700			2500			1.5	0.50	56
1,2-Ethylene-bis/di(1-propyl)phosphate7				4720	925	-	10.8	2.78		0.76	50
Di-1-butyl benzenephosphonate				1840	342	-	5.17	1.63		0.85	50
Trinonyl phosphate	257.2/5	450	842		7900		19.0	4.0		0.73	242
Di-p-tolyl 1-naphthyl phosphate	226-228/0.16	473	883				126.9	8.89		0.85	248
Tritolyl phosphate		420	788				35.11	4.37		0.88	95
Diisooctyl benzenephosphonate				49,300	4571	-	11.7	2.63		0.82	50
Tetraethyl dithionopyro phosphate				248	-	-	3.81	1.43		0.81	50
Dinonyl phosphite				4870	708		7.92	2.39		0.73	50

Conclusions. It does not seem likely that any phosphorus compound containing a single phosphorus atom will be developed that will answer the viscosity specifications as a single fluid.

The stability specifications appear to be answered by the aromatic phosphates which, if not useful as the base material of a fluid, may serve as thermally stable anti-wear additives. Alkyl phosphates with hydrogen on the β-carbon atom do not possess the desired thermal stability.

Data on the decomposition temperature of neopentyl-type phosphate, phosphonate and phosphite esters should establish the maximum thermal stability for these classes of aliphatic esters.

More data on the relationship of structure to viscosity are needed on phosphorus compounds.

Boron Compounds

Thermal Stability. The thermostability of borates, from our own test data (Table 25) and as judged from some boiling point data (Table 18), is as good as that of silicates. The boron-oxygen bond energy is reported as 110 ±5 kcal/mole (51), which is slightly greater than that of 106 kcal/mole reported for the silicon-oxygen bond (98).

Triphenyl borate boils at 360°C without decomposition (16). Boric acid triesters of a mixture of isomeric α-hydroxyethylxylenes decompose at 250°C/10 mm (73). Tris(hydroabietyl) borate is stable at 330°C (207).

Nothing was found on the thermal properties of boronates. Trisubstituted boron is oxidatively unstable.

Viscosity. On this project viscosity data were determined at 100°F and at 212°F for an aliphatic and an aromatic borate; the results are shown in Table 19 and are plotted in Fig. 3. Based on these two examples, borates offer no improvement viscositywise over phosphates or silicates.

Hydrolysis. Boric acid esters are generally quite susceptible to hydrolysis and are hygroscopic (218, 249). In certain configurations, however, the esters are extremely difficult to hydrolyze. *n*-Alkyl borates are rapidly hydrolyzed by water, secondary alkyl borates more slowly; branching of the chain slows down the rate, as shown by the unusually slow hydrolysis of tri-(neopentyl) borate. The most hydrolysis-resistant of the borates studied was tris(diisopropylcarbinyl) borate which did not hydrolyze at 100°C in an alkaline solution (218).

Di-*n*-butyl *n*-butylboronate is fairly stable to water and 10% sodium hydroxide (136).

Table 18

PHYSICAL PROPERTIES OF REPRESENTATIVE BORATES AND BORONATES

Compounds	Lit. BP °C/mm Hg	Lit. MP °C	Calc NBP °C	Calc NBP °F	Ref.
Tris(decyl) borate	274-6/0.5	-	540	1004	261
Tris(octyl) borate	200-1/2	-	400	752	261
Tris(nonyl) borate	228-30/1.5	-	450	842	261
Tris(hexadecyl) borate	328-90/<0.5	43-44	610	1130	261
Tris(2,2-dimethylpropyl) borate	229-230	57-59	-		218
Tris(2,4-dimethylpentyl-3) borate	285-290	54-55	-		218
Tris(cyclohexyl) borate	137-41/1.5	-	330	626	274
Triphenyl borate	141.6-8/1.5	38-40			274
Tris(2-phenyl-4-chlorophenyl) borate	242-8/3.8	-	440	824	206
Tris(2-phenylphenyl) borate	320-30/3.8	-	540	1004	206
Tris(benzyl) borate	255/17	-	400	752	58
Tris(β-naphthyl) borate		116	-	-	Beil., II, 648
Tris(α-naphthyl) borate		84-85	-	-	Beil., VI, 611
Tris(p-tolyl) borate	248-250/12	58-61	-	-	249
Tris(o-chlorophenyl) borate	242/6	47-49	-	-	249
Tris(p-chlorophenyl) borate	258-260/5	60-64	-	-	249
Tris(hydroabietyl) borate	Stable 330	59	-	-	207
Phenyl o-phenylene borate	166-167/12	40-44	-	-	249
Phenyl ethylene borate	262-268	Solid	-	-	249
Tri-o-cresyl borate	189-195/2	Liquid	-	-	195
Tris[2-cyclohexylcyclohexyl) borate		172-175	-	-	195
Tris(hexyleneglycol) diborate	143-149/2	Liquid	-	-	195
Di-n-butyl n-butylboronate	110/19	-	220	428	136
Diisobutyl m-tolylboronate	195-207/66	-	295	563	Beil., XVI, 921
Diisobutyl phenylboronate	180-187/30-35	-	295	563	Beil., XVI, 921
Diisobutyl benzylboronate	189-96/36	-	302	576	142

Dibutyl chlorophenylboronate improves oiliness and film strength of a hydrocarbon lubricating oil (156).

Conclusions: In view of the outstanding hydrolytic stability of the tris(diisopropylcarbinyl) borate, tertiary alkylcarbinyl borates should have good hydrolytic stability and improved thermal stability.

Aliphatic borates are more thermally stable than aliphatic phosphates and equal to or slightly better than aliphatic silicates. Borates in general are no better in viscosity than phosphates and are not quite as good as silicates. Straight-chain aliphatic and aromatic borates are less stable hydrolytically than phosphates and silicates. They possess one possible advantage in the ease of synthesis.

The properties of aryl borates need further elucidation.

Table 19

VISCOSITY OF BORATES

	BP °C/mm Hg	Viscosity cs 100°F	Viscosity cs 212°F	ASTM Slope 100°-210°F	Ref.
Tris(2-ethyl-1-hexyl)borate	350/760	6.071	1.844	0.82	203
Tris(m,p-cresyl) borate	179-210/0.1	43.4	4.109	0.97	203

Silicates and Siloxanes

Thermal Stability. Data on the thermal stability of aliphatic silicates and siloxanes above 400°F are meager. Tetra-(2-ethylhexyl) silicate and tetra(C_6-C_8) silicate are stable at 600°F in glass but unstable at 700°F; incipient decomposition is shown at 650°F in a stainless steel pressure cylinder (200).

Aromatic silicates are more stable than aliphatic silicates. A sample of tetraphenyl silicate, a yellowish oil, (bp 407°-408°C, mp 48°C) was heated for six weeks in glass under a nitrogen pressure of 1 in. Hg. The boiling point dropped and became constant at 396° ±2°C. There was no evidence of decomposition although the liquid toward the end became more viscous and tended to resinify when cooled (140). Tetracresyl silicate (bp 426°-430°C, mp below -65°C) behaved about as the phenyl compound after four weeks of heating, with the boiling point stabilizing at 385° ±3°C (140).

The tendency to resinify can be largely, if not completely, eliminated by using mixtures of tetraaryl silicates with other compatible organic silicates. A mixture of 15 parts of tetraethyl silicate and 85 parts of tetraphenyl silicate was heated at the boiling point (371° ± 10°C) for six weeks with no sign of resinification or decomposition (140).

The phenyl radical is reported to exhibit higher heat stability than substituted phenyl radicals, although the tolyl radical is considered equivalent to the phenyl radical (66).

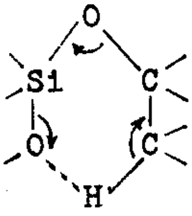
Mixed (n-amyl, phenyl) silicates, in which the phenyl and n-amyl radicals are in the proportion of 0.75 - 3.25 phenyl radicals to 3.25 - 0.75 n-amyl radicals for each silicon atom, have excellent heat stability in the range 525°-600°F (66).

Ester chlorides of silicic acid increase in stability with molecular weight and decrease from normal ester to isoester. Aromatic ester chlorides are more stable than aliphatic (263).

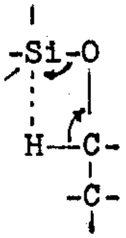
The spontaneous ignition temperature of tetraaryl silicate was reported as 1070°F (134).

Table 20 gives some physical data indicative of stabilities of some additional silicates.

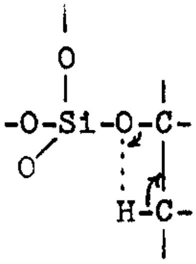
In the absence of much data on the thermal decomposition of silicates, it is useful to consider likely paths of decomposition from a theoretical viewpoint, in order to point up the most probable sites of decomposition in the molecule. Several transition states which might provide a lower energy path for decomposition than by direct fission of a bond can be written for silicates.



A



B



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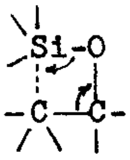
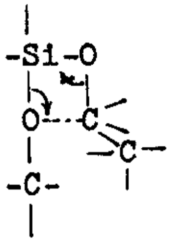


D



E

Decomposition by routes A or E is unfavorable because a silicon-oxygen double bond must be formed. It has been shown that a carbon-silicon double bond is unlikely: the Si-C bond is longer than the C-C bond, and this greater bond distance makes the overlap of π orbitals on the singly bonded atoms too small

Table 20

PHYSICAL PROPERTIES OF SOME SILICATES AND SILOXANES

Compound	Lit. BP °C/mm Hg	Lit. MP °C	Calc NBP °C	Calc NBP °F	Ref.
Methyl triphenyl orthosilicate	366			691	204
Methyl tri-o-cresyl orthosilicate	383			721	204
Ethyl triphenyl orthosilicate	365			689	204
Ethyl tri-o-cresyl orthosilicate	388			730	204
Di-(ethyl ricinoleate) diethyl silicate	308-311/1		560	1040	214
Hexadecyl tripropyl silicate	235-240			455	26
Di-(hexadecyl)diethyl silicate	312-316/15		480	896	214
Tetra-m-tolyl orthosilicate	443-446/720			829/720	Beil., VI, 381
Tetraphenyl orthosilicate	417-420			782	Beil., VI, 182
Tetrathymyl orthosilicate	450	47-48		842	Beil., VI, 539
Tetra-o-tolyl orthosilicate	435-438	Liq.		815	Beil., VI, 358
Tetra-p-tolyl orthosilicate	442-445	69-70		827	Beil., VI, 402
Tetra-α-naphthyl orthosilicate	425-430/130	needles		797/130	Beil., VI, 611
Tetra-β-naphthyl orthosilicate	430/133	crystals		806/133	Beil., VI, 648
Tetraoctadecyl orthosilicate		56-58			82
Tetra(3,5,5-trimethylhexyl) silicate	210/1		440	824	45
Decakis(1,3-dimethylbutoxy) tetrasiloxane	240-242/0.05		550	1022	177
Octakis(2-ethylhexoxy)trisiloxane	260-269/0.05		590	1094	177
Tetra-p-chlorophenoxysilane		70			240

for double bond formation (98, 205). Similar considerations rule out a silicon-oxygen double bond (98). Routes B and D are unfavorable because they require breaking an Si-O bond which is 25 kcal stronger than a C-O bond (98). Thus, route C remains the most likely route for the decomposition of silicate esters.

Some experimental evidence supports this mode of decomposition. The silanol formed as a decomposition product should form a disiloxane or polysiloxanes as the decomposition proceeds (98), and it is observed that silicates resinify on heating (140). In addition, terminal double bonds have been detected in the volatile decomposition products by infrared analysis (203).

It is of interest that route C is analogous to a possible mode of decomposition of ethers designated as route B (see section on ethers). Since it was shown that this is a high energy route for ethers, it would be expected that aliphatic silicates would have a higher thermal stability than the corresponding ether. If route C does in fact require a high activation energy, then other modes of decomposition, such as a free radical attack on the hydrocarbon chain, may also be important in silicate decomposition.

Viscosity. A report by the California Research Corporation discusses the alkyl silicates and siloxanes extensively (50). Table 21 contains viscosity data on many silicates and siloxanes taken largely from this report.

The tetraalkyl silicates, in general, exhibit good viscosity characteristics at low temperatures. Straight-chain silicates are the optimum structures for the best ASTM slopes, both at 100° to 210°F and -65° to 210°F. This is to be expected from general considerations carried over from knowledge on the viscosity characteristics of hydrocarbons. Highly branched silicates tend to exhibit unusual viscosities at low temperatures, in that for a given compound the -65° to 210°F slope is less than the 100° to 210°F value.

The tetra(mixed alkyl) silicates are superior both in overall slope and in low-temperature viscosity characteristics.

The glycol silicate derivatives, the dialkyldialkoxy silanes and the tetra(mixed alkyl) silicates all have good slope characteristics and may have advantages over tetraalkyl silicates and silicones.

The disiloxanes have higher viscosities than the corresponding orthosilicates and have higher refractive indexes and densities as well. Furthermore, they possess, in general, better ASTM slopes than the corresponding orthosilicates but

Table 21

VISCOSITIES OF SILICATES AND SILOXANES

Compound	BP, °C at 1 mm Hg	Viscosity cs -65°F	Viscosity cs -40°F	Viscosity cs 100°F	Viscosity cs 210°F	ASTM Slope 65° to 210°F	ASTM Slope 100° to 210°F	Hydrolytic Stability "Coke Bottle" Test(3)
Orthosilicates								
Tetra(ethyl) silicate	168.1/760							Bad
Tetra(2-propyl) silicate	70-71/10 mm	Solid	-	1.03	0.56	-	0.89	Good
Tetra(1-pentyl) silicate	143-147	65.5	-	2.6	1.2	0.73	0.74	Bad
Tetra(3-pentyl) silicate	121-124	326	-	3.79	1.43	0.79	0.81	Good
Tetra(2-methyl-1-butyl) silicate	124-32	95.0	36.2	2.81	1.17	0.78	0.82	Good
Tetra(2-methyl-2-butyl) silicate (1)	107-108	23.3		2.26	1.10	0.66	0.73	-
Tetra(2,2-dimethylpropyl) silicate	110-120	melt range 67°-69°C.			2.16	-	-	-
Tetra(cyclopentyl) silicate		solid at room temp.				-	-	-
Tetra(benzyl) silicate	215-220/0.2 mm	-	-	7.1	2.3	-	0.72	-
Tetra(4-methyl-2-pentyl) silicate	137-138	846	146	3.88	1.44	0.84	0.88	Good
Tetra(2-ethyl-1-butyl) silicate	163-166	204	67	3.94	1.55	0.73	0.76	Good
Tetra(1-methoxy-2-propyl) silicate	125-128	315	-	3.19	1.25	0.83	0.84	Bad
Tetra(2-heptyl) silicate	175-178	867	215	5.07	1.73	0.79	0.80	Good
Tetra(2,4-dimethyl-3-pentyl) silicate	142-149	4900	763	7.60	2.25	0.79	0.77	-
Tetra(4-methylcyclohexyl) silicate	208-211		33,900(2)	64.6	6.44	-	0.84	Poor
Tetra(2-octyl) silicate	204-207	1720	410	7.12	2.20	0.74	0.76	Fair
Tetra(2-ethyl-1-hexyl) silicate	192-193	1320	260	6.83	2.36	0.71	0.68	Good
Tetra(2-butoxyethyl) silicate	224-226	359	104	4.35	1.67	0.74	0.74	Bad

Table 21 (Cont'd)

Compound	BP, °C at 1 mm Hg	Viscosity cs -65°F	Viscosity cs -40°F	Viscosity cs 100°F	Viscosity cs 210°F	ASTM Slope 65° To 210°F	ASTM Slope 100° To 210°F	Hydrolytic Stability "Coke Bottle" Test$^{(3)}$
Tetra(1-butoxy-2-propyl) silicate	205-206	1010	236	5.68	1.92	0.75	0.75	Poor
Tetra(3-phenyl-1-propyl) silicate	Approx. 168/1μ		720$^{(2)}$	20.7	4.41	-	0.77	Bad
Tetra(1-diethylamino-2-propyl silicate	182-190		-	6.79	2.17	-	0.77	Bad
Tetra(5-diethylamino-2-pentyl) silicate	222-225	278$^{(2)}$	2860	13.4	3.32	-	0.72	Bad
Disiloxanes								
Hexa(2-propoxy)disiloxane	95-97	Solid	-	3.04	1.34	-	0.73	Good
Hexa(2-methyl-1-butoxy)disiloxane	183-186	230	85.8	5.80	2.26	0.62	0.63	Good
Hexa(2-methyl-1-pentoxy)disiloxane	216-220	1770	396	11.0	3.70	0.62	0.57	Good
Hexa(4-methyl-2-pentoxy)disiloxane	193-194	4430	761	11.4	3.53	0.67	0.62	-
Hexa(2-ethyl-1-butoxy)disiloxane	213-216	621	204	9.40	3.41	0.58	0.56	Good
Hexa(1-methoxy-2-propoxy)disiloxane	182-183	1210	-	7.38	2.57	0.69	0.72	Bad
Special Types								+ 1% PAN
1,2-Bis/tri(2-ethyl-1-butoxy)siloxy7-ethane	>108$^{(7)}$	956	262	9.20	3.16	0.62	0.60	Bad
2,5-Bis/tri(2-propoxy)siloxy7hexane	136-143	246	77.6	4.26	1.65	0.72	0.72	Good
Diethyldi(2-ethyl-1-hexoxy)silane	135-137	190	61.8	3.28	1.32	0.78	0.78	Good

Table 21 (Cont'd)

Compound	BP, °C at 1 mm Hg	Viscosity cs -65°F	Viscosity cs -40°F	Viscosity cs 100°F	Viscosity cs 210°F	ASTM Slope 65° to 210°F	ASTM Slope 100° to 210°F	Hydrolytic Stability "Coke Bottle" Test(3)
Mixed tetraalkyl Silicates								
Tetra(2-propyl,4-methyl-2-pentyl) silicate	93-96	79	-	2.25	0.99	0.83	0.86	-
Tetra(2-propyl,4-methyl-2-pentyl) silicate	116-119	282	-	3.07	1.22	0.85	0.85	-
Tetra(2-propyl,4-methyl-2-pentyl) silicate (5)	142-204	2420	461	8.06	2.39	0.74	0.75	-
Tetra(ethyl,2-methyl-2-butyl, 4-methyl-2-pentyl) silicate	93-100	216	67	3.40	1.30	0.79	0.84	Good
Tetra(ethyl, 2-methyl-2-butyl, 4-methyl-2-pentyl) silicate	123-130	1010	176	4.17	1.50	0.84	0.82	Good
Tetra(ethyl, 2-methyl-2-butyl, 4-methyl-2-pentyl) silicate	130-201	2650	417	6.83	2.20	0.76	0.74	-
Polysiloxanes								
Poly(2-propoxy)polysiloxane (4)	131-142	143	-	7.85	2.9	0.52	0.58	-
Poly/1-(1-methoxy-2-propoxy)-2-propoxy/polysiloxane (6)	Not distilled	12,800	-	11.1	3.18	0.63	0.68	Bad
Poly(4-methyl-2-pentoxy)polysiloxane	Not distilled >177	-	-	633	81.8	-	0.42	Bad
Poly(1-pentoxy)polysiloxane	Not distilled >155	229	-	6.12	2.45	0.59	0.59	Bad
Poly(3-pentoxy)polysiloxane	Not distilled >204	56,400	-	88.1	17.8	0.50	0.48	Bad
Poly(2-methyl-1-butoxy)polysiloxane	Not distilled >184	649	-	12.4	4.51	0.52	0.46	Bad
Poly(2-methyl-1-butoxy)polysiloxane	Not distilled >216	1450	474	21.6	7.23	0.48	0.45	Fair
Poly(2-methyl-2-butoxy)polysiloxane	Not distilled >108	6830	-	102	28.3	0.36	0.35	Bad
Poly(1-methoxy-2-propoxy)polysiloxane	Not distilled >210	2590	564	10.98	3.61	0.63	0.58	Bad

Table 21 (Cont'd)

Compound	BP, °C at 1 mm Hg	Viscosity cs -65°F	Viscosity cs -40°F	Viscosity cs 100°F	Viscosity cs 210°F	ASTM Slope 65° to 210°F	ASTM Slope 100° to 210°F	Hydrolytic Stability "Coke Bottle" Test(3)
Poly(4-methyl-2-pentoxy)polysiloxane	Not distilled >125	Flow	-	81.6	15.5	-	0.51	-
Poly(2-propoxy)polysiloxane	Not distilled >130	15,200	3710	72.1	15.8	0.47	0.47	Bad
Poly(2-propoxy)polysiloxane (9)	Not distilled >100	628	-	14.9	4.91	0.50	0.52	Bad
Isoamyl triphenyl orthosilicate (10)								
Hexa(1-hexoxy)disiloxane (11)				6.62	2.45			
Hexa(2-octoxy)disiloxane (11)				18.34	4.67			
Hexa(2-ethyl-1-hexoxy)disiloxane (11)				13.37	4.17			
Hexa(1-decylthio)disiloxane (11)				40.0	7.84			
Tetra(2-ethyl-1-hexyl) silicate (12)	213-16/1			6.80	2.20(8)		0.72	
Tetra(2-ethyl-1-hexyl) silicate after 10 hrs. at 690°F (12)				7.38	2.42(8)		0.68	
n-Amyl triphenyl orthosilicate (13)	396/766	370	108	4.3	1.63		0.75	

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(1) Identity doubtful. (2) Visc. at 0°F. (3) 1% Phenyl-α-naphthylamine inhibitor. (4) Believed largely octa(2-propoxy)-trisiloxane. (5) May contain dimers. (6) Contains monomers. (7) Not distilled. (8) Visc. at 212°F. (9) Preceding compounds taken from Ref. 50. (10) Ref. 204. (11) Ref. 194. (12) Ref. 203. (13) Ref. 66.

are more prone to have a -65° to 210°F slope which is greater than the 100°-210°F slope. This is undesirable, being indicative of poorer low temperature characteristics.

Certain slightly branched-chain tetraalkyl silicates and hexaalkoxydisiloxanes, the best silicate derivatives, have ASTM viscosity-temperature slopes second only to the silicones, have good stabilities and good wear properties, show low volatilities and cost about one-third to one-eighth as much as the silicones. The slopes decrease in the series from orthosilicates to disiloxanes to polysiloxanes. Compounds with about five to six carbon atoms per alkyl group are optimum for good viscosity properties in the -65°F region. The phenomenon wherein the -65° to 210°F slope is less than the 100° to 210°F slope is more prevalent for silicate derivatives containing a mixture of long- and short-chain alkyl groups.

Polysiloxanes are more viscous and have better slopes than either the disiloxanes or the orthosilicates. These polymeric products approach closely the viscosities of the silicone polymers, except that the viscosities of the polysiloxanes "hook" upward at low temperatures in the ASTM plot of viscosity vs. temperature.

Alkyl aryl orthosilicates are reported to have reduced viscosities and improved pour points over straight aryl silicates. Numerous ones are reported with kinematic viscosities (204).

Plots of the data on tetra(2-ethyl-1-hexyl) silicate (Table 21) and on a mixed silicate, n-amyl triphenyl silicate, are shown in Fig 3. Tetra(2-ethyl-1-hexyl) silicate decreased in slope from 0.72 to 0.68 after 10 hrs of heat treatment at 690°F (Table 21). This indicates the possible formation of di- or polysiloxanes. The aromatic silicates have poorer viscosity characteristics than the aliphatic silicates.

It will be noted from Table 21 that tetra(2-ethyl-1-butyoxy)-disiloxane and poly(2-methyl-1-butoxy)polysiloxane are lower in viscosity than the specifications but approach the slope requirements. With a larger alkyl group of the desired thermal properties it may be possible to obtain a disiloxane and polysiloxane that approach the specifications as a single fluid.

Hydrolysis. A disadvantage of the tetraalkyl silicates (Table 21) is their instability to hydrolysis in the presence of small amounts of acidic material. Introduction of basic groups in the molecule, such as in tetra(diethylaminoalkyl) silicate, did not improve the hydrolytic stability. Chain branching at the two position in the silicates is requisite for good hydrolytic stability. In all probability the steric hindrance resulting from such branching enhances this stability. If this were true, it would be expected that the bulkiest groups would prove to be the most beneficial in promoting stability. There is certain evidence that indicates such is actually the case: mixed ethyl, t-amyl, 2-methyl-2-pentyl tetraalkyl silicates are stable to hydrolysis, ethyl silicate and mixed tetra(ethyl and 4-methyl-2-pentyl) silicates are unstable. It thus appears that the highly branched groups stabilize the ethyl groups.

To obtain hydrolytic stability in glycol silicates the glycol must contain at least one carbon atom between the carbons holding the hydroxyl groups. Ethylene glycol derivatives are unstable while 2,5-hexanediol derivatives are stable. It has not been determined whether the hydroxy groups must be secondary groups.

Dialkyldialkoxysilanes exhibit good hydrolytic stability and an important feature is that they do not form silica on hydrolysis but probably a silicone.

Polysiloxanes are much poorer in hydrolytic stability than the disiloxanes. No polymers higher than trimers have been found that are stable, even in the presence of phenyl-α-naphthylamine inhibitor (50).

The tetraaryl orthosilicates when heated with water hydrolyze and become unfit for use as heat transfer media. The mixed alkyl aryl silicates have better resistance to hydrolysis (65, 204).

Conclusions. Alkyl silicates and siloxanes with hydrogen on the β-carbon atom are unstable at 700°F. The tetraaryl silicates are stable at this temperature but possess poor hydrolytic stability; the latter property can possibly be improved.

It is possible to approach quite closely the viscosity slope specifications of 0.50 with an aliphatic disiloxane or polysiloxane. What is needed in this case is better thermal stability, which might be obtained through tertiary alkylcarbinyl esters.

Silanes and Silicones

Thermal Stability. Compounds of the type SiR_4, in which all of the organic radicals (R) are alkyl or aryl hydrocarbon groups, are the most stable substances known to organosilicon chemistry. In comparing the chemical properties of organosilicon and carbon compounds, it should be noted that the strength of the C-C bond (84.9 kcal/mole) is slightly greater than that of the Si-C bond (75.0 kcal/mole). It would be expected, in consequence, that the Si-C bond should be slightly the more reactive.

This is exemplified by the greater ease of thermal decomposition of the tetraalkylsilanes, compared to their carbon analogs. The difference is not great, however, and does not imply an instability of the Si-C bond under ordinary conditions. Thus, such compounds as tetraphenylsilane (154) and tetraphenylmethane can be boiled undecomposed at high temperatures (428°C and 431°C, respectively) and are stable at temperatures of 500°C and higher (98). It would be a mistake, however, to conclude that Si-C bonds impart exceptional stability to the rest of the molecule. In molecules with very high organic content the effect of a silicon atom is greatly diluted or is entirely lost (49).

Diethylsilane is reported to decompose at 480°C (93). The decomposition of silicon tetraethyl is rapid at 580°C (264). At pressures down to 10 cm of Hg, temperatures of 660°-720°C were required to give a measurable rate to the decomposition of tetramethylsilane (117).

The thermal stability of silanes is further illustrated by the compounds in Table 22 that boil above 400°C.

The thermal stability of the fluorosilanes is remarkable. Even so complex a member as dibutyldifluorosilane can be heated in a sealed glass tube to 300°C without evident decomposition. Methyltrifluorosilane is quite stable at 400°C and decomposes only slowly at 600°C (197).

The low bond strength of the Si-Si bond (51 kcal) indicates that toward homolytic cleavage this bond would be relatively unstable. However, the few known disilanes show good thermal stability. Hexaphenyldisilane melts undecomposed at 355°C, and octaphenylcyclotetrasilane decomposes only slowly above 300°C; in these cases the silicon compounds are more stable than their carbon analogs. Disilane and trisilane pyrolyze at 311°C and 319°C respectively, decomposition temperatures which, while less than those of ethane and propane, compare favorably with many hydrocarbons (98). The unexpected stability of the Si-Si bond is probably related to reduced steric factors around it as compared to a C-C bond and the fact that the silyl free radical cannot be resonance-stabilized as much as a hydrocarbon free radical.

Polymethylsiloxane, a silicone, pyrolyzed in 30 to 40 min at 550°F with gel formation. Cracking was also thought to take place at 550°F, as shown by the viscosity decrease of 1% at 250°F. Polyethylsiloxane showed gel formation at 450°F. The viscosity of poly(methyl, phenyl)siloxane could be measured at 700°F, which indicates increased stability over polymethylsiloxane (184). A branched methylpolysiloxane formed by the cohydrolysis of dimethyldichlorosilane and methyltrichlorosilane, undergoes thermal rearrangement under nitrogen above 350°C with

Table 22

PHYSICAL PROPERTIES OF SOME REPRESENTATIVE SILANES

Compound	Lit. BP °C/mm Hg	Lit. MP °C	Calc NBP °C	Calc NBP °F	Ref.
Tetramethyldiphenyldisiloxane	111/1				68
Naphthyltriethoxysilane	308-320/744				151
$CH_3[(CH_3)_2SiO]_9Si(CH_3)_3$	203/10		355	671	271
$CH_3[(CH_3)_2SiO]_{10}Si(CH_3)_3$	202/4.7		380	716	271
Dibenzyldiphenoxysilane	230/1		470	878	113
Diethyldiphenoxysilane	150/4		315	599	113
Dibenzyldibutoxysilane	206/10		360	680	113
R.P. of $(C_2H_5)_2SiCl_2$ and $C_4H_8(SH)_2$	-		-	-	209
Decyltriethylsilane	241/200		295	563	269
Myristyltrimethylsilane	300	Solid	300	572	269
Diphenyldiethoxysilane	117-20/0.12		350	662	103
Tetra-2-naphthylsilane		216-217			100
Trimethyl-p-chlorophenylsilane	119-20/50		210	410	48
Dimethyl-bis(p-chlorophenyl)silane	191/7	45			48
Diphenyl-p-dimethylaminophenylsilane	186-187/0.15		445	833	101
Di-(1-naphthyl)dibutylsilane	400-405/760		400	752	202
Tetrabenzylsilane		127			161
Tetra-p-tolylsilane		223			27
Tris(p-ethylphenyl)methylsilane		50-50.5			27
Octamethyltrisilmethylene	202/720		205	401	238
Diphenyldifluorosilane	157		157	315	164a
Dibutyldifluorosilane	156		156	313	164a
Difluoro-di-1-naphthylsilane	210-13/3	79-81			201
Tri-[("lorol")dodecyl]siliconfluoride	255-265/0.25	3	540	1004	174

Table 22 (Cont'd)

Compound	Lit. BP °C/mm Hg	Lit. MP °C	Calc NBP °C	Calc NBP °F	Ref.
Tetra-n-dodecylsilane	435-440		435	815	102
Tetra-n-tetradecylsilane	435-440		435	815	102
Tetra-n-hexadecylsilane	455-460		455	851	102
Dodecyltrimethylsilane	61-62/0.14				213
Dodecyltripropylsilane	107/0.12	≤-73	330	626	213
Dodecyltrioctylsilane	217/0.27	≤-70	475	887	213
Dodecyltridecylsilane	245/0.15	-70	530	986	213
Dodecyltriundecylsilane	264/0.14	-65	560	1040	213
n-Hexadecyltritolylsilane	430	Liq.			99
n-Dodecyltri-(m-fluorophenyl)silane	420	Liq.			99
Tri-n-octadecylbenzylsilane	302/0.0005	Liq.			99
Octadecyltri-(o-biphenyl)silane	435	Liq.			99

distillation of lower molecular weight products; at 450°C the product gels and continues to undergo rearrangement as the temperature is raised to 600°C (228, 266).

Dow-Corning 710, a silicone, can be heated in the presence of air for over 1200 hrs at 482°F (250°C) without gelling or decomposing to form gums, sludge or other residue. At lower temperatures it can be heated indefinitely without decomposition (71).

Poly(methyl, phenyl)siloxanes are more stable to high temperature oxidation than polymethylsiloxanes. Oxidation attack ruptures the methyl group and oxidizes it to formaldehyde. At 200°C poly(methyl, phenyl)siloxane was stable to oxidation; at 250°C significant viscosity increases took place in the dynamic oxidation test; and at 275°C in dry air gelation occurred in 90-150 hrs; at 300°C, gelation occurred between 8 and 24 hrs and under helium no gelation occurred. Lead, selenium and tellurium accelerated oxidation (62).

The oxidation stability of the polymethylsiloxanes decreases rapidly above 200°C, the maximum temperature at which they can be used advantageously in an oxidizing atmosphere. Metals affect the oxidation (7). The upper service temperature limit of the silicone oils can be raised if oxygen is excluded, for it is the oxidation of the methyl group that imposes the limit (212). Organosiloxanes are stabilized by amines (164).

Viscosity. Insufficient viscosity data were available for any firm generalizations on silanes. Based on the limited data available, however, silanes appear to be inferior to silicones but as good as the siloxanes and silicates. Viscosity data for some silanes are plotted in Fig 1 and listed in Table 23.

Dow-Corning 550 as a single fluid satisfies the viscosity requirements of the specifications (Fig 3, Table 23). Dow-Corning 710 as a single fluid satisfies the slope requirements but is too high in viscosity at 0°C (Fig 3, Table 23).

The uniquely high viscosity index of silicones, as compared to their ether and hydrocarbon analogs, is due to the size of the silicon atom which permits freedom of rotation and gives the molecule an ability to coil not found in hydrocarbons or molecules containing only carbon, hydrogen and oxygen (87,186).

Certain physical measurements on toluene solutions of dimethylpolysilicone and diethylpolysilicone support the view that macromolecules of these polymers consist of systems in which many rings are joined like links in a chain (92).

The slope of the viscosity-temperature plot of polymethylsiloxane increases in going from methyl to ethyl to phenyl, which

Table 23

VISCOSITIES OF SELECTED SILANES AND SILICONES

Compound	Viscosity cs -40°F	0°F	32°F	100°F	210°F	250°F	300°F	350°F	400°F	450°F	500°F	550°F	600°F	650°F	700°F	ASTM Slope 100°-210°F	Ref.
Specifications		2500													1.5	0.50	
Dow-Corning 550		2960	612	95.4	20.68	14.34	9.77	6.99	5.22	4.01	3.16	2.53	2.066	1.698	1.42	0.44	184
Decyltriethylsilane			8.001	4.61(2)	2.12(3)											0.76	269
Tri(lorol)silicon fluoride				22.6	5.21											0.64	174
Dodecyltripropylsilane	671	100		6.83	1.95											0.85	213
Dodecyltrioctylsilane	4862	549		16.36	4.77											0.58	213
Dodecyltridecylsilane	7531	853		24.67	6.11											0.59	213
Dodecyltriundecylsilane	8495	1073		29.66	6.81											0.57	213
Dow-Corning 710				235.6	29.39(1)	19.6	12.7	8.80	6.40	4.90	3.88	3.15	2.64	2.24	1.92	0.52	174
Dow-Corning 710 (10 hrs. at 545°F)				244.5	30.01(1)											0.52	174
Dow-Corning 710 (10 hrs. at 690°F)				249.9	30.02(2)											0.51	174
Aroclor 1254				490	6.0	3.25	1.96	1.35	1.01	0.78	0.64	0.55	0.48	0.43	0.40	0.31	203

(1) Run at 212°F; (2) Run at 68°F; (3) Run at 140°F.

is analogous to the rule for hydrocarbons that the slope increases with the ratio of the cross-sectional diameter of the molecule to its length. The convexity of the graph at high temperatures is ascribed to the statistical uncoiling of long chain molecules as the temperature rise increases the disorganizing effect of thermal agitation. As the molecules exhaust their capacity to uncoil, there is a rapid dropping away from the straight line (184).

Hydrolysis. In contrast to hydrocarbons, silanes can be hydrolyzed by acids and bases. The fact that the silicon atom is larger, less electro-negative and capable of a greater maximum coordination number than the carbon atom makes the Si-C bond considerably more reactive than the C-C bond toward a number of reagents. For example, aryltrimethylsilanes are cleaved by acids under fairly mild conditions to give trimethylsilanol and a substituted benzene, while tert-butylbenzenes are relatively stable towards acids. Presumably, the partial ionic character of the Si-C bond facilitates attack by a proton at the negative (carbon) end of the dipole. The Si-C bond is also more susceptible to basic cleavage. Thus, benzyltriphenylsilane and many related compounds are readily cleaved by potassium hydroxide in alcohol, acetone or dioxane, to give triphenylsilanol and a hydrocarbon, while benzyltriphenylmethane, is relatively inert towards bases.

Any substituent which tends to increase the polarity of the bond has a greater effect on the reactivity of a Si-C bond than on its C-C analog. For example, in compounds of the type X_3C-AY_3, where A is a carbon or silicon atom attacked by base, cleavage of the C-A rather than the X-C bond occurs in the carbon analog only if all three X atoms are halogen and at least two of the Y positions are occupied by oxygen. When A is silicon, only one X need be a halogen atom and only one Y an oxygen atom in order to get cleavage of the C-A bond. In the case of trichloro(trichloromethyl)silane, cold water alone cleaves the C-Si bond readily. In hexachloroethane the C-C bond is not cleaved even by alcoholic potassium hydroxide at 100°C. Cleavage is probably facilitated in the case of silicon compounds by the positive character of the silicon atom, its greater size (which decreases shielding by the surrounding groups) and its ability to increase its coordination number, all of which make nucleophilic attack easier (98).

The alkylfluorosilanes are much less reactive toward metathesis than the corresponding chlorosilanes. The trifluoro compounds fume in moist air and are largely hydrolyzed by water. The difluorides do not fume in air and are not readily hydrolyzed by dilute ammonium hydroxide, but they will react with aqueous sodium hydroxide. The higher trialkylfluorosilanes are not detectably hydrolyzed by aqueous base, nor do they react with sodium in liquid ammonia. The variation of activity with the size of the alkyl substituent is demonstrated by the fact that the trimethylfluorosilane can be titrated as an acid. This same variation in activity is evident in the reaction of silicon tetrafluoride with the Grignard reagent: tetraethylsilane and triethylfluorosilane are formed in about equal amounts, while the propyl, butyl and amyl Grignard reagents do not form the tetraalkylsilane to any appreciable extent under the same conditions (197).

Lubrication. From an application standpoint the silicones are covered rather comprehensively by a group of seven articles (43, 63, 64, 84, 111, 185, 278).

The silicones possess many of the desirable characteristics for a good lubricant, but they do not provide an adequate lubricating film between sliding ferrous surfaces under boundary conditions. Where one or both sliding surfaces are nonferrous much equipment can be adapted to use silicone fluids. Other difficulties are the leak tendencies of silicones where the contact is metal to metal.

Silicone oils blended with 15 to 33% of a solvent such as benzene, cyclohexane, adipates, etc. show excellent lubricating properties even when the solvent and the silicone separately are extremely poor lubricants. An explanation is that in bulk the silicone molecules assume a helical configuration with little adhesion while in solution the solvent causes an uncoiling to a maximum energy of adhesion resulting in a closely packed oriented film on ferrous surfaces (139).

Conclusions. Tetraalkyl- and tetraarylsilanes have sufficient thermal stability to be distilled above 400°C. No data are available to indicate the thermal stability vs. time at high temperatures.

Dow-Corning 710, as shown by our own test in the absence of air, has excellent thermal stability at 370°C. It is, however, too high in viscosity at 0°C to be used as a single fluid. Dow-Corning 550 satisfies the viscosity requirements as a single fluid. Data are needed on thermal stability.

Points of architectural change in the silicone molecule to bring about improvements are two in number, namely at the end of the molecule in the "end stoppers" which retard or prevent further thermal polymerization and at the silicon atom where a change in substitution may alter the hydrolytic or oxidation stability.

The silicones can approach very closely the specifications for this contract without additives as shown by Dow-Corning 550. On the basis of data at hand they have a much better slope than the silanes.

Organo Compounds of the Higher Elements of Groups III, IV and V

Most of the compounds that have shown promise as high temperature hydraulic fluids have been based on the Group III element boron, the Group IV elements carbon and silicon, and the Group V elements phosphorus and nitrogen. It is of interest to consider the higher elements in these groups to learn if any of their derivatives have more desirable properties than the derivatives of the lower elements.

Group III. In addition to boron, the elements of Group III are aluminum, the A elements, scandium, yttrium and the lanthanides, and the B elements, gallium, indium and tellurium.

Like the borines, the trialkyl derivatives of aluminum are violently attacked by air or water; towards heat alone the aluminum compounds are fairly stable and trimethylaluminum decomposes gradually at 300°C. The triarylaluminum compounds are less readily attacked by air and water than the trialkyl, but are sufficiently reactive to react at once with iodine (230).

The aluminic esters, $Al(OR)_3$, are analogous to the boric esters but are higher melting and somewhat more reactive. They distill without decomposition at relatively high temperatures ($Al(OC_2H_5)_3$, mp, 139°C, bp, 320°C/760) and are hydrolyzed at once by water. Their reactivity is illustrated by their use as reducing agents in the Meerwein reduction (230).

The chemistry of the organo derivatives of the III-A elements has not been developed. With increasing atomic number the properties of their trialkyl and trialkoxy derivatives should approach the properties of the corresponding magnesium compounds, so that derivatives of the III-A elements would be even less promising than the aluminum compounds. In addition, the rarity of the III-A elements removes them from further consideration.

The trialkyl and triaryl derivatives of the III-B elements are also unstable to air and water. Gallium trialkyls ignite spontaneously in air and hydrolyze immediately in water. Indium trialkyls oxidize readily and lose methane in the presence of moisture. Thallium trialkyls fume in air but do not ignite spontaneously; thallium triethyl hydrolyzes in water to diethylthallium hydroxide, $(Et_2Tl)OH$, while gallium triethyl hydrolyzes to ethylgallium hydroxide, $EtVa(OH)_2$. Gallium triphenyl, mp 166°C, is fairly reactive; indium triphenyl, mp, 208°C, is readily oxidized by air; and thallium triphenyl, mp, 169°C, is oxidized by air and reacts with water. In general, indium alkyls and aryls are more reactive than those of gallium and much more than those of thallium (230).

Esters of the trihydroxides of the III-B elements have not been reported, but they would probably have no better hydrolytic stability or wider liquid range than the aluminic esters.

Group IV. Besides carbon and silicon, Group IV includes the B elements germanium, tin and lead and the A elements titanium, zirconium, hafnium and thorium.

In contrast to the trialkyl boron and aluminum compounds, the tetraalkylated derivatives of silicon, germanium, tin and lead are stable to air and are not easily hydrolyzed by water (151). The tetraaryl derivatives are very thermally stable, the degree of thermal stability decreasing from silicon to lead. Table 24 shows the similarity in melting points of the tetraaryl derivatives and the variation in their decomposition points. The tetraaryl derivatives are fairly stable to chemical attack, and again stability decreases from silicon to lead. While tetraphenylsilane can be nitrated or sulphonated, tetraphenyllead loses all of its phenyl groups on treatment with glacial acetic acid (230).

Table 24

TETRAARYL DERIVATIVES OF GROUP IV-B ELEMENTS

Compound	MP °C	Decomp. Point °C	Ref.
Tetraphenylmethane	285	500	230
Tetraphenylsilane	237.5	530	230,102
Tetraphenylgermane	233.4	435	230,102
Tetraphenyltin	229.2	432	230
Tetraphenyllead	227.8	270	230,102
Tetra(p-tolyl)tin		342	151
Tetra(m-tolyl)tin		287	151
Tetracyclohexyltin		290	151
Tetracyclohexyllead		290	107

The triarylfluoro derivatives are also thermally stable. It was shown in Table 25 that triphenylfluorosilane was very stable at 370°C. Triphenylfluorogermane is the most stable of the halotriphenylgermanes, and hydrolyzes very slowly even when boiled with alcoholic potassium hydroxide. The dihalo and trihalogermanes hydrolyze readily (138). Triphenylfluorostannane is somewhat less stable than the silane and begins to decompose at 350°C (151).

Aryl substituents appear to be more readily removed by chemical action than alkyl, as shown by the fact that diethyldiphenylgermane on treatment with bromine loses phenyl but not ethyl groups to give diethyldibromogermane and bromobenzene (230). Towards heat, aryl substituents appear to impart greater stability than alkyl. While tetraphenylgermane is stable above 435°C, tetraalkylgermanes decompose at 420°-450°C. This reaction is homogeneous and monomolecular and is thought to proceed according to the following equation (225).

$$Ge(C_2H_5)_4 = Ge + 4\ C_2H_5\cdot$$

The tetraalkylsilanes, stannanes and plumbanes are believed to decompose in a similar manner in this temperature range (265). Hexaalkyldistannanes are as stable as the tetraalkylstannanes but are slowly oxidized by air (151). Most tetraalkyllead compounds can be distilled undecomposed below 140°C (151), but dibenzyldiphenylplumbane turns brown at 127°C (151).

Gilman, after testing the thermal stability of a large number of germanes, stannanes and plumbanes, reported that for use at high temperatures the lead compounds were not promising, the tin compounds were better than the lead but not good enough and, in general, the silicon compounds were better than the germanium (102, 99).

Few esters of acids of the type $E(OH)_4$ are known where E is germanium, tin or lead. Tetraethoxygermane is extremely hygroscopic and hydrolyzes readily in air with the separation of germanium dioxide (138). The corresponding esters of tin and lead would be expected to behave similarly. In view of the promising thermal properties of the silicates the thermal stability of the germanates should be tested, in spite of their poor hydrolytic stability.

The chemistry of the organo derivatives of the Group IV-A metals has not been extensively developed. In Table 25 it is shown that tetra(2-ethylhexyl) titanate, while stable at 545°F, suffered an 85% weight loss at 690°F in 30 min. This indicates that the ortho esters of titanium are less stable than the corresponding silicon and boron compounds. Since it would be expected that the ortho esters of the other IV-A elements would be less thermally stable than those of titanium, this class of compounds is not promising for the development of a high temperature fluid.

<u>Group V.</u> Besides nitrogen and phosphorus, Group V includes the A elements vanadium, niobium, tantalum and protoactinium and the B elements arsenic, antimony and bismuth.

Few organic compounds of the V-A elements have been prepared. The ortho and meta esters of vanadic acid change from one form to another almost as rapidly as the ions of ortho- and metavanadic acid. The ortho esters, R_3VO_4, are hydrolyzed at once in water to colloidal vanadic acid. Pyrovanadic esters, $R_4V_2O_7$, do not seem to exist. The metavanadic esters $R_3V_3O_9$, are hydrolyzed with great ease; they are unstable and even in a carbon dioxide atmosphere undergo internal oxidation and reduction with the formation of aldehydes (230). With these properties this class of compounds could not be used as high temperature fluids, and there is no reason to expect that similar esters of the other V-A elements would be any more promising.

Although few organo derivatives of the V-A elements have been reported, literally thousands of organo derivatives of the V-B elements are known, largely because of the interest in their chemotherapeutic properties.

The trialkyl derivatives of the V-B elements are less stable than the triaryl, but the tribenzyl are the least stable of all. In general, derivatives of the type ER_3, where E is arsenic, antimony or bismuth, become less stable as E becomes larger (230).

Trialkylarsines oxidize readily in air (230), and decompose when heated in sealed tubes at high temperatures (200°-300°C) to give compounds of the type $(RAs)_4$ and higher aliphatic hydrocarbons (67). The structure and properties of the compounds $(RAs)_4$ do not seem to be well-known, but they might be interesting as high temperature materials. The trialkylstibines decompose in air and the trimethyl and triethyl derivatives ignite spontaneously (52). Trimethylbismuthine fumes in air (106).

Triarylarsines distill unchanged in a carbon dioxide atmosphere at temperatures above 360°C (208) and tetraphenyldiarsine, which oxidizes in air, is stable to heat alone up to 400°C (230). Triarylstibines are stable to air and have fair thermal stability; tri-4-biphenylstibine, mp, 177°C, decomposes into biphenyl, antimony and other products at the boiling point (105). Mixed arylalkylstibines are readily oxidized, and phenyldimethylstibine fumes faintly in air and oxidizes in solution (105). The triarylstibines are solids [$(C_6H_5)_3Sb$, mp, 48°-50°C; $(p\text{-}CH_3C_6H_5)_3Sb$, mp, 107°C] while the mixed stibines are mostly liquids (230). The triarylbismuthines are also more stable than the trialkyl derivatives and are not oxidized by air (230).

The triaryl and trialkyl derivatives of the V-B elements are fairly stable to hydrolysis; for example, trimethylbismuthine is volatile with steam and decomposes only slowly in boiling water (106). The trialkoxy derivatives, however, are hydrolyzed at once by water (230).

Other types of organoarsenic, antimony and bismuth compounds are known which have better resistance to chemical attack than the trialkyl and trialkoxy derivatives. Most of these are solids, however, and few display any high degree of thermal stability.

Phenylarsonic acid, $C_6H_5AsO(OH)_2$, mp, 158°C with loss of water, is extraordinarily stable to attack of hot concentrated nitric or sulfuric acid (230). Dialkyl or diarylarsinic acids, such as cacodylic acid, $(CH_3)_2AsO(OH)$, mp, 200°C, are also extremely stable toward oxidizing or reducing agents (230). Esters of these acids might be of interest as high temperature fluids.

The stibonic acids, $R\text{-}SbO(OH)_2$, melt with decomposition and polymerize readily (230). The dialkyl or diarylstibinic acids, $R_2SbO(OH)$, also are highly polymerized and have a varying water content (230). The trialkyl and triarylstibine oxides, which are formed by the oxidation of the stibines, may be fairly resistant to heat; they are, however, solids. The distibines are oxidized by air (230).

The bismuthonic and bismuthinic acids are not known and dibismuthines have not been isolated (230).

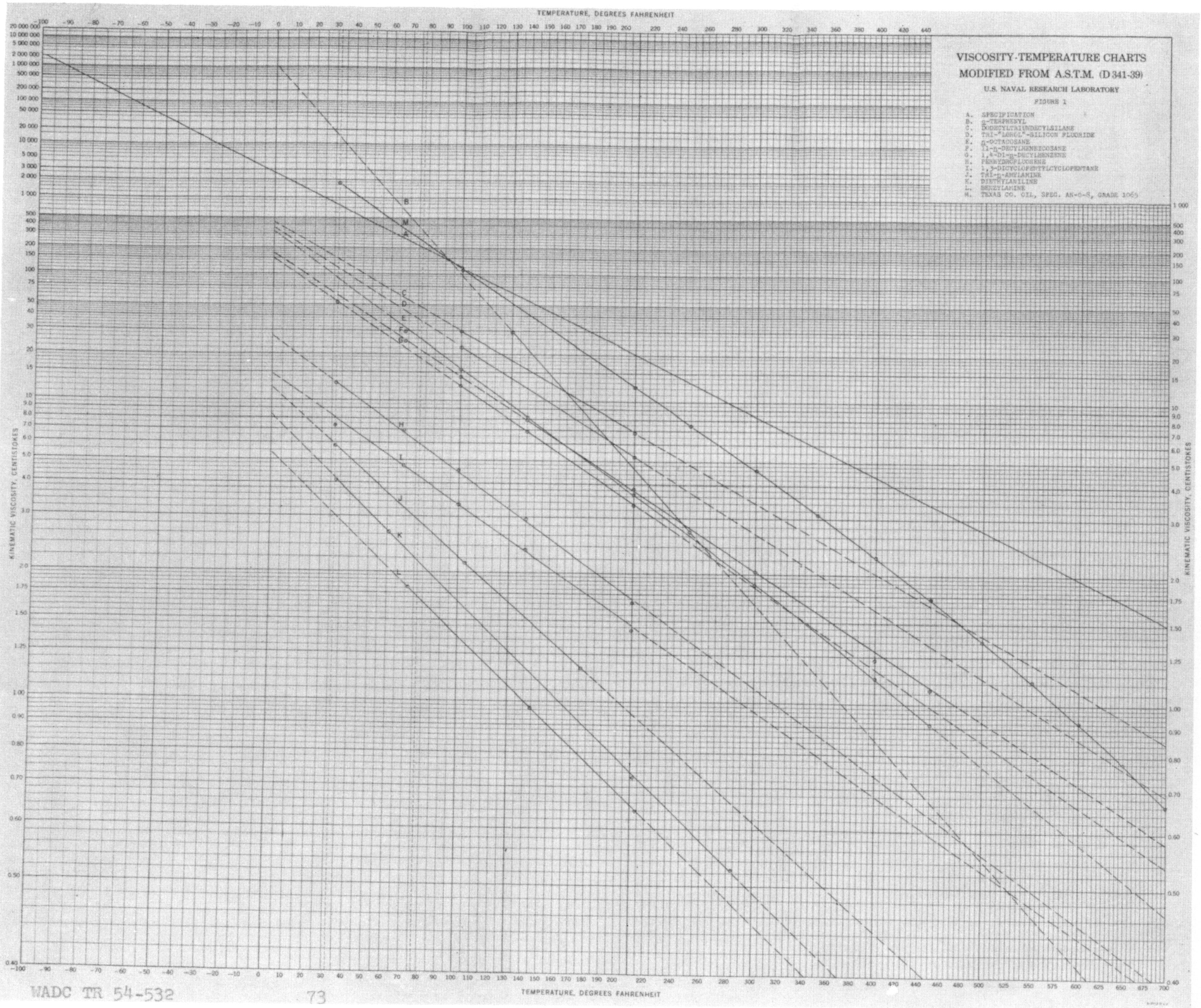
Conclusions. This cursory review of the chemistry of the organic derivatives of the Group III, IV and V elements other than boron, carbon, silicon, nitrogen and phosphorus did not uncover any really promising leads. The most likely classes of compounds for use as a high temperature fluid appear to be the germanes, esters of germanic acid, $Ge(OH)_4$, esters of arsonic acids, $RAsO(OH)_2$, and esters of arsinic acids, $R_2AsO(OH)$. There are no obvious advantages to any of these classes, however, to compensate for the cost of the germanes, the hydrolytic instability of the germanic esters and the toxicity of the arsenic compounds.

Oxidation Inhibitors; Metal Deactivators; Anti-Wear Additives

In all three of these applications the chemical employed will vary with the severity and specific conditions of each requirement. An intensive search for such materials should be made, if needed, when a promising base material is found.

A comprehensive survey of the literature on antioxidants and corrosion inhibitors for lubricants was made by the University of Virginia and reported in WADC Technical Report 53-353. Listing is made of all compounds noted in the literature which are applicable as inhibitors above 300°F.

A WADC Technical Report 53-16 (in two parts) on corrosion preventative additives has been issued by Armour Research Foundation. Two articles by Baker et al deal with the theory, properties and test methods for polar-type rust inhibitors (8a, 8b).



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

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FIGURE 1

A. SPECIFICATION
B. p-TERPHENYL
C. DODECYLTRIUNDECYLSILANE
D. TRI-"LOROL"-SILICON FLUORIDE
E. n-OCTACOSANE
F. 11-n-DECYLHENEICOSANE
G. 1,4-DI-n-DECYLBENZENE
H. PERHYDROFLUORENE
I. 1,3-DICYCLOPENTYLCYCLOPENTANE
J. TRI-n-AMYLAMINE
K. DIETHYLANILINE
L. BENZYLAMINE
M. TEXAS CO. OIL, SPEC. AN-O-8, GRADE 1065

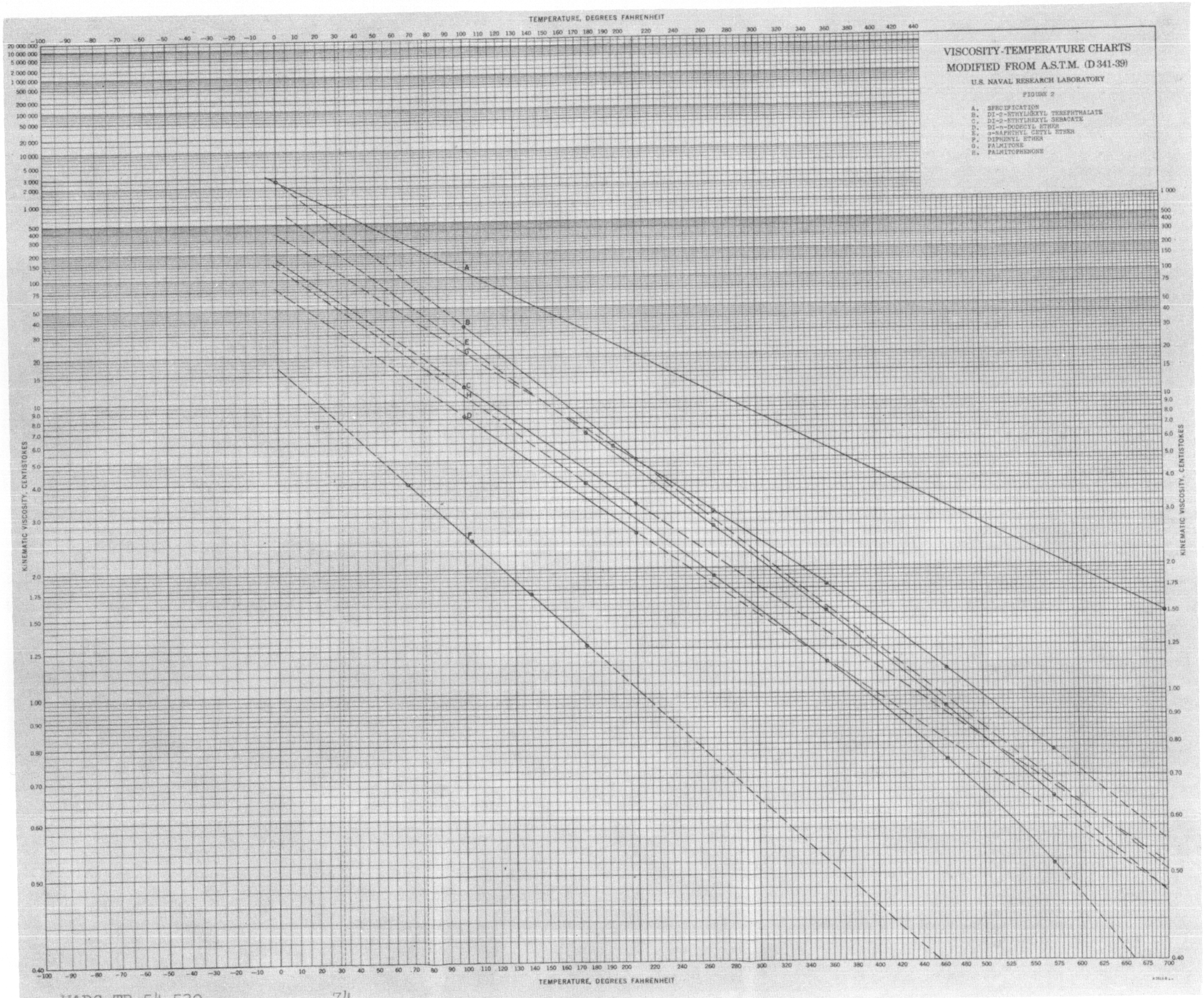

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FIGURE 2

- A. SPECIFICATION
- B. DI-2-ETHYLHEXYL TEREPHTHALATE
- C. DI-2-ETHYLHEXYL SEBACATE
- D. DI-n-DODECYL ETHER
- E. α-NAPHTHYL CETYL ETHER
- F. DIPHENYL ETHER
- G. PALMITONE
- H. PALMITOPHENONE

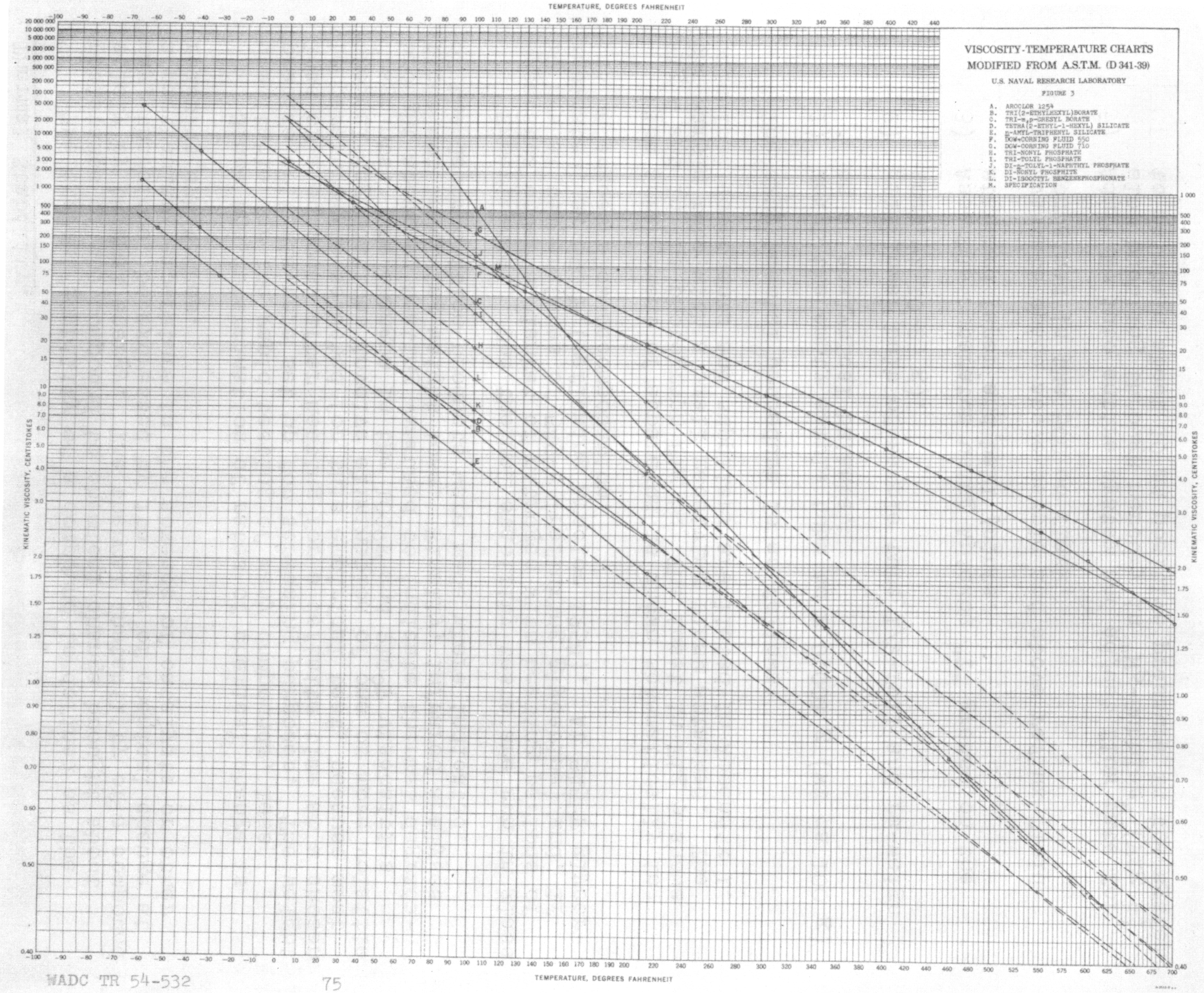

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FIGURE 3

A. AROCLOR 1254
B. TRI(2-ETHYLHEXYL)BORATE
C. TRI-m,p-CRESYL BORATE
D. TETRA(2-ETHYL-1-HEXYL) SILICATE
E. n-AMYL-TRIPHENYL SILICATE
F. DOW-CORNING FLUID 550
G. DOW-CORNING FLUID 710
H. TRI-NONYL PHOSPHATE
I. TRI-TOLYL PHOSPHATE
J. DI-p-TOLYL-1-NAPHTHYL PHOSPHATE
K. DI-NONYL PHOSPHITE
L. DI-ISOOCTYL BENZENEPHOSPHONATE
M. SPECIFICATION

III. PHYSICAL TESTING

Thermal Stability.

The thermal stability of a compound is defined as the resistance of the compound to chemical change brought about solely by thermal energy. The thermal instability of a compound may, therefore, be expressed by its rate of chemical change at a particular temperature in the absence of catalysts or other reactive substances.

Since the determination of rates of chemical change is unsuitable for the rapid testing of many compounds, less precise criteria were set up for screening purposes. The weight loss of a compound after heating for a definite time at a chosen temperature was selected for this empirical test, because most thermal degradations involve elimination of one or more volatile fragments. The changes in the 100°F and 210°F viscosities brought about by heating were used to indicate thermal degradations not involving weight loss. Finally, infrared analyses of the decomposition products were made where indicated.

Experimental. The thermal stability tests are run in glass apparatus under a blanket of nitrogen with heating periods of 10 hrs at temperatures of 545°F (refluxing glycerine) and, if indicated, at 690°F (refluxing Aroclor 1254). At 545°F glycerine undergoes slow decomposition.

The arrangement of apparatus is shown schematically in Fig 4 and in the photograph Fig 5. The inset in Fig 5 shows the sample tube with a small receiving flask attached. The principal components and suppliers are listed in Appendix I.

The experimental procedure is as follows:

1) Weigh the empty sample tube to ± 0.001 g (wt ca 100 g) on an analytical balance.

2) Fill lower bulb of sample tube 1/2-full and re-weigh (net wt 10-25 g).

3) Assemble apparatus using Apiezon "T" grease on the standard taper and ball joints.

4) Evacuate space above sample and above reflux fluid contained in the 500 cc flask.

5) Admit N_2 into entire system and adjust flow rate for slow bubbling through mercury in "N_2-Bubbler" (Fig 4) to maintain about 10 mm positive pressure in the system.

Table 25

THERMAL STABILITY TESTS

Compound	Source(1)	MP °C(2)	BP°C	Weight Percent Loss at 545°F	Weight Percent Loss at 690°F
n-Octacosane	a	59-61	412.5	0.2	4.3
Polybutene	b	L	-	9.3	-
Amylbiphenyl	a	L	155-165 at 7 mm	0.3	distills below
1,2-Bis(2-biphenylyloxy)ethane	a	100-102	-	0.01	59.2
4,4'-Bis(2-ethylhexoxy)-x,x,x,x-tetrachlorobiphenyl	c	L	255-265 at 0.2 mm	0.4	44
Aroclor 1254	c	8-12 (pour)	367	-	0.04
Polyglycol P-2000 (polypropylene glycol)	f	-38°F (pour)	-	9.4	-
Ucon Lubricant 50-HB-280-X	d	-20°F	-	1.3	43 (1/2 hr.)
Ucon Lubricant LB-285	d	L	-	3.6	-
4-Acetyl-o-terphenyl	a	92-94	-	-	3.8
Tri-n-amyl orthoformate	a	-	152-155 at 8 mm	55(5)	-
Di-p-tolyl carbonate	a	109-111	-	0.4	53(4)
Dioctyl sebacate	j	L	-	2.3	31.3 (1 hr)
Di-2-ethylhexyl phthalate	c	L	-	4.2 6.8	50 (1/2 hr)
Dibenzyl phthalate	a	42-44	-	0.8	42.5 (1 hr)
Diphenyl phthalate	a	73-75	-	2.1	51.5
Phenyl stearate	a	50-52	-	2.0	36.7
Pentaerythritol tetrabenzoate	c	S	-	-	3.4(3)
2-Butyl-2-ethylpropanediol 1,3-laurate and pelargonate (mixture)	c	L	-	-	26 (1 hr)
Benzoflex 2-45 Lot E3-13	i	L	-	1.5	39

Table 25 (Cont'd)

Compound	Source(1)	MP °C(2)	BP°C	Weight Percent Loss at 545°F	Weight Percent Loss at 690°F
Tris(2-ethyl-2-butylpropanediol-1,3) diborate	c	L	-		26.0
2,2'-(2-Ethylhexanamido)-diethyl di-2-ethylhexoate	d	L	-	53	-
Tri-m,*p*-cresyl borate	g	L	-	0.8	4.2
Tri-*n*-dodecyl borate	g	L	-	0.3	3.1 2.8
Tri(2-ethylhexyl) borate	g	L	-	1.8	4.8
Trihexylene glycol diborate	k	L	-	12.9	-
Tetra-2-ethylhexyl titanate	l	L	-	0.8	84
Triisooctyl phosphite	h	L	-	70 (3 hrs)	-
Tri-*p*-tolyl phosphite	k	L	-	0.05	0.33
Tri-2-ethylhexyl phosphate	d	L	-	ca. 100	-
Tricresyl phosphate	c	L	-	0.3	0.5
Bis(2-ethylhexyl) 2-ethylhexylphosphonate	h	L	-	57 (1/2 hr)	-
Tri-*p*-tolyl thiophosphate	a	90-92	-	0.2	37.5
Tetra-2-ethylhexyl silicate	c	L	-	1.5	9.2
Dow-Corning 710 Fluid (methyl phenyl silicone?)	e	-10°F	-	0.2	0.2
Tris(*n*-octyl)silicon fluoride	c	L	195-200 at 1 mm	0.3	6.9
Tris(octadecyl)silicon fluoride	c	S	345-370 at 2 mm	0.2	2.5
Triphenylsilicon fluoride	c	S	182-184 at 5 mm	0.1	0.9
N,*N*-Dimethyloctadecylamine	a	S	-	1.0	11.7
Tribenzylamine	c	92-93	-	-	36 (1/2 hr)
N,*N*'-Di-2-naphthyl-*p*-phenylenediamine	a	227-230	-	0.3	2.0

Table 25 (Cont'd)

Compound	Source(1)	MP °C(2)	BP°C	Weight Percent Loss at 545°F	Weight Percent Loss at 690°F
p,p'-Methylenebis(N,N-dimethyl aniline)	a	89-90	-	0.1	12.6
N,N,N',N'-Tetraethyl phthalamide	a	37-39.5	-	2.2	6.5 (1 1/2 hr)

---

(1) Source of samples: (a) Eastman Kodak Co., (b) Oronite Chem. Co., (c) Monsanto Chem. Co., (d) Carbide and Carbon Chem. Co., (e) Dow-Corning Corp., (f) Dow Chem. Co., (g) American Potash and Chem. Corp., (h) Victor Chem. Co., (i) Tennessee Products and Chem. Corp., (j) Pittsburgh Coke and Chem. Co., (k) Pacific Coast Borax Co., (l) Titanium Pigment Oorp.

(2) The symbols S and L indicate the physical state, solid or liquid, at room temperature.

(3) The change in appearance of this sample suggests considerable decomposition into non-volatile decomposition products.

(4) This compound distilled over as shown by comparison of X-ray diffraction patterns of starting material, distillate, and residue; however, the moist appearance of both distillate and residue indicates considerable decomposition.

(5) Test stopped when temperature reached 455°F.

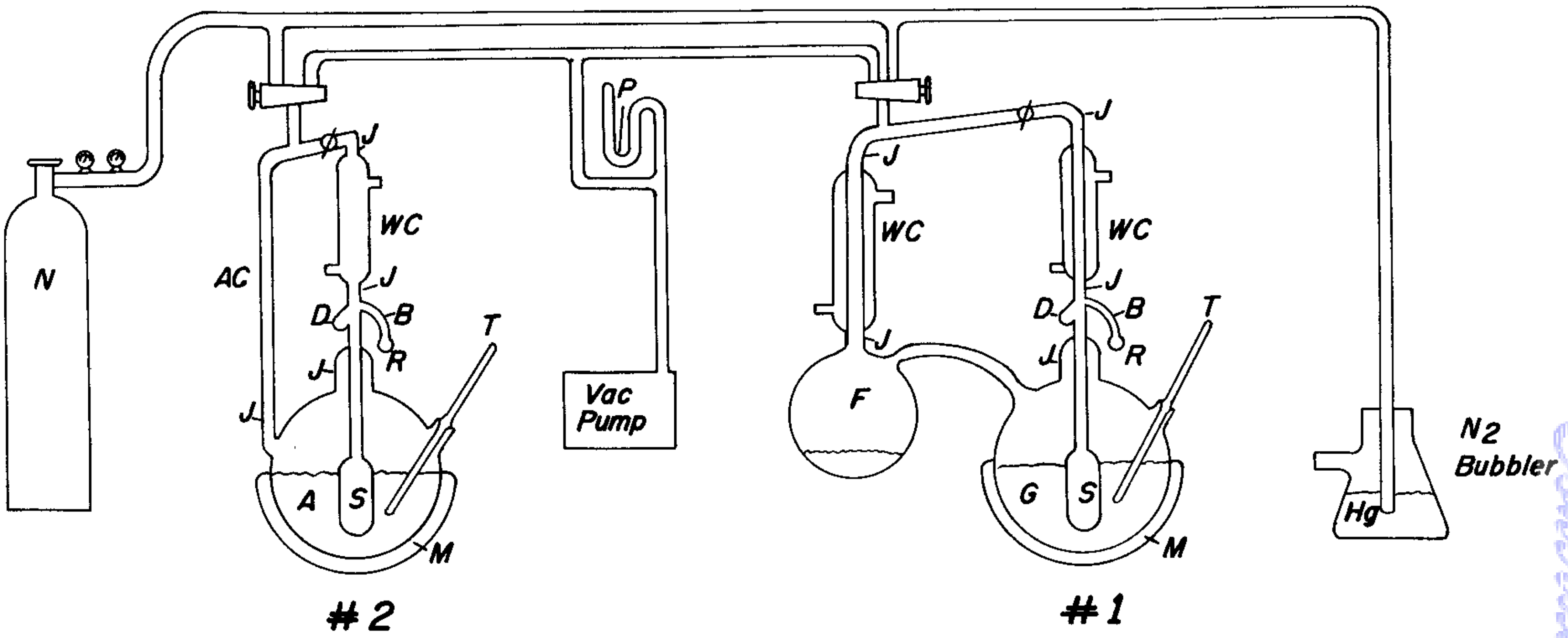


Fig. 4 "THERMAL STABILITY APPARATUS"

Legend:

A- Aroclor 1254 fluid
AC-Air Condenser
B- Ball Joint
D- Drain Shoulder
F- Receiver for glycerine decomposition products
G- Glycerine
Hg- Mercury
J- Standard taper joints
M- Heating Mantle
N- Nitrogen Tank
P- Manometer
R- Receiver Flask
SC1-Oneway Stopcock; SC 2-Two way Stopcock
S- Sample
T- Thermometer

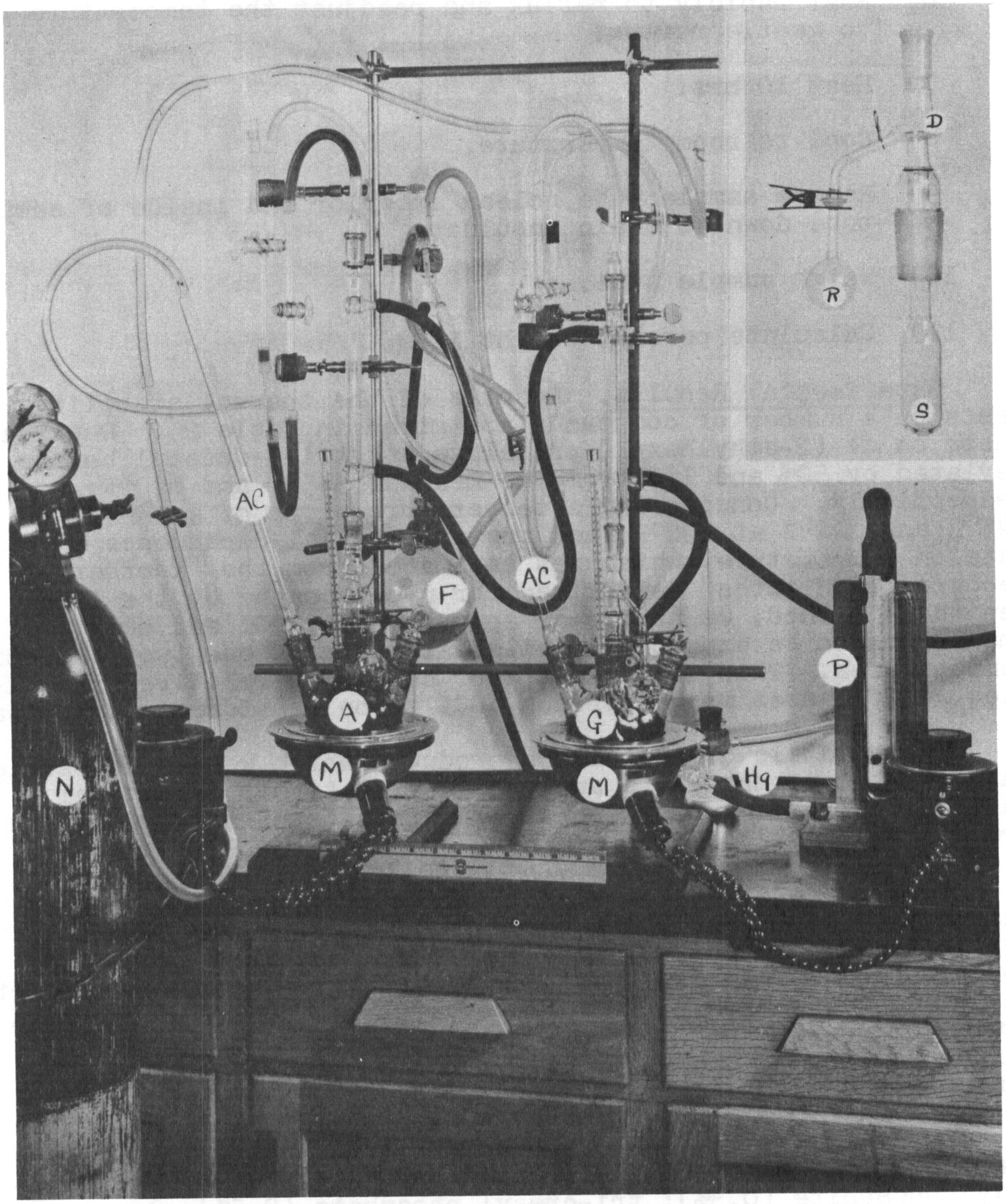


Fig. 5 THERMAL-STABILITY APPARATUS

6) Heat rapidly to reflux and readjust the temperature to gentle reflux.

7) Heat 10 hrs.

8) Cool to room temperature.

9) Remove sample tube, clean exterior and inside of sample tube down to drain shoulder.

10) Weigh sample tube.

11) Calculate percent weight loss.

Experimental Results. Results of the thermal stability tests on a number of compounds are given in Table 25. Duplicate tests on di-(2-ethylhexyl) phthalate and tri-n-dodecyl borate deviated by 50% and 10% from the mean at 545°F and 690°F, respectively. Considering a temperature error of ± 3°F at 545°F and ± 2°F at 690°F, and the exponential dependence of rate on temperature, which was estimated from the "isothermal decomposition rates" determined for n-octacosane by the isoteniscope method, we arrive at approximately 90% and 60% for the errors to be expected in single tests at these two respective temperatures. This means that, for comparing relative stabilities, differences must approach 100% to be considered significant.

The volatile decomposition products which were condensible in a water condenser were analyzed qualitatively in several cases by infrared spectroscopy. The results of these analyses are given in Table 26.

Infrared analyses of some of the starting materials were also made. Weak absorption bands for P=O bonds were found in tri(isooctyl) phosphite. This indicates that this sample was not a pure material and these impurities may have played a part in its decomposition. The infrared spectrum of Dow-Corning Fluid 710 showed that it contains aliphatic and aromatic C-H; strong absorption bands for Si-O-C bonds were observed and bands were present for $Si-CH_3$ and/or $Si-C_6H_5$.

Discussion. Five substances were found which lose less than 1% of their weight in 10 hrs at 690°F. These are: tri-p-tolyl phosphite (0.3%); tri-cresyl phosphate (0.5%); Dow-Corning 710 Fluid (0.2%); triphenylsilicon fluoride (0.9%) and Aroclor 1254 (0.04%). Configurations contained in these molecules which may, therefore, be considered thermally stable are phenyl, tolyl, methyl, phenyl-O-Si, phenyl-O-P, phenyl-Si and CH_3Si.

Nine compounds were found which undergo weight loss to the extent of 2-13% at 690°F. These are n-octacosane (4.3%); tri-n-dodecyl borate (3.1%); tetra-2-ethylhexyl orthosilicate (9.2%);

Table 26

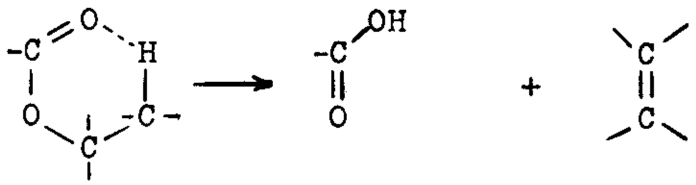
INFRARED ANALYSES OF DISTILLED DECOMPOSITION PRODUCTS

Compound	Temp °F	Results
n-Octacosane	690	$-CH{=}CH_2$ predominant; plus *cis* and *trans* $-CH{=}CH-$
Dioctyl sebacate	690	$>C{=}CH_2$ predominant; plus $-CH{=}CH_2$, and $-COO$ (acid and/or ester)
Di-2-ethylhexyl phthalate	690	$>C{=}CH_2$
Tri-*n*-dodecyl borate	690	$-CH{=}CH_2$ and $-CH_2-OH$ predominant; plus weak carbonyl and $-CH{=}CH-$ (*trans*)
Triisooctyl phosphite	545	$-CH{=}CH_2$, branched hydrocarbon
Tri-*p*-tolyl thiophosphate	690	Toluene
Tetra-2-ethylhexyl silicate	545	Aliphatic primary alcohol plus weak $-CH{=}CH-$ (*trans*)
Tetra-2-ethylhexyl silicate	690	Hydrocarbon(s) containing $-CH{=}CH-$ and $>C{=}CH_2$, not conjugated; weak hydroxyl and carbonyl (ester or aldehyde).
Tri-*n*-octylsilicon fluoride	690	$-CH{=}CH_2$ and $-CH{=}CH-$ (*trans*)
Tri octadecyl silicon fluoride	690	$-CH{=}CH_2$ and $-CH{=}CH-$ (*trans*); weak carbonyl absorption.

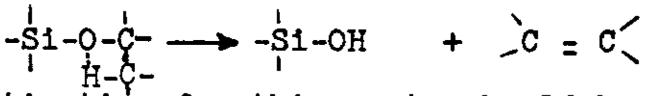
tri-n-octylsilicon fluoride (6.9%); trioctadecylsilicon fluoride (7.5%); N,N-dimethyloctadecylamine (11.7%); N,N'-di-2-naphthyl-p-phenylenediamine (2.0%); p,p'-methylenebis-(N,N-dimethylaniline) (12.6%); and 4-acetyl-o-terphenyl (3.8%). Since the first six compounds contain between 8 and 28 carbon atoms in the hydrocarbon chain, it is not unreasonable to expect the same degradation mechanism to be operating on the hydrocarbon portion of these compounds as prevails in the case of n-octacosane. It may be inferred from the isoteniscope studies on n-octacosane (see section on vapor pressure measurement) that decomposition in the range 2-13% will cause a pressure development in 10 hrs at 700°F in excess of the 600 mm limit imposed by the specifications. Further study of the reactions involved might lead to the development of suitable inhibitors in case the reaction proceeds by a chain mechanism rather than a thermal decomposition mechanism.

It will be noted that generally alkyl esters of acids containing double-bonded oxygen decompose extensively. The alkyl phosphates and phosphonates decompose at 545°F, and the carboxylic esters, which are somewhat more stable at 545°F, decompose rapidly at 690°F. The aryl esters of phosphoric acid are much more stable than the alkyl esters.

These results are consistent with the ideas on the mechanisms of thermal decompositions discussed in the section on the literature survey. The quasi six-membered ring



provides a facile route for the decomposition of esters containing a doubly-bonded oxygen and a β-hydrogen atom on the alcohol moiety. This is in accordance with the observation that dioctyl sebacate and tri-2-ethylhexyl phosphate decomposed rapidly at 545°F. Tricresyl phosphate, which has the β-hydrogen atoms on an aromatic ring, decomposes only slightly at 690°F; the lower stability of phenyl stearate may be due to the susceptibility of the acid moiety to free radical attack. Esters having no doubly-bonded oxygen, such as silicates and borates, cannot decompose via a six-membered ring, and the most likely route for decomposition which requires less energy than simple bond dissociation is one analogous to "route b" discussed under ethers.



$$-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{H-C-}}{\overset{|}{\mathrm{C}}}- \longrightarrow -\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{OH} \quad + \quad \rangle\mathrm{C}=\mathrm{C}\langle$$

The energy of activation for this route should be greater than for a quasi six-membered ring, because a six-membered ring involves less strain than a four, and a hydrogen bond to a carbonyl group should be stronger than one to an ether oxygen. It follows then that alkyl silicates and borates should be more stable than the corresponding carboxylates and phosphates, a conclusion which agrees with the data.

Conclusions. A satisfactory test has been devised for screening hydraulic fluid base stock compounds for thermal stability. A number of compounds were tested with results as given above. Tentative conclusions regarding several classes of compounds are given in the above discussion.

Vapor Pressure Measurement

Apparatus has been set-up for direct measurement of the equilibrium vapor pressure of base stock materials. The isoteniscope method of A. Smith and A. W. C. Menzies was adopted for this work (235). This method is accurate and applicable over a wide pressure range. It is useful to detect the threshold temperature at which base stock materials begin to decompose and is thus superior to dynamic methods for our purposes (8).

Experimental. The isoteniscope consists of a bulb joined to a manometric U-tube. Both bulb and U-tube contain the liquid under investigation and the assembly is either immersed in a constant temperature bath or in a furnace having low thermal gradients. The second arm of the U-tube connects to an external system for 1) producing and measuring high vacuum and 2) admitting and measuring the pressure of an inert gas which is admitted for balancing pressure on the two arms of the U-tube, the pressure measured being equal to the equilibrium vapor pressure of the substance in the sample bulb.

The apparatus is shown schematically in Fig 6. To the right in this figure is a full scale sectional drawing of the isoteniscope bulb (B) and U-tube (M-1). The indentation in the bulb is for the hot junction of the calibrated chromel-alumel thermocouple used for temperature measurement. The U-tube (M-2) is a mercury reservoir provided for ease in producing a "Torricellian" vacuum on the closed side of the large manometer (M-3). Briefly, M-3 is set-up with M-2 empty, SC-2 open, the meter bar removed, and the system evacuated to about 10^{-6} mm Hg. The mercury is flamed to drive out dissolved and adsorbed gas. Then SC-2 is closed and air is admitted to the system to force sufficient mercury up the right arm of M-3 to half-fill M-2. When the mercury is lowered in M-3, a vacuum is left between M-2 and M-3 which is quite permanent but which can be easily renewed if the system becomes contaminated and needs to be reflamed.

A photographic view of this experimental set-up is shown in Fig 7 in which some auxiliary apparatus may also be seen.

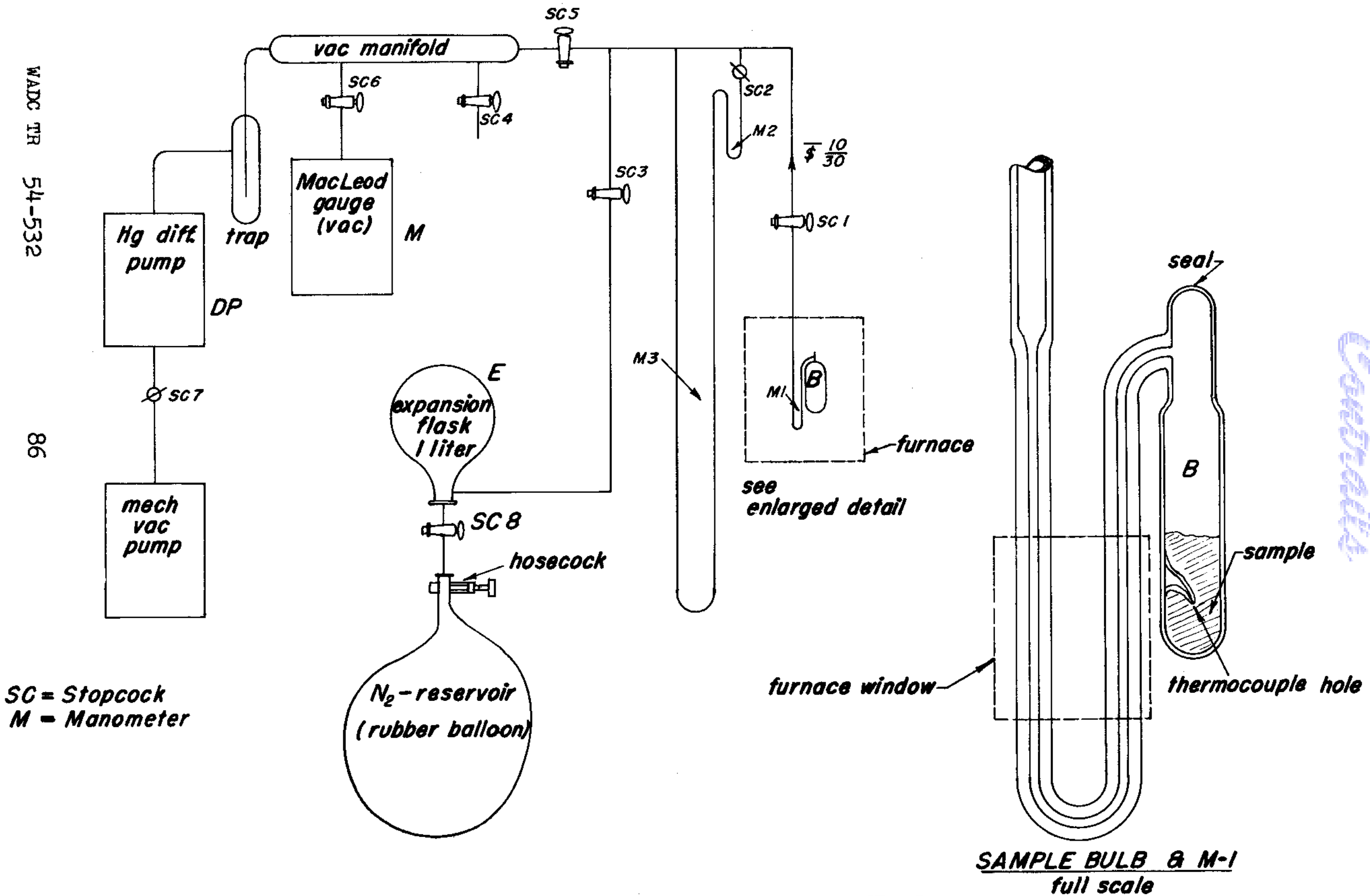


Fig. 6 VAPOR PRESSURE APPARATUS

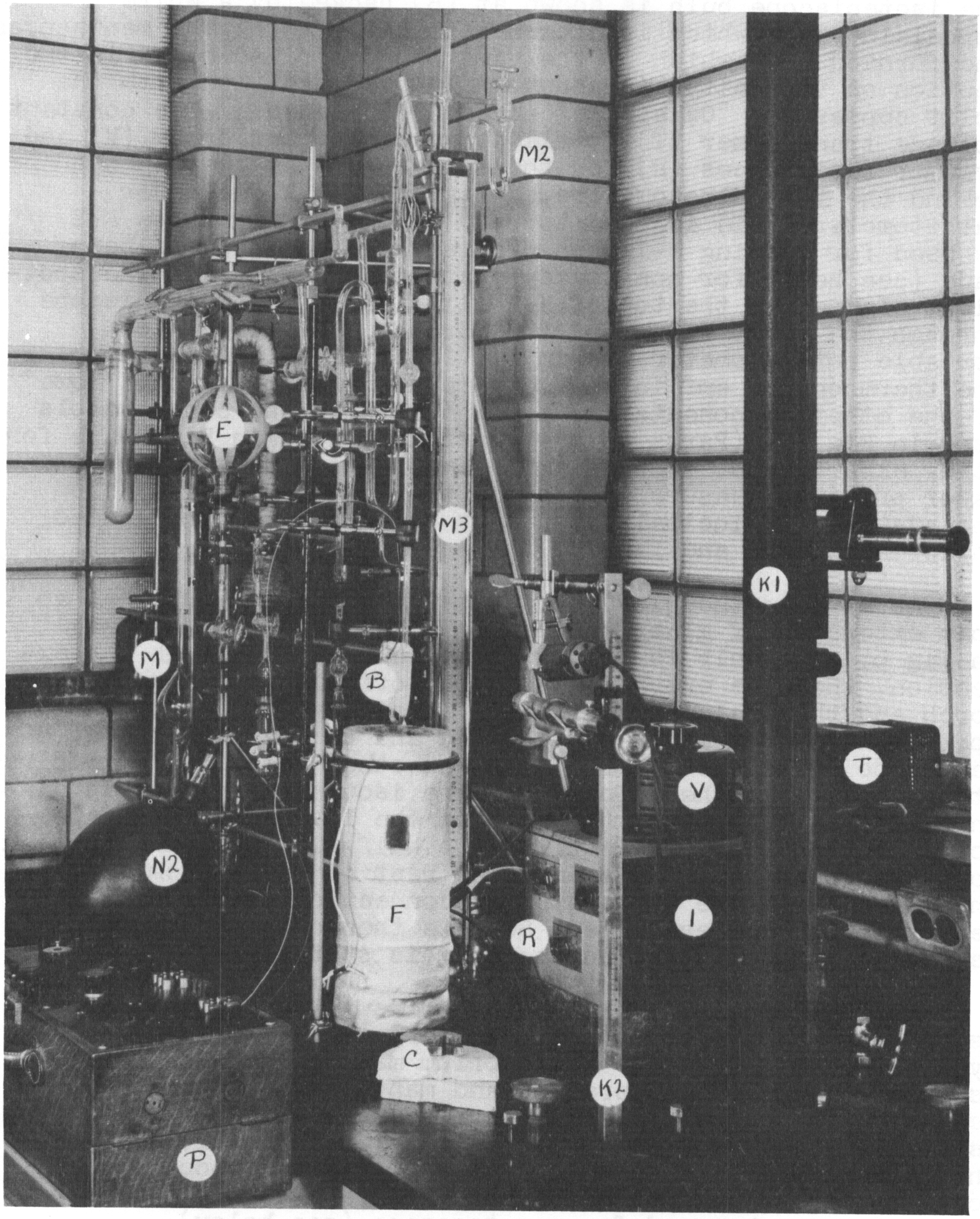


Fig. 7 VAPOR PRESSURE APPARATUS

The isoteniscope bulb is shown at (B) backed by a white porcelain plate which is attached to aid viewing the meniscuses. The furnace (F), which is the same one described below in the section on viscosity, is shown in lowered position with the split copper and "Calsilite" covers (C) removed. The constant voltage transformer (T), variable voltage transformer (V) and trimmer resistances (R) for the furnace are at the right behind the two cathetometers, K-1 and K-2. A one-meter cathetometer (K-1) is used to read manometer (M-3) and K-2 is used for reading M-1 when precise measurements are being made (see below for non-steady-state measurements). The spotlight clamped to the top of K-2 illuminates the isoteniscope through the sight window of the furnace. The precision portable potentiometer (P) in the lower left is for measuring the thermocouple emf in the temperature determination. Some of the other components are designated with the same symbols used in Fig 6. (Parts of the glass apparatus in Fig 7 are for other experiments. These extra components do not affect the vapor pressure measurements since they can be isolated from the system). Principal components and suppliers are listed in Appendixes II and IV.

As made in the glass shop, the isoteniscope tube has an open extension of glass tubing above the point marked "seal" in Fig 6. The bulb is filled about half-full through the extension, then the extra glass is cut off with a glass-blowing torch and the seal is completed. This leaves the U-tube (M-1) open. The system is then evacuated and the sample is heated gently to drive off absorbed gas and other volatile impurities. Stopcock SC-1 is then closed and the isoteniscope tube is disengaged from the system (by parting the 10/30 standard taper joint above SC-1). It is tilted to half-fill M-1, and is then connected back to the system. The rest of the system down to the hosecock on the rubber tubing connection to the nitrogen reservoir is then evacuated, SC-5 is then closed, the furnace is raised into position and heating is started.

As the temperature rises the pressure in the sample bulb is balanced by admitting nitrogen very slowly with the screw-type hosecock. For true equilibrium measurements the furnace is held at a fixed temperature and manometers M-1 and M-3 are read with the cathetometers. At a temperature where a compound is stable the manometer levels should remain stationary when the temperature is constant; however, if the compound decomposes the pressure should steadily change. Both patterns of behavior were observed for n-octacosane (see below).

As a means for studying thermal stability, pressure readings can be made as the temperature is steadily rising with the power applied to the furnace being sufficient to take it from room temperature to above 700°F in about four hrs. So long as the compound is stable the curve of log p vs. 1/T (where p = vapor pressure and T = absolute temperature) should be very nearly a straight line; however, if the substance begins to undergo a chemical change the curve should pull away from the straight line. The point of departure (point of tangency) may be defined as the "decomposition point".

Experimental Results and Discussion. The vapor pressure of n-octacosane (Eastman) was measured under both equilibrium and non-steady-state temperature conditions. The results are shown graphically in Fig 8, along with smoothed literature values, for comparison (246).

The "decomposition point" is seen to be about 571°K (≡ 569°F). This is consistent with the thermal stability tests in which very little weight loss occurred at 545°F (0.21%) but considerably more at 690°F (4.3%).

Under equilibrium temperature conditions only three data points were obtained below the decomposition point and one of these, at the lowest temperature, appears to be a "sport", i.e., inconsistent with the other data and subject to some accidental error. The straight line between the two remaining points gives 413°C for the normal boiling point which agrees surprisingly well with Stull's value of 412.5°C (246). The straight line part of the curve for the non-steady-state measurements also extrapolates to give about 412° for the boiling point. Lack of agreement of the vapor pressures with Stull's data at low temperature may be due to impurities in the sample.

In making the pressure measurements at steady-state temperatures above the decomposition point the pressure change was followed over a period of time in several instances. This gave the several series of points falling on a vertical straight line. Isothermal rates of pressure increase were calculated, with results given in Table 27.

Table 27

ISOTHERMAL RATE OF PRESSURE CHANGE OF n-OCTACOSANE

T°K	10^3/T°K	$\frac{dp}{dt}\left(\frac{mm}{sec}\right)$
593	1.688	0.0012
609	1.641	0.0067
639	1.565	0.080
644(≡700°F)	1.554	(0.120, interpolated from graph)
655	1.527	0.329

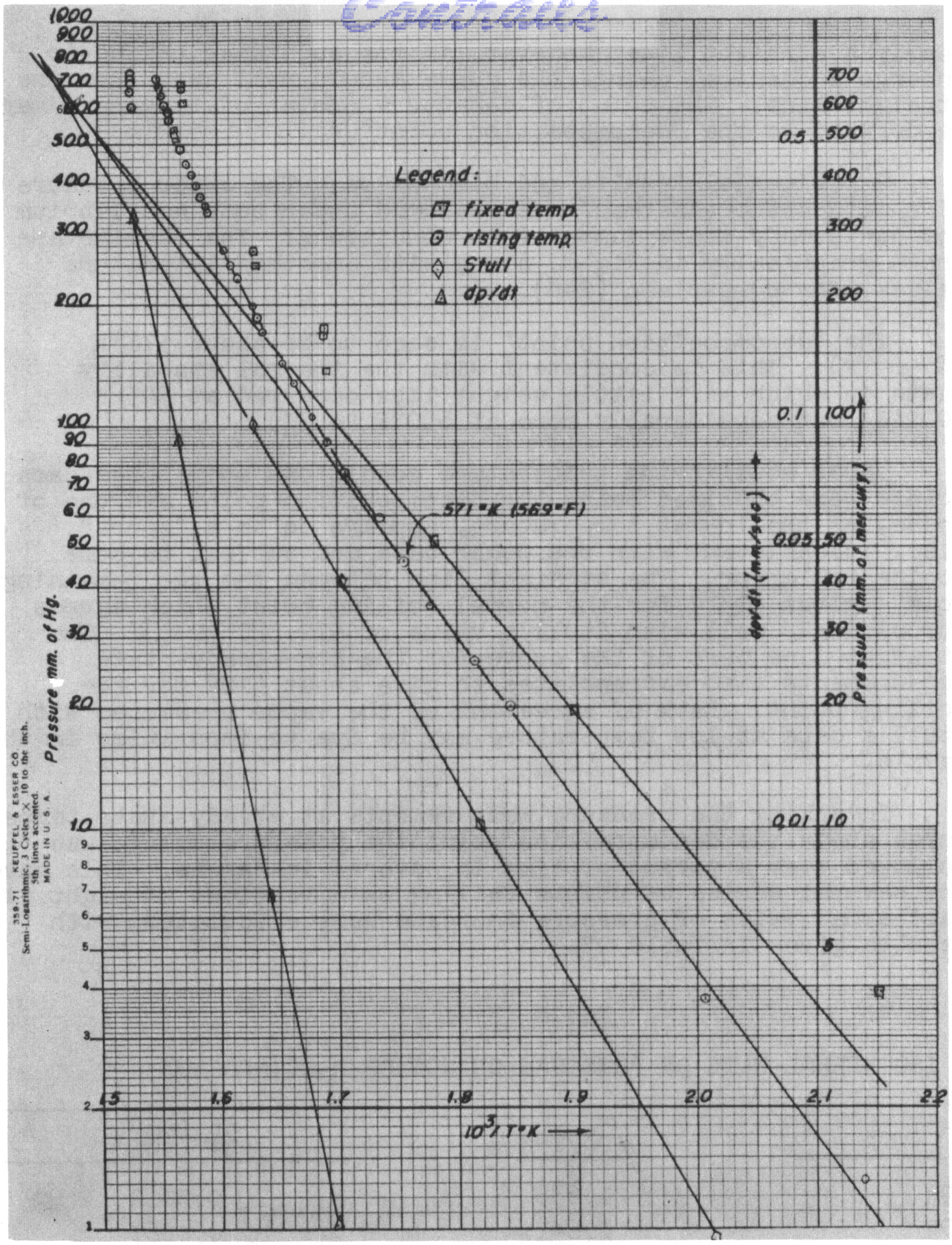


Fig. 8 VAPOR PRESSURE OF n-OCTACOSANE

A plot of these rates in Fig 8 as log dp/dt vs. $10^3/T^\circ K$ gave a straight line from which the rate at 700°F (=644°K) was found to be 0.120 mm/sec, a rate which, if sustained for 10 hrs in this system, would develop a pressure of about 4320 mm or 5.7 atm.

Conclusions. The isoteniscope method as set-up appears to be satisfactory for determining vapor pressure, detecting decomposition and measuring the rate of decomposition.

The rate of pressure increase for n-octacosane at 700°F is sufficient to cause the vapor pressure to exceed 600 mm in a brief period of heating. It is also expected that the compounds in Table 25 that decomposed to the extent of about 1% or more in 10 hrs at 690°F would develop excessive vapor pressures at 700°F, just as n-octacosane does.

Kinematic Viscosity Measurements

Apparatus has been set up for kinematic viscosity measurements at 100°F, 210°F and the range 210° to 700°F. Standardized procedures for ordinary temperatures have been given in detail in ASTM Method D445-53T entitled "Tentative Method of Test for Kinematic Viscosity". The detailed procedure described in Appendix A of this ASTM method for Cannon-Fenske viscometers was adopted for measurements at 100° and 210°F, and constant temperature baths were assembled for these two temperatures. These baths meet the ASTM requirement of temperature fluctuations of less than ± 0.02°F. The photograph of these baths, given in Fig 9, and the parts list in Appendixes III and IV should provide sufficient description of this apparatus.

For measurements above 210°F a special furnace was constructed; it is shown in the sectional drawing in Fig 10 and which was pictured as "F" in Fig 7. The furnace is constructed of a 2-1/2 in. diameter copper tube with 1/4 in. wall thickness covered with a layer of asbestos paper. This asbestos-covered tube is wound with nichrome wire with windings spaced 1/8 to 1/4 in., the closer spacing being used near the ends and at the level of the 1-1/2 x 1 in. window. The insulated machine screws by each side of the window hold the wire which is wound back and forth around the tube at the level of, but not crossing, the window. Alundum cement is used to hold the winding in place. "Unibestos" pipe insulation is used to insulate the sides and "Calsilite" mineral insulation is used at top and bottom. Several taps in the winding allow external trimmer resistances to be placed parallel to sections of the winding for adjusting power to the several sections so that thermal gradients can be reduced. It was found that the settings of the variable trimmer resistances were not very critical. The external electrical circuit is shown schematically in Fig 10.

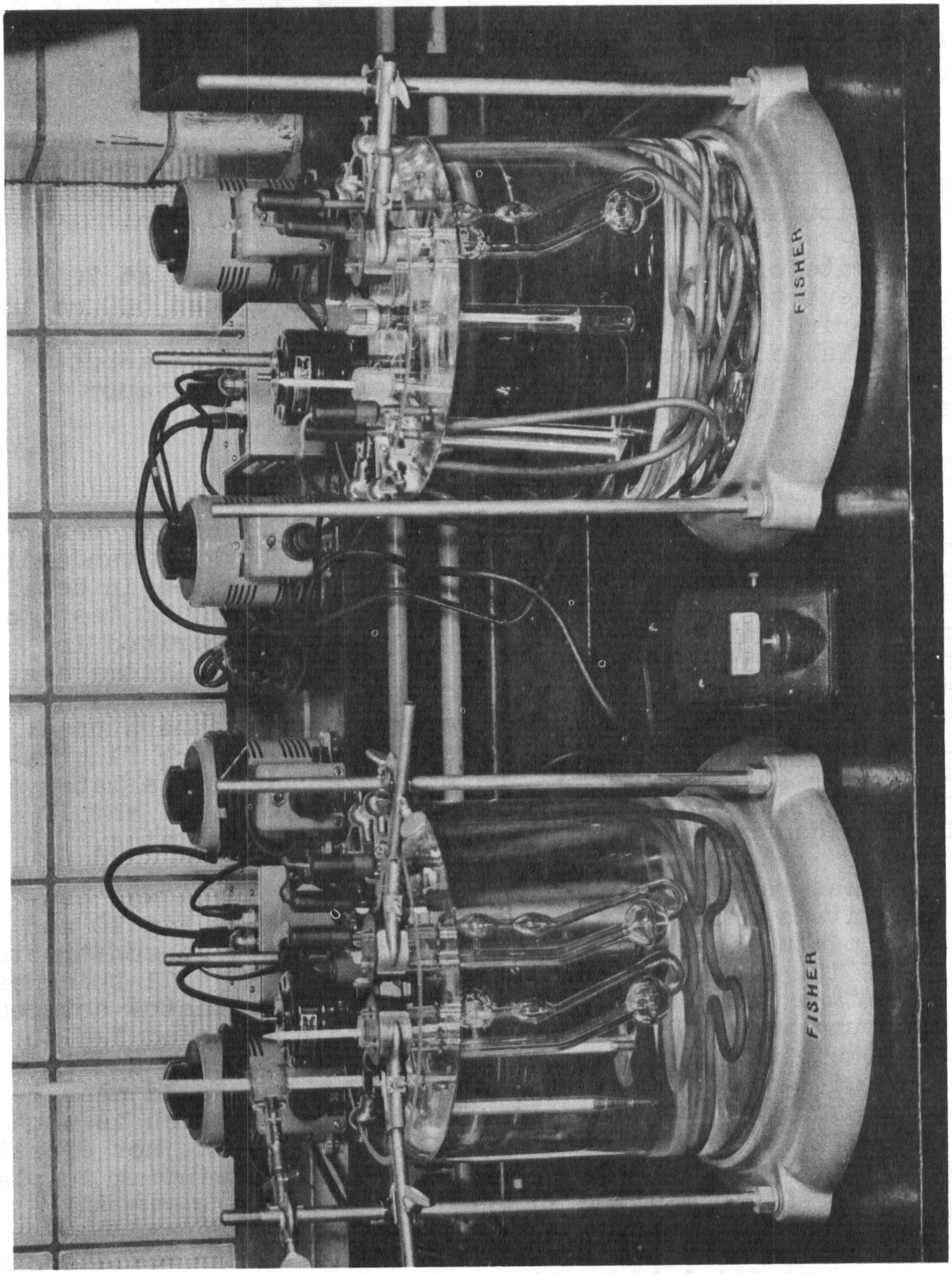


Fig. 9 VISCOSITY APPARATUS

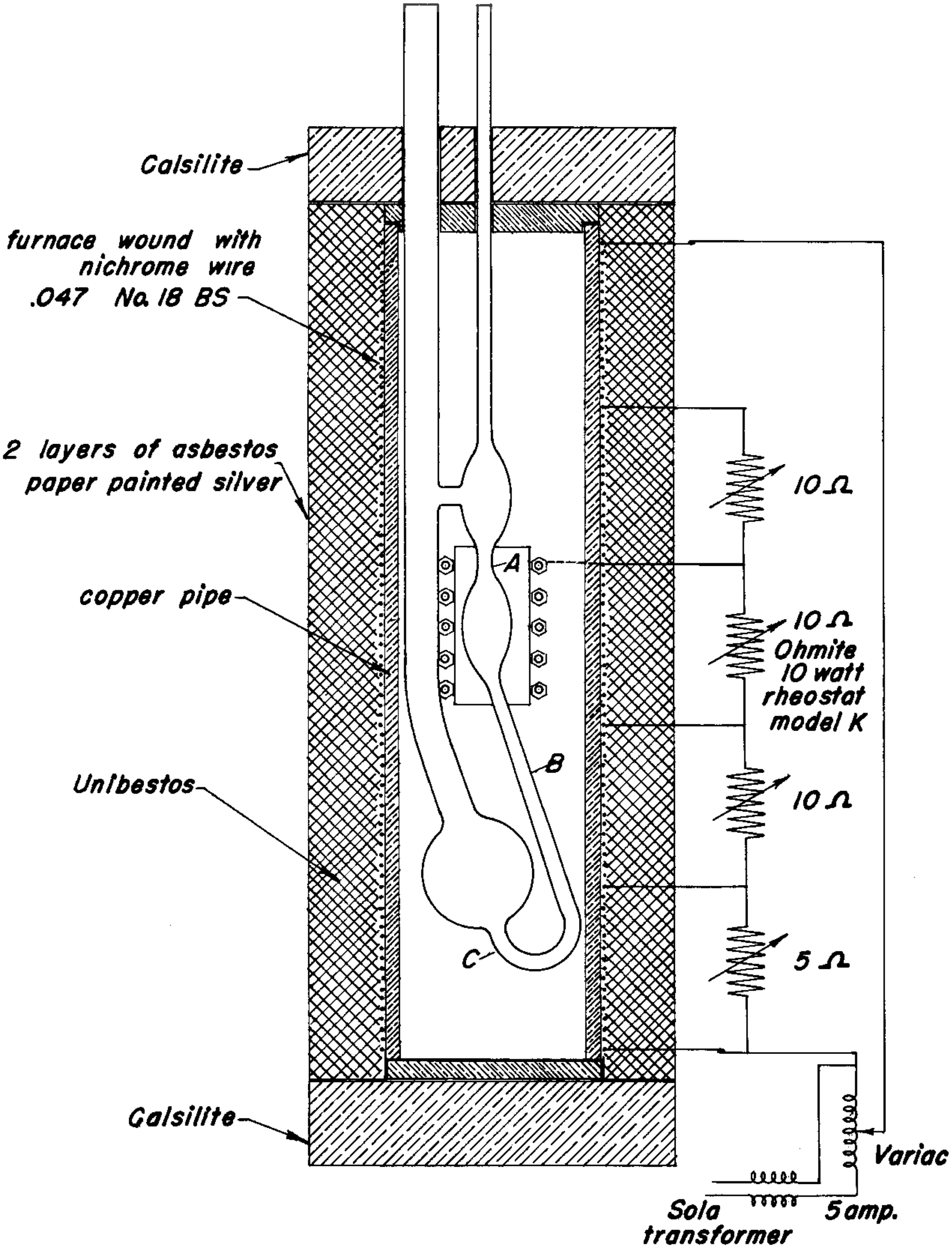


Fig. 10 HIGH TEMPERATURE FURNACE

scale : half size

The viscometer used in the high temperature measurements was modified by adding a 3-in. extension to the filling tubes of a Cannon-Fenske viscometer. This viscometer was then recalibrated at 100°F and 210°F according to procedures given in ASTM D445-53T. The calibration constant at higher temperatures was obtained by extrapolation from these two points.

Temperature is determined with thermocouples placed at three points on the viscometer (A, B and C in Fig 10). The three thermocouples are used in order to check against excessive thermal gradients. At 693°F the thermocouples at A and C had a difference in emf corresponding to a temperature spread of 1.5°F. This represents an error of about 0.3% of the viscosity in the range 500°-700°F which is considered a sufficient accuracy for these measurements.

Experimental Results. The results of the viscosity measurements are given in tables and figures in the literature survey sections as follows:

Compound	Temp °F	Table	Figure
Aroclor 1254	100-618	23	3
Tri(2-ethyl-1-hexyl) borate	100-212	19	3
Tri-m,p-cresyl borate	100-212	19	3
Tetra-2-ethyl-1-hexyl silicate	100-212	21	3
after 10 hr at 690°F	100-212	21	-
Dow-Corning Fluid 710	100-692	23	3
after 10 hr at 545°F	100-212	23	-
after 10 hr at 690°F	100-212	23	-

The viscosities of Aroclor 1254 and Dow-Corning Fluid 710 were determined at five temperatures between 350° and 700°F to demonstrate the operability of the described technique for high-temperature viscosity measurements. The data are plotted in Fig 3 and data reported in Table 23 were read from this curve. It is of interest that the ASTM curve for Aroclor 1254 is linear above 450°F in contrast to the concave downward curve of Dow-Corning Fluid. The high-temperature behavior of the Dow-Corning Fluid is typical of that shown by hydrocarbons, esters, ethers, silicones and silicates (184).

Conclusion. The procedure described for viscosity measurements above 210° and up to 700°F is considered practical and satisfactory.

IV. RECOMMENDATIONS

It is recommended that:

(1) Organic and inorganic esters be prepared in which thermal decomposition by the elimination of an olefin is inhibited by molecular structure. Esters of tertiaryalkylcarbinols and 2,2-difluoro alcohols are two possibilities.

(2) Several n-alkyl-p-terphenyls be prepared in which the length of the alkyl group is varied systematically. The thermal stability of these compounds should be determined to obtain information on variation of thermal stability with chain length. This information is essential for the design of other molecules in which a long chain is incorporated.

(3) Some carefully chosen examples of phosphates, phosphites and phosphonates be prepared with the view to improvement in thermal stability, viscosity and hydrolytic stability.

(4) Modifications be made in aryl silicates and borates directed toward improvements in viscosity and hydrolytic stability.

(5) Modifications be made in diaryl ethers to improve their viscosity properties.

(6) Further thermal data be obtained on phenol esters of aromatic and carbonic acids.

(7) Alicyclic compounds and alkylated aromatic compounds designed to have the optimum balance between thermal and viscosity properties be prepared and evaluated.

In the arrangement of these recommendations, consideration was given to priority in the numbering.

V. BIBLIOGRAPHY

(1) Alexander, E. R., and Mudrak, A., J. Am. Chem. Soc., 72, 1810, 3194 (1950).

(2) Allen, P. Jr., J. Org. Chem., 7, 23 (1942).

(3) Anscheitz, R., and Wirtz, Q., Ber., 18, 1947 (1885).

(4) Appeldorn, J. H., and Matuszak, A. H., Synthetic Lubricants 2nd Quarterly Report, A.T.I. 94277, Jan. 12, 1951.

(5) Arbuzov, B. A., and Vinogradova, V. S., CA, 47, 10458 (1953).

(6) Arnold, R. T., Smith, G. G., and Dodson, R. M., J. Org. Chem., 15, 1256 (1950).

(7) Atkins, D. C., Murphy, C. M., and Saunders, C. E., Ind. Eng. Chem., 39, 1395 (1947).

(8) Ballentine, O. M., Private Communication, WADC, Dayton, Ohio.

(8a) Baker, H. R., Jones, D. T. and Zisman, W. A., Ing. Eng. Chem., 41, 137 (1949).

(8b) Baker, H. R. and Zisman, W. A., Ing. Eng. Chem., 40, 2338 (1948).

(9) Bamberger, E., Ber., 19, 1818 (1896).

(10) Banchero, J. T., U. of Mich. Microfilm Pub. No. 1682.

(11) Barton, D.H.R., J. Chem. Soc., 1949, 2174.

(12) Bass, S. L., and Van Duzee, E. M., U. S. Patent 2,109,458.

(13) Bauly, J. R., and Mahan, R., U. S. Patent 2,237,541.

(14) Behaghel, O., and Freiensehuer, H., Ber., 67B, 1368 (1934).

(15) Beilsteins Handbuch der Organischen Chemie, 4th Edition, Julius Springer, Berlin, (1934). Vol. VI, p. 147.

(15a) Ibid., I, 379, 406.

(16) Ibid., VI, 183.

(17) Ibid., VI, 300.

(18) Ibid., VI, 370.

(19) Ibid., VI, 419.

(20) Ibid., VI, 455.

(21) Ibid., VI, 607.

(22) Ibid., VI, 642.

(23) Ibid., XII (2), 99.

(24) Ibid., XII (1), 166.

(25) Ibid., XII, 1277.

(26) Bejk-Guldenwerke Chem. Fab. A. G., CA, 32, 7678 (1938).

(27) Benkeser, R. A., and Riel, F. J., CA, 46, 5539 (1952).

(28) Benz, G., Ber., 16, 14 (1883).

(29) Bergmann, E., CA, 33, 4225 (1939).

(30) Bingham, E. C., Klooster, H. S., and Kleinspehn, J. Phys. Chem., 24, 1 (1919).

(31) Bingham, E. C., and Larver, L. A., J. Am. Chem. Soc., 42, 2011 (1920).

(32) Bingham, E. C., and Spooner, L. W., J. Rheol., 3, 222 (1932).

(33) Bistrzycki, A., and Landtwing, A., Ber., 41, 686 (1908).

(34) Boehner, R. S., and Ward, A. L., J. Am. Chem. Soc., 38, 2505 (1916).

(35) Boelhouwer, J.W.M., Nederbragt, G. W., and Verberg, G., Appl. Scientific Res., A2, 249 (1950).

(36) Bone, W. A., and Wheeler, R. V., J. Chem. Soc., 1902, 542.

(37) Bordroux, D., and Thomassin, R., CA 33, 5832 (1939).

(38) Bowden, S. T., J. Chem. Soc., 1939, 310.

(39) Braun, J. V., Hahn, E., and Seeman, J., Ber., 55, 1687 (1922).

(40) Brewster, C. M., Putnam, I. J., Jr., J. Am. Chem. Soc., 61, 3083 (1939).

(41) Brice, T. J., and Coon, R. I., J. Am. Chem. Soc., 75, 2921 (1953).

(42) Brooks, B. T., "The Chemistry of the Non-benzenoid Hydrocarbons", 2nd Edition, Reinhold Publishing Company, New York, (1950).

(43) Brophy, J. F., Militz, R. O., and Zisman, W. A., Trans. A.S.M.E., 68, 355 (1946).

(44) Brunner, L., Ann., 151, 135 (1869).

(45) Bruner, W. M., Ind. Eng. Chem., 41, 2860 (1949).

(46) Burger, A., and Dawson, N. D., J. Org. Chem., 16, 1250 (1951).

(47) Burk, R. E., Laskowski, L., and Lankelma, H. P., J. Am. Chem. Soc., 63, 3248 (1941).

(48) Burkhard, C. A., U. S. Patent 2,561,178.

(49) Burkhard, C. A., Rochow, E. G., Booth, H. S., and Hartt, J. Chem. Rev., 41, 97-149 (1947).

(50) California Research Corporation, Contract No.AF-33(038) 9831, Jan. (1951).

(51) Charnley, T., Skinner, H. A., and Smith, N. B., CA, 46, 8506 (1952).

(52) Christiansen, W. G., "Organic Derivatives of Antimony", Chemical Catalog Company, New York, (1925), p. 25.

(53) Coleman, G. H., and Perkins, R. P., U. S. Patent 2,170,809.

(54) Colson, A., Compt. rend., 147, 1054 (1908).

(55) Connerade, E., CA, 30, 1373 (1936).

(56) Contract No. AF 33(616) 2623.

(57) Contractor's Meeting WADC, Sept., 1954.

(58) Cook, H. G., Ilett, J. D., Saunders, B. C., and Stacey, G. J., J. Chem. Soc., 1950 3125.

(59) Coover, H. W., and Dickey, J. B., U. S. Patent 2,585,230, Feb. 12, 1952.

(60) Cramer, P. L. and Mulligan, M. J., J. Am. Chem. Soc., 58, 373 (1936).

(61) Cristol, S. J., Hayes, R. A., and Haller, H. L., CA, 40, 4050 (1946).

(63) Currie, C. C., and Hommel, M. C., Ind. Eng. Chem., 42, 2452 (1950).

(64) Currie, C. C., and Smith, B. F., Ind. Eng. Chem., 42, 2457 (1950).

(65) Da Fano Ettore, U. S. Patent 2,640,032.

(66) Da Fano Ettore, U. S. Patent 2,684,945.

(67) Dehn, W. M., Am. Chem. Jour., 40, 88 (1908).

(68) De Malde M., and Pirani, R., CA, 46, 4273 (1952).

(69) Dilthey, W., and Harenberg, F., CA, 27, 1878 (1933).

(70) Doss, M. P., "Physical Constants of the Principal Hydrocarbons", 4th Edition, The Texas Company, New York, (1943).

(71) Dow-Corning Silicone Notes, Oct. 25, 1951.

(72) Driesbach, R. R., Physical Properties of Chemical Substances, The Dow Chemical Company, Midland, Mich., (1952).

(73) Dreisbach, R. R., Martin, R. A., and Erbel, A. J., U. S. Patent 2,507,506.

(74) Eastwood, T. A., and Hinshelwood, C., J. Chem. Soc., 1952, 733-8.

(75) Egloff, G., and Parish, C. I., Chem. Rev., 19, 145 (1936).

(76) Egloff, G., "The Reactions of Pure Hydrocarbons", Reinhold Publishing Company, New York (1937).

(77) Elbs, K., and Larsen, E., Ber., 17, 2849 (1884).

(78) Engler, C., and Dengler, L., Ber., 26, 1444 (1893).

(79) Engler, C., and Grimm, J., Ber., 30, 2922 (1897).

(80) Engler, C., and Löw, E., Ber., 26, 1436 (1893).

(81) Evans, D. P., Davies, W. C., and Jones, W. J., J. Chem. Soc., 1930 1310.

(82) Falkenburg, L. B., Teeter, H. M., and Cowan, J. C., J. Am. Chem. Soc., 69, 486-7 (1947).

(83) Fedosew, P. N., CA, 31, 8527 (1937).

(84) Fitzsimmons, V. G., Pickett, D. L., Militz, R. O., and Zisman, W. A., Trans. A.S.M.E., 68, 361 (1946).

(85) Foster, A. B., Overend, W. G., and Stacey, M., J. Chem. Soc., 1951, 980.

(86) Fox, R. B., and Lockhart, L. B., "The Chemistry of Organophosphorus Compounds", p. 49, Naval Research Lab., Washington, D. C., (1948).

(87) Fox, H. W., Taylor, P. W., and Zisman, W. A., Ind. Eng. Chem., 39, 1401 (1947).

(88) Frank, C. E., and Blackham, A. U., CA, 46, 5303 (1952).

(89) Freiser, H., and Glowoski, W. S., J. Am. Chem. Soc., 70, 2575 (1948); ibid., 71, 514 (1949).

(90) Frey, F. E., Ind. Eng. Chem., 26, 198 (1934).

(91) Friend, J. N., and Hargraves, W. D., Phil. Mag., 35, 57, 619 (1944).

(92) Frisch, H. L., Martin, I., and Mark, H., CA, 47, 9659 (1953).

(93) Fritz, G., CA, 47, 12223 (1953).

(94) Gallaugher, A. F., and Hibbert, H., J. Am. Chem. Soc., 59, 2521 (1937).

(95) Gamrath, H. R., Hatton, R. E., and Weesner, W. E., Ind. Eng. Chem., 46, 208 (1954).

(96) Gault, H., and Sigwalt, R., CA, 22, 379 (1928).

(97) Gerrard, W., J. Chem. Soc., 1944, 85.

(98) Gilman, H., Chem. Rev., 52, 77 (1953).

(99) Gilman, H., Contractors' Meeting WADC, September, 1954.

(100) Gilman, H., and Brannen, C. G., CA, 45, 2921 (1951).

(101) Gilman, H., and Dunn, G. E., J. Am. Chem. Soc., 73, 3404 (1951).

(102) Gilman, H., Ingham, R. K., and Gorsick, R. D., "Organo-Metallic and Organo-Metalloidal High Temperature Lubricants and Related Materials", WADC Technical Report 53-426.

(103) Gilman, H., and Miller, L. S., CA, 45, 7972 (1951).

(104) Glass, J.V.S., and Hinselwood, C. N., J. Chem. Soc., 1929, 1804.

(105) Goddard, A. E., In "A Textbook of Inorganic Chemistry", Edited by J. N. Friend, Vol. XI, Part III, p. 198, C. Griffin and Company, Ltd., London, (1936).

(106) Ibid., p. 268.

(107) Goddard, A. E., and Goddard, D., In "A Textbook of Inorganic Chemistry", Edited by J. N. Friend, Vol. XI, Part I, p. 341 C. Griffin and Co., Ltd., London, (1928).

(108) Graebe, C., and Knecht, W., Ann., 202, 1 (1880).

(109) Graebe, C., and Ullmann, F., Ber., 29, 1877 (1896).

(110) Graf, R., Ber., 85, 9 (1952).

(111) Grant, G., 3d, and Currie, C. C., Mech. Eng., 73, 311 (1951).

(112) Hall, S. A., and Jacobson, M., Ind. Eng. Chem., 40, 694 (1948).

(113) Hanford, W. E., U. S. Patent 2,386,793.

(114) Hartley, G. S., J. Chem. Soc., 1939, 1828.

(115) Hatt, H. H., Pilgrim, A., and Stephenson, E.F.M., CA, 36, 445 (1942).

(116) Hein, F., and Retter, W., Ber., 61, 1790 (1928).

(117) Helm, D. F., and Mack, E. Jr., J. Am. Chem. Soc., 59, 60 (1937).

(118) Hennion, G. F., and de C. McLeese, S. F., J. Am. Chem. Soc., 64, 2421 (1942).

(119) Herndon, L. R., and Reid, E. E., J. Am. Chem. Soc., 50, 3066 (1928).

(120) Hickenbottom, W. J., J. Chem. Soc., 1937, 1119.

(121) Hinshelwood, C. N., and Askey, P. J., Proc. Roy. Soc., 115, 215 (1927).

(122) Hofmann, F., and Lang, K., Chem. Zentr., 1929 II, 164.

(123) Holt, H. S., U. S. Patent 2,287,249.

(124) Howard, J. W., and Derick, C. G., J. Am. Chem. Soc., 46, 166 (1924).

(125) Hurd, C. D., "The Pyrolysis of Organic Compounds", The Chemical Catalog Company, Inc., New York, 1929.

(126) Hurd, C. D., and Bennett, C. W., J. Am. Chem. Soc., 51, 1200 (1929).

(127) Hurd, C. D., and Blunck, F. H., J. Am. Chem. Soc., 60, 2419 (1938).

(128) Hurd, C. D., and Dull, M. F., J. Am. Chem. Soc., 54, 2432 (1932).

(129) Hurd, C. D., and Tallyn, W. H., J. Am. Chem. Soc., 47, 1779 (1925).

(130) Ingold, C. K., "Structure and Mechanism in Organic Chemistry", Chapter XIV, Cornell University Press, Ithaca, New York, 1953.

(131) Ipatiev, V., and Orlov, N., Ber., 60, 1967 (1927).

(132) Ipatiev, V. N., and Petrov, A. D., Ber., 60, 1956 (1927).

(133) Jackson, I. K., Davies, W. C., and Jones, W. J., J. Chem. Soc., 1931, 2109.

(134) Jackson, J. L., Ind. Eng. Chem., 43, 2869 (1951).

(135) Jaehne, O., Ann., 256, 269 (1890).

(136) Johnson, J. R., and Van Campen, M. G. Jr., J. Am. Chem. Soc., 60, 121 (1938).

(137) Johnson, J. R., Van Campen, M. G., Jr., and Grummett, O., J. Am. Chem. Soc., 60, 111 (1938).

(138) Johnson, O. H., Chem. Rev., 48, 259 (1950).

(139) Johnson, R. L., Swikert, M. A., Bisson, E. E., CA, 47, 4068 (1953).

(140) Johnston, L. H., U. S. Patent 2,335,012.

(141) Jones, D. T., J. Chem. Soc., 1915, 1582.

(142) Kholinsky, E., and Melamed, M., Ber., 42, 3090 (1909).

(143) Kleene, R. D., CA, 35, 1044 (1941).

(144) Knoevenagel, E., Ber., 21, 1344 (1888).

(145) Kosolapoff, G. M., J. Am. Chem. Soc., 72, 5508 (1950).

(146) Kosolapoff, G. M., J. Am. Chem. Soc., 67, 2259 (1945).

(147) Kosolapoff, G. M., J. Am. Chem. Soc., 67, 1180 (1945).

(148) Kosolapoff, G. M., "Organophosphorus Compounds", John Wiley and Sons, New York (1950).

(149) Kossiakoff, A., and Rice, F. O., J. Am. Chem. Soc., 65, 590 (1943).

(150) Kotera, A., CA, 45, 6598 (1951).

(151) Krause, E., and van Grosse, A., "Die Chemie der metallorganischen Verbindungen", Borntrager, Berlin (1937).

(152) Lachman, A., J. Am. Chem. Soc., 45, 2356 (1923).

(153) Larsen, R. G., and Bondi, A., Ind. Eng. Chem., 42, 2421 (1950).

(154) Lewis, R. N., and Newkirk, A. E., J. Am. Chem. Soc., 69, 701 (1947).

(155) Lieberman, C., and Speigel, L., Ber., 22, 779 (1889).

(156) Lincoln, B. H., and Byrkit, G. D., U. S. Patent 2,413,718.

(157) Löb, W., Ber., 34, 918 (1901).

(158) Long, L. M., and Henze, H. R., J. Am. Chem. Soc., 63, 1939 (1941).

(159) MacGregor, J. H , and Ward, F., Jour. Soc. Chem. Ind., 66, 344 (1947).

(160) Mann, F. G., and Purdie, D., J. Chem. Soc., 1935, 1549.

(161) Manulkin, Z., and Yakubova, F., CA, 35, 3240 (1941).

(162) McCready, D. W., Vaughan, W. R., Braown, B. B., Goheen, D. W., Dick, M. F., Turner, H., Univ. of Michigan Engineering Research Institute, Project M779, WADC, Contract No. W-33-038-ac-21457, Project MX-982.

(163) McElvain, S. M., Anthes, H. I., and Shapiro, S. H., J. Am. Chem. Soc., 64, 2525 (1942).

(164) McGregor, R. R., and Warrick, E. L., U. S. Patent 2,389,802.

(164a) Marans, N. S., Sommer, L. H., and Whitmore, F. C., J. Am. Chem. Soc., 73, 5127 (1951).

(165) Mentschutkin, N., Ber., 15, 2512 (1882).

(166) Meyer, H., and Hofmann, A., Monatsh., 37, 681, (1916); CA, 11, 780 (1917).

(167) Meyer, H., and Hofmann, A., Monatsh., 38, 343 (1917).

(168) Meyer, H., and Hofmann-Meyer, A., J. prakt. Chem., [2], 102, 287 (1921); Chem. Zent., 1921 III, 1122.

(169) Michaelis, A., and Kaehne, R., Ber., 31, 1058 (1898).

(170) Michaelis, A. von., Ann. 293, 193, 261 (1896).

(171) Michaelis, A. von., Ann. 326, 129, (1903).

(172) Mikeska, L. A., Ind. Eng. Chem., 28, 970 (1936).

(173) Miron S., and Lowy A., J. Am. Chem. Soc., 73, 1872 (1951).

(174) Monsanto compound.

(175) Monsanto Tech. Bulletin No. P-106, Nov. 6, 1950.

(176) Monsanto Chemical Co., unpublished work.

(177) Morgan, C. R., Olds, W. F., and Rafferty, A. L., J. Am. Chem. Soc., 73, 5193 (1951).

(178) Morrison, D. C., J. Am. Chem. Soc., 72, 4820 (1950).

(179) Moyle, C. L., U. S. Patent 2,170,833.

(180) Moyle, C. L., U. S. Patent 2,220,113.

(181) Moyle, C. L., U. S. Patent 2,220,845.

(182) Moyle, C. L., U. S. Patent 2,255,434.

(183) Muller, A., Bull. soc. chim., [2], 45, 438 (1886).

(184) Murphy, C. M., Romano, J. B., and Zisman, W. A., Trans. of the A.S.M.E., 71, 561 (1949).

(185) Murphy, C. M., Saunders, C. E., and Smith, D. C., Ind. Eng. Chem., 42, 2462 (1950).

(186) Murphy, C. M., and Zisman, W. A., Ind. Eng. Chem., 42, 2414 (1950).

(187) Muskat, I. E., U. S. Patent 2,379,249, June 26, 1945.

(188) Newman, M. S., J. Am. Chem. Soc., 72, 4783 (1950).

(189) Neunhoeffer, O., and Nerdel, F., CA, 31, 379 (1937).

(190) Nietzki, R., Ber., 10, 474 (1877).

(191) Norris, J. F., and Young, R. C., J. Am. Chem. Soc., 52, 753 (1930).

(192) N.V.de Bataafsche Petroleum Maatschappij, CA, 46, 8145 (1952).

(193) Oppenheim, A., and Precht, H., Ber., 9, 325 (1876).

(194) Orkin, B. A., U. S. Patent 2,626,957.

(195) Pacific Coast Borax Company.

(196) Pauling, L., The Nature of the Chemical Bond, 2nd Edition, pp. 53, 131, Cornell University Press, Ithaca, New York (1948).

(197) Pearlson, W. H., Brice, T. J., and Simons, J. H., J. Am. Chem. Soc., 67, 1769 (1945).

(198) Pease, R. N., and Martin, J. A., J. Am. Chem. Soc., 50, 1779 (1928).

(199) Pennsylvania State College, Petroleum Refining Laboratory, Report No. PRL 3.49 - Jan. 51.

(200) Pennsylvania State University, State College, Pa. Progress Statement, May, 1954 on "Fluids, Lubricants, Fuels, and Related Materials".

(201) Petrov, A. D., and Chernysheva, T. I., CA, 46, 7556 (1952).

(202) Petrov, A. D., and Chugunov, V. S., CA, 46, 480 (1952).

(203) Physical Testing Section of this Report.

(204) Pierce, J. B. Foundation, N. Y., Brit. Patent 670, 630.

(205) Pitzer, K. S., J. Am. Chem. Soc., 70, 2140 (1948).

(206) Prescott, R. F., Dosser, R. C., and Sculate, J. J., U. S. Patent 2,300,006.

(206a) Prutton, C. F., U. S. Patent 2,555,371.

(207) Raczynsky, W. A., U. S. Patent 2,510,904.

(208) Raiziss, G. W., and Gavron, J. L., "Organic Arsenical Compounds", p. 221, Chemical Catalog Co., New York (1923).

(209) Richter, F. P., and Orkin, B. A., U. S. Patent 2,590,039.

(210) Rinkes, I. J., CA, 40, 6061 (1946).

(211) Ritchie, P. D., J. Chem. Soc., 1935, 1054.

(212) Rochow, E., Chem. and Eng. News, 23, 612 (1945).

(213) Rosenberg, H., Groves, J. D., and Bartholomew, E. J., Absrts. of the 126th National ACS Meeting, Sept. 1954, 86-0.

(214) Rosenmund, K. W., CA, 32, 9403 (1938).

(215) Sabatier, P., and Senderens, J. B., Compt. rend., 133, 323 (1901).

(216) Sachanen, A. N., "Conversion of Petroleum", 2nd Edition, Reinhold Publishing Company, New York, 1949.

(217) Sachanen, A. N., and Tilicheev, M. D., Ber., 62, 528 (1929).

(218) Scattergood, A., Miller, W. H., and Gammon, J. Jr., J. Am. Chem. Soc., 67, 2150 (1945).

(219) Schiessler, R. W., Unpublished data, The Pennsylvania State University.

(220) Schiessler, R. W. et al, A.P.I. Research Project 42, Quarterly Reports 1951, 1952.

(221) Schiessler, R. W., Clarke, D. G., Rowland, C. S., Sloatman, W. S., and Herr, C. H., Trans. of the A.P.I. III, 24, 49, Nov. 10, 1943.

(222) Schiessler, R. W., Cosby, J. N., Clarke, D. G., Rowland, C. S., Sloatman, W. S., and Herr, C. H., Trans. of the A.P.I. III, 23, 1, Nov. 10, 1942.

(223) Schiessler, R. W., Herr, C. H., Rytina, A. W., Weisel, C. H., Fischl, F., McLaughlin, R. L,, and Kuehner, H. H., Trans. of the A.P.I. III, 1, June 2, 1947.

(224) Schiessler, R. W., and Sutherland, H., Trans. of the A.P.I. III, 32, 1, Nov. 10, 1952.

(225) Schmidt, J., "Organo Metallverbindungen", p. 232, Wissenschaftliche Verlagsgesellshaft. M.B.H., Stuttgart, (1934).

(226) Schönberg, A., Schütz, O., Bruckner, V., and Peter, J., Ber., 62B, 2550 (1929).

(227) Schroeder, W. D., and Brewster, R. Q., J. Am. Chem. Soc., 60, 751 (1938).

(228) Scott, D. W., J. Am. Chem. Soc., 68, 356 (1946).

(229) Sherman, A., Quimby, Q. T., and Sutherland, R. O., J. Chem. Physics, 4, 732 (1936).

(230) Sidgwick, N. V., "The Chemical Elements and Their Compounds", Vol. I, Oxford University Press (1950).

(231) Skraup, S., and Beifuss, W., Ber., 60, 1070 (1927).

(232) Skraup, S., and Beng, E., Ber., 60, 950 (1927).

(233) Skraup, S., and Nieten, F., Ber., 57, 1308 (1924).

(234) Skraup, S., and Schwamburger, E., Ann., 462, 153 (1928).

(235) Smith, A., and Menzies, A.W.C., J. Am. Chem. Soc., 32, 897, 907, 1412 (1910).

(236) Smith, L. I., "The Synthesis of Hydrocarbons", A.T.I., 30467, September 15, 1941.

(237) Smith, R. A., J. Am. Chem. Soc., 55, 3718 (1933).

(238) Sommer, L. H., Goldberg, G. M., Gold, J., and Whitmore, F. C., J. Am. Chem. Soc., 73, 5127 (1951).

(239) Southwest Research Inst., Tech. Report No. 4, July 31, 1953.

(240) Sperer, J. L., J. Am. Chem. Soc., 74, 1003 (1952).

(241) Spilker, A., Z. Angew. Chem., 48, 368 (1935).

(242) Standard Oil Co. Indiana, Tech. Bull. No. 15.

(243) Starokadomskaya, E., CA, 32, 6933 (1938).

(244) Staudinger, H., and Rathsam, G., Helv. Chim. Acta., 5, 645 (1922).

(245) Staudinger, H., and Rössler, K., Ber., 69, 49, 61 (1936).

(246) Stull, D. R., Ind. Eng. Chem., 39, 517-540 (1947).

(247) Szwarc, M., Chem. Rev., 47, 75 (1950).

(248) Tech. Report No. 4, Contract AF-33(616)-276.

(249) Thomas, L. H., J. Chem. Soc., 1946, 820.

(250) Tilicheev, M. D., and Shchitikov, V. K., Chem. Zeit., 1937, 4583.

(251) Tilicheev, M. D., and Shchitikov, V. K., CA, 32, 2721 (1938).

(252) Tilicheev, M. D., and Shchitikov, V. K., CA, 32, 4762 (1938).

(253) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds", pp. 360, 475, Elsevier Publishing Co., Inc. New York (1950).

(254) Timmermans, J., and Hennault-Roland, Mme., J. Chim. phys., 34, 733 (1937).

(255) Toy, A.D.F., J. Am. Chem. Soc., 70, 186 (1948).

(256) Toy, A.D.F., J. Am. Chem. Soc., 70, 3882 (1948).

(257) Toy, A.D.F., U. S. Patent 2,400,577 (1946).

(258) Ungnade, H. E., Kline, E. F., and Crandall, E. W., J. Am. Chem. Soc., 75, 3333 (1953).

(259) Upson, F. W., and Sands, L., J. Am. Chem. Soc., 44, 2306 (1922).

(260) Van Duzee, E. M., and Adkins, H., J. Am. Chem. Soc., 57, 147 (1935).

(261) Vinogradova, V. S., CA, 47, 10458 (1953).

(262) Voge, H. H., and Good, G. M., J. Am. Chem. Soc., 71, 593 (1949).

(263) Vol'Nov, Yu N., CA, 42, 2230 (1948).

(264) Waring, C. E., Trans. Faraday Soc., 36, 1142 (1940).

(265) Waring, C. E., and Horton, W. S., J. Am. Chem. Soc., 67, 540 (1945).

(266) Warrick, E. L., Hunter, M. J., and Barry, A. J., Ind. Eng. Chem., 44, 2196 (1952).

(267) Weselsky, P., Ber., 2, 519 (1869).

(268) Westphal, O., and Jerchel, D., Ber., 73B, 1002 (1940).

(269) Whitmore, F. C., et al., J. Am. Chem. Soc., 68, 475 (1946).

(270) Wibaut, J. B., and Smithenberg, J., Rec. trav. chim., 61, 348 (1942).

(271) Wilcock, D. F., J. Am. Chem. Soc., 68, 691 (1946).

(272) Wiley, K. B., J. Am. Chem. Soc., 75, 2665 (1953).

(273) Williams-Gardner, A., Fuel in Science and Practice, 4, 430 (1925); CA, 20, 280 (1926).

(274) Wuyts, H., and Dequesne, A., Bull. Soc. chim. Belg., 48, 77-93 (1939).

(275) Zelinsky, N. D., and Gawerdowskoja, M. W., Ber., 60, 713 (1927).

(276) Zelinsky, N. D., Titz, I., and Gaverdovskaja, M., Ber., 59, 2593 (1926).

(277) Zisman, W. A., Ind. Eng. Chem., 45, 1406 (1953).

(278) Zisman, W. A., and Brophy, J. E., Mech. Eng., 73, 754 (1951).

APPENDIX I

PARTS LIST FOR THERMAL STABILITY APPARATUS (Fig. 5)

Quantity	Description	Source	Approximate Cost
2	Type 116 Powerstat, 115-volt, 50-60 cycle, 7-1/2 amp output	Srepco, Inc. Dayton, Ohio	$ 46.00
2	S-900 Quartz-fabric heating mantle for 500 cc flask	Glas-Col Apparatus, Inc. Terre Haute, Ind.	39.50
2	Westclox Model TS-1 time switch clock	Rike-Kumler Co., Dayton, Ohio	25.00
2	Thermometer, Special J-2304 range 200° to 425°C, 3 in. stem	Scientific Glass App. Co. Bloomfield, N. J.	20.00
1 oz	Apiezon Grease "T"	J. G. Biddle Co. Philadelphia, Pa.	17.60
3	C-8075 Condensers, jacket length 200 mm	Scientific Glass App. Co. Bloomfield, N. J.	10.83
2	500 cc, 3-neck flask with 34/45 ₸ center and 24/40 ₸ side necks, and 10/30 ₸-thermometer joints	Ace Glass Inc. Vineland, N. J.	19.00
1	500 cc, single-neck flask with 19/38 ₸ joint and side arm	Ace Glass, Inc. Vineland, N. J.	6.00
1	Cenco Hyvac Vacuum Pump, Cat. No. 91105 No. 1 with Motor	Central Scientific Co. Chicago, Ill	91.00

APPENDIX I (CONT'D)

PARTS LIST FOR THERMAL STABILITY APPARATUS (Fig. 5)

Quantity	Description	Source	Approximate Cost
1	11-292 Mercury manometer, vacuum, Bennert type, metric	Fisher Scientific Co. Pittsburg, Pa.	$ 21.00
2	7280 One-way stopcock, Code No. 441200, 2 mm	Corning Glass Works Corning, N. Y.	5.36
2	7380 Two-way stopcock, Code No. 441282, 2 mm	Corning Glass Works Corning, N. Y.	8.46
2	Air condensers, 24/40 ₸ joint with 2 ft x 16 mm glass tube necked to 7 mm	Laboratory Glass Shop	7.00
2	7570 24/40 ₸ plugs, Code No. 408330	Corning Glass Works Corning, N. Y.	3.50
2	Sample tubes (see inset photograph, Fig. 5) 19/38 ₸ joint at center, and 12/5 male ball joint on drain tube	Laboratory Glass Shop	70.00
2	Receiver bulbs, 20 cc bulb with 8 mm tube to 12/5 female ball joint	Laboratory Glass Shop	3.50
2	Male 19/38 ₸ joints necked down to 7 mm tube	Laboratory Glass Shop	6.00

APPENDIX II

PARTS LIST FOR ISOTENISCOPE (Fig. 7)

Quantity	Description	Source	Approximate Cost
1	Welch Duo-Seal Vacuum pump, with motor and base	W. M. Welch Mfg. Co. Chicago, Ill.	$ 115.00
1	7558 Stopcock, one-way, 8 mm bore, Code No. 400257	Corning Glass Works Corning, N. Y.	6.68
1	93201 Mercury diffusion pump	Central Scientific Co. Chicago, Ill.	43.50
1	Cold trap	Laboratory Glass Shop	10.00
1	9333 MacLeod gauge, high vacuum, 200-0.5 microns	Will Corp. Rochester, N. Y.	50.00
1	4320 Single-neck flask, 1000 cc, 24/40 ₮ joint, code No. 400223	Corning Glass Works Corning, N. Y.	2.10
7	7546 Stopcocks, 2 mm Code No. 400301	Corning Glass Works Corning, N. Y.	31.15
1	N_2 reservoir balloon		3.00
1	12-620 Cathetometer, vertical or horizontal, 40-cm scale	Eberbach & Son Co. Ann Arbor, Mich.	135.00
1	19-204 Cathetometer, vertical, 102-cm scale	Gaertner Scientific Corp. Chicago, Ill.	450.00

APPENDIX III

PARTS LIST FOR KINEMATIC VISCOSITY BATHS (Fig. 9)

Quantity	Description	Source	Approximate Cost
2	15-445-5 Base for thermostat jar	Fisher Scientific Co. Pittsburgh, Pa.	$ 32.00
2	11-823 Size J (12 in. dia. x 12 in. high) jar, Pyrex	Fisher Scientific Co. Pittsburgh, Pa.	31.50
2	14-503 Stirrer, economy	Fisher Scientific Co. Pittsburgh, Pa.	45.00
2	(Set of 3) 15-445-10 Rods for jars 12 in. high	Fisher Scientific Co. Pittsburgh, Pa.	6.00
8	15-445-80 Water bath clamp, small	Fisher Scientific Co. Pittsburgh, Pa.	10.00
4	15-445-75 Water bath clamp, large	Fisher Scientific Co. Pittsburgh, Pa.	6.00
6	5-757 Jumbo clamp holder	Fisher Scientific Co. Pittsburgh, Pa.	4.50
2	15-445 Electronic Control Units for 115-volt, 50-60 cycle, AC only	Fisher Scientific Co. Pittsburgh, Pa.	94.00
1	H-1265 Heater, immersion, size D, 300-watt	Kauffman-Lattimer Co. Columbus, Ohio	6.25
2	H-1265 Heater, immersion, size E, 500-watt	Kauffman-Lattimer Co. Columbus, Ohio	14.00
1	H-1265 Heater, immersion, size F, 750-watt	Kauffman-Lattimer Co. Columbus, Ohio	7.00

APPENDIX III (CONT'D)

PARTS LIST FOR KINEMATIC VISCOSITY BATHS (Fig. 9)

Quantity	Description	Source	Approximate Cost
1	T-5750 Micro-set thermoregulator, size A	Kauffman-Lattimer Columbus, Ohio	$ 60.00
1	T-5750 Micro-set thermoregulator, size B	Kauffman-Lattimer Co. Columbus, Ohio	60.00
4	Type 116 Powerstat, 115-volt 50-60 cycle, 7-1/2 amp output	Srepco, Inc. Dayton, Ohio	92.00
5 gal	Mineral oil	Standard Oil Co.	15.00
1	13-618-D Thermometer, kinematic viscosity, range 97.5°-102.5°F	Fisher Scientific Co. Pittsburgh,Pa.	15.13
1	13-618-J Thermometer, kinematic viscosity, range 207.5°-212.5°F	Fisher Scientific Co. Pittsburgh,Pa.	15.13
4	5-733 Fisher castalloy apparatus clamps, large size	Fisher Scientific Co. Pittsburgh, Pa.	4.00
1	14-653 Stopwatch, electric, direct reading, 1/10 second	Fisher Scientific Co. Pittsburgh, Pa.	42.50
7	No. 27876 Viscosity pipet, Ostwald, Cannon Fenske, calibrated, ASTM, exax blue line. Two of No. A, and one each of Nos. B,C,D,E, and F	Central Scientific Co. Chicago, Ill.	96.60

APPENDIX IV

PARTS LIST FOR FURNACE, VAPOR PRESSURE AND HIGH-TEMPERATURE VISCOSITY MEASUREMENT (Figs. 7 & 10)

Quantity	Description	Source	Approximate Cost
1	General Radio Variac, V5MT	General Radio Co. Cambridge, Mass.	$ 25.00
2	Ohmite Rheostat 10Ω Model K, 100-watt	Ohmite Mfg. Co. Chicago, Ill.	22.00
1	Ohmite Rheostat 5Ω Model K, 100-watt	Ohmite Mfg. Chicago, Ill.	11.70
35 ft	Nichrome wire, .047 No.18 BS	Driver-Harris Co. Harrison, N. J.	3.00
1	Copper pipe, 2-1/2 in. dia. x 11 in., 1/8 in. wall		8.00
1	Unibestos insulation	C. W. Booher & Sons Dayton, Ohio	2.00
1	Metal box for rheostat	Bud Radio Corp. Cleveland, Ohio	3.00
1	30806 Sola constant voltage transformer, 120 VA	Sola Electric Co. Chicago, Ill.	115.00
1	Chromel-Alumel thermocouple	Leads & Northrup Philadelphia, Pa.	2.50
1	8662 Portable Precision Potentiometer, double range	Leeds & Northrup Philadelphia, Pa.	364.00