NRL REPORT C-3396

FR3396

VISCOSITIES AND DENSITIES OF LUBRICATING FLUIDS FROM -40 TO 700°F

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December 22, 1948

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ABSTRACT

The viscosities and densities of a large group of high-boiling synthetic and petroleum fluids have been investigated over a wide range of temperatures. They were chosen because of their promise for use at extreme temperatures or their ability to supply fundamental data for viscometry and lubrication. The variation of density with temperature was practically linear over the range investigated, A modified A.S.T.M. viscosity-temperature chart, extending from -100° to 700°F, proved very satisfactory for analysis of viscometric data. Deviations from linearity at the extreme temperatures were studied and classified, and nearly all could be explained on the basis of certain physical or chemical transformations shown to occur at the extreme temperatures. The linear portions of the graphs are qualitatively explained in terms of the ability of many types of linear molecules to coil as helices. Convexity at high temperatures is believed general and is caused by the disappearance of the helical configuration under conditions of violent thermal agitation.

PROBLEM STATUS

This is an interim report; work is continuing on the problem of lubricants for turbo-jet engines and for propeller-drive gas turbines.

AUTHORIZATION

NRL Problem No. C02-06D

VISCOSITIES AND DENSITIES OF LUBRICATING FLUIDS FROM -40 to 700°F

INTRODUCTION

Viscosity is generally considered the most important single characteristic of a lubricating fluid. Unfortunately, very little is known at present about the viscosity of either petroleum or synthetic oils under high temperature conditions. Without such data it is impossible to ascertain the reliability of the many empirical and theoretical equations proposed for relating viscosity with temperature.

Controversy exists as to whether in many applications the absolute viscosity (η) or the kinematic viscosity ($\mu = \eta/\rho$ where ρ= density) of a lubricant is the more significant. Since at ordinary temperatures the densities of a large number of petroleum oils do not differ greatly from unity, their kinematic and absolute viscosities do not differ significantly. However, as the density of fluids usually decreases with increasing temperature, the difference between the kinematic and absolute viscosities of petroleum oils may be considerable at high temperatures, while even greater differences will be observed in denser fluids such as the perfluorocarbons. Furthermore, since the temperature coefficients of viscosity and density are not comparable, the coefficients of the absolute and kinematic viscosities may be very different.

In order to obtain more information, particularly in view of the high temperatures encountered in gas turbines and turbo-jet engines, a systematic investigation was undertaken of the density and viscosity-temperature characteristics, over a wide temperature range, of a variety of synthetic and conventional mineral-base oils.

MATERIALS

The fluids selected for investigation were considered representative of both petroleum and synthetic types. These included silicones, polymeric ethylene glycols, petroleum oils, diesters, and fluids containing fluorine and/or chlorine. The silicones, obtained from the Dow-Corning Corp., included commercial samples of the polymethyl-, polyethyl-, and poly(methyl-phenyl) siloxanes.[1,2,3,4] The poly(methyl-phenyl) siloxanes, arranged in increasing order of aromaticity[5] are the DC 500, the DC 703, and the DC 702. An infrared spectrum analysis of the DC 710 fluid has not been made, but from its other properties this material is believed to have a higher phenyl-to-methyl ratio than the DC 550.

The polymeric ethylene glycols[6] were obtained from Carbide and Carbon Chemicals Corporation and the polymers of 1,2-propanediol from the Dow Chemical Co.[7] The latter glycols have methyl branches and would be expected to have lower pour points and less favorable V.I.'s than the polyethylene glycols which contain no branch chains. Similar polymers were the "Ucon" fluids.[8,9,10,11,12] The LB series are derivatives of 1,2-propanediol, while the HB series are derived from copolymers of ethylene glycol and 1,2-propanediol. Samples were available with and without the recommended antioxidant.

The low-V.I. petroleum oils (Navy Symbol 2135 and 2250),[13] were procured from the Socony-Vacuum Oil Company and the Texas Company respectively, while those having high-V.I.'s (Grades 1065 and 1120 of Specification AN-0-8)[14] were from The Texas Company.

The diester oils were represented by the n-butyl, 2-ethylhexyl, and 1-methyl-4-ethyloctyl (or undecyl) esters of sebacic acid.[15] The first two fluids were procured from the Resinous Products and Chemical Co. and the Rhom and Haas Co. respectively, while the undecyl sebacate was made in this Laboratory.

A fraction of a fully fluorinated petroleum oil designated as Fluoro Lubricant FCD-331 and having a boiling range of 266 to 302°F at 10 mm[16] was procured from E. I. DuPont de Nemours & Company. Two polymers of monochlorotrifluoroethylene[17,18,19,20] designated as Fluorolube-Standard and Fluorolube-Light Grease, were obtained from the Hooker Electrochemical Company.

EXPERIMENTAL

Previous experience had dictated the advisability of removing any volatile impurities from the fluids under investigation in order to assure better reproducibility of results at the higher temperatures. These impurities were removed by passing the fluids dropwise from a reservoir through a 2-cm-diameter glass column filled to a height of 50 cm with glass helices. For all materials except the halocarbons, the pressure within the system was maintained at 5 mm of mercury while the column was heated to 220°F. The halocarbons were treated at 165°F because of the high vapor pressures of these fluids.

Several of the silicones were slightly turbid as received and were clarified with activated Fuller's earth.

The densities and viscosities were determined in thermostated constant-temperature baths maintained within ±0.05°F of the desired temperature over the range -40° to 700°F. For temperatures from 77° to 210°F, a conventional water bath was sufficient. Lower temperatures were obtained with a Precision Scientific Company bath using methyl cellosolve for the bath liquid and dry ice as the coolant while the temperature was controlled as described in earlier work.[15] For maintaining temperatures above 210°F, there was employed a well insulated Pyrex glass bath provided with double windows and using DC 550 silicone as the bath liquid. Except for the use of a three-junction iron-constantan thermopile in this bath, the temperature control systems of the high- and low-temperature baths were the same.

Densities were determined in dilatometers of approximately 12-cc capacity made by sealing to a small Erlenmeyer flask a precision bore capillary of approximately 2.25 mm diameter. Calibrations were made at 77°F with mercury, and all weights in air were reduced to weights in vacuo.[21] At the other temperatures from -40 to 700°F the volumes of the dilatometers were calculated from the coefficient of cubical expansion of "Pyrex" glass ($5.33^{\circ}F \times 10^{6}/^{\circ}F$).

In filling the dilatometer, the oil sample was introduced into a small glass reservoir attached to the open end of the instrument by means of a glass joint. The system was evacuated to a pressure of 5 mm of mercury while the oil was heated to facilitate removal of dissolved and entrained air. When foaming stopped, the system was inverted, air admitted to the reservoir, and the dilatometer filled with the liquid to a height that would insure oil being in the capillary at the lowest temperature. To reduce drainage errors to a minimum at the higher temperatures, runs on all fluids were begun at the lowest temperature encountered. Determinations were made at increasing temperature increments until there was evidence of decomposition or until the vapor pressure was so great that liquid condensed on the cooler parts of the capillary. Densities were calculated from the weights of the fluid in vacuo and the values for intermediate temperatures were obtained by graphical interpolation.

All kinematic viscosities were determined by conventional methods in Cannon-Fenske modified Ostwald-type viscometers according to Federal Standard Method 30.5[22] (ASTM Method D 445-46-T).[23]

Each viscometer was calibrated at 100°F with two reference petroleum-type oils obtained from the National Bureau of Standards, and the value of the calibration constants in the two cases agreed within 0.1 percent. As the viscometers were filled at room temperature, it was necessary to apply a temperature correction factor for tests at other temperatures since the hydrostatic head of the liquid varies with the temperature and the coefficient of expansion of the liquid according to the following equation:[22,23]

$$C_{t_2} = C_{t_1}\left[1 - \frac{Vol_2 - Vol_1}{0.785Hd^2}\right]$$

where

C_{t_1} = calibration constant at reference temperature,

C_{t_2} = calibration constant being calculated,

Vol_1 = volume of liquid in viscometer (6.5cc) at t_1,

Vol_2 = volume of liquid in viscometer at t_2,

H = fluid head (9.0 cm), and

d = inside diameter of lower reservoir (3.0 cm).

The temperature correction factor, which is the term enclosed by brackets, was calculated for each temperature interval and for each type of fluid. The factors agreed within 0.1 percent from -40° to 210°F and are given in Table I.

TABLE I

Temperature Correction Factors

Temp., °F	Petroleum Oils	Ucons and Poly-Glycols	Silicones and Diesters	Fluorolube Standard	Fluoro Lubricant FCD-331
-40	1.006	1.005	1.006		
-20	1.005	1.005	1.005		
0	1.004	1.004	1.004		
32	1.003	1.003	1.002	1.003	1.003
77	1.001	1.001	1.001	1.001	1.001
210	0.995	0.995	0.995	0.994	0.994
250	0.993	0.993	0.993	0.992	0.991
300	0.991	0.990	0.990	0.989	0.988
350	0.989	0.988	0.987	0.986	0.984
400	0.986	0.985	0.984	0.983	0.980
450	0.984	0.982	0.981	0.979	0.976
500	0.981	0.979	0.977	0.975	0.970
550	0.978	0.975	0.974		
600	0.975	0.972	0.970		
650	0.972		0.967		
700	0.967		0.963		

When Ostwald-type viscometers are used, it is necessary to apply slight corrections to the calibration constant if the samples under investigation have surface tension characteristics different from those of the calibrating fluids. From the equation for surface tension, $\gamma = \frac{1}{2}h\rho g r$, an equation may be derived for correcting the calibration constant for changes in surface tension:

$$\text{Surface tension correction} = \frac{2}{Hg}\left[\frac{1}{r_1} - \frac{1}{r_2}\right]\left[\frac{\gamma_1}{\rho_1} - \frac{\gamma_2}{\rho_2}\right]$$

where

H = fluid head (9.0 cm),

g = gravitational constant,

r_1 = mean effective radius of upper bulb (0.6 cm),

r_2 = mean effective radius of lower reservoir (1.5 cm),

γ_1 = surface tension of calibrating liquid (dynes/cm),

γ_2 = surface tension of test liquid (dynes/cm),

ρ_1 = density of calibrating liquid, and

ρ_2 = density of test liquid.

Barr[24] has discussed the surface tension corrections and has shown that a correction factor for the change in head due to capillarity must be applied for any but small capillaries. The correction factor depends on the form of the meniscus.

The petroleum calibrating liquids had surface tensions of 31.5 ± 1 dynes/cm at 77°F, "Ucon" fluids and the polyglycols had values of 30 to 32 dynes/cm, while the diesters had values of 29 to 30 dynes/cm. However, the densities of these liquids are all sufficiently close to unity to make the surface tension corrections less than 0.1 percent. It is well known that the surface tensions of most liquids vary linearly with temperature until close to the critical temperature.[25] Winchester and Reber[26] found that the temperature coefficient of surface tension between 180 and 600°F was constant for several petroleum oils, the average value being 0.033 dynes/cm/°F, and the maximum variation from the mean being 0.0017 dynes/cm/°F. Unpublished investigations of this Laboratory[27] reveal that the temperature coefficient of surface tension of the "Ucons," polyglycols, and diesters is approximately 0.03 dynes/cm/°F. Differences between surface tensions of the petroleum oils and the fluids mentioned above will remain practically constant, since the surface tensions are decreasing at the same rate. Corrections due to surface tension differences will therefore become even smaller at elevated temperatures.

Surface tension data at 77°F for the other fluids investigated are as follows:

Fluid	Surface tension dynes/cm	Temp. Coef. of surface tension	Surface Tension corrections, percent
Polymethylsiloxanes	19.5-21.0	0.037/°F	0.3
Polyethylsiloxanes	23-25	0.036/°F	0.2
Polymethyl-phenyl-siloxanes	20-26	0.044/°F	0.25
Halocarbons	23 (approximately)	0.027/°F	0.4

It is seen from this data that appropriate surface tension corrections can be made at temperatures other than 77°F. The temperature coefficients of surface tension of the halocarbons[27] were not linear, and it is possible that the coefficients of other fluids also deviate from linearity at high temperatures. This would not introduce an appreciable error in the calculated corrections as the differences in surface tension become smaller at the elevated temperatures.

Viscosities were determined at temperatures of -40, -20, 0, 32, 100, 130, 210, and 250°F and at 50°F increments thereafter up to the point where reproducible results could not be obtained. Above 400°F it was impossible to obtain efflux times reproducible within 0.2 percent with some fluids. Viscometers were selected so that the kinetic energy corrections were negligible except at very high temperatures where some of the fluids had efflux times less than the minimum.[23] In order to minimize the effect of atmospheric oxygen, the bath was blanketed with carbon dioxide which was discharged from a funnel inverted over the top of the bath, thus permitting the viscometers to breathe an inert atmosphere. Prior to filling, the viscometers were swept out with carbon dioxide.

DISCUSSION OF RESULTS

Densities

The densities of the fluids investigated are accurate to ±0.1 percent and are arranged in Table II for each group of homologous fluids. Data at intermediate temperatures can be obtained with an accuracy of 0.2 percent from a straight line graph of density vs. temperature over the range given in the second from last column in Table II. The cubical coefficient of expansion at 77°F was calculated from $d\rho/dt$ and the density at that temperature.

The densities of the diesters agree within the limits set by the lesser accuracy of our earlier work,[15] while those for the silicones and polyglycols and derivatives agree well, over the comparable temperature range, with values already reported.[4,6,7,8,12,28] Although the data obtained on the petroleum oils seem to contradict values reported by Winchester and Reber,[28] this is only an apparent inconsistency since their oils were very viscous fractions having viscosities above 30 centistokes at 210°F.

Except for the halocarbons, the density-temperature graphs deviate from linearity only very slightly at the extreme temperatures. The graph for fluoro-lubricant FCD-331 is not linear anywhere, but the two polymers of trifluoromonochlorethylene behaved linearly up to 300 and 450°F respectively.

In general, $d\rho/dt$ and the cubical coefficient of expansion decrease as the viscosity increases in any homologous series of fluids. This is readily seen in Table II, particularly in the last column where the cubical coefficient of expansion is highest for the fluoro-lubricant FCD-331 and the lowest-viscosity polymethylsiloxane and least for the petroleum oils and most aromatic silicones.

Kinematic Viscosities

Viscosities are given in Table III, and all values reported from -40° to 400°F are believed accurate to within 0.2 percent relative to the accepted

Table II

Densities of Fluids

Identification	Density, Grams/cc. at °F. -40	77	210	550	$-(d\rho/dt)\times10^4$	Applicable Range, °F.	Coefficient* of Expansion x 10^4
			SILICONES				
Polymethylsiloxanes							
DC 500 "A"	1.011	0.950	0.886	0.720	4.86	32 to 600	5.12
DC 500 "B"	1.022	0.962	0.898	0.737	4.74	32 to 600	4.93
DC 500 "C"	1.026	0.965	0.902	0.743	4.71	32 to 600	4.88
DC 200 "D"	1.030	0.969	0.906	0.749	4.67	32 to 600	4.82
DC 200 "E"	1.031	0.970	0.908	0.751	4.65	32 to 600	4.79
Polyethylsiloxanes							
DC 400 "A"	1.003	0.952	0.895	0.792e	4.31	-40 to 450	4.53
DC 400 "C"	1.042	0.994	0.941	0.825f	4.02	-40 to 500	4.04
Poly(methyl-phenyl)siloxanes							
DC 702	1.107b	1.071	1.008	0.845	4.74	0 to 500	4.43
DC 703	1.117b	1.081	1.022	0.869	4.52	0 to 500	4.18
DC 710	1.125b	1.092	1.037	0.898	4.13	0 to 550	3.78
DC 550	1.104b	1.070	1.016	0.876	4.09	77 to 600	3.82
			POLYALKYLENE GLYCOLS AND DERIVATIVES				
Polyethylene Glycols							
Polyethylene Glycol 200	1.175a	1.122	1.062	0.895	4.50	-40 to 300	4.01
Carbowax 1000		1.098d	1.064	0.937f	4.33	130 to 400	3.94
Polypropylene Glycols							
Polyglycol P-400	1.053a	1.007	0.945	0.784	4.69	-20 to 400	4.66
Polyglycol P-750	1.047a	1.004	0.945	0.794	4.44	-20 to 550	4.42
Polyglycol P-1200	1.045a	1.002	0.944	0.798	4.33	-20 to 550	4.32
Polypropylene Glycol Derivatives							
Ucon LB-100	1.022	0.970	0.911	0.762	4.41	-40 to 550	4.55
Ucon LB-100-X	1.027	0.975	0.917	0.767	4.41	-40 to 550	4.52
Ucon LB-250	1.042	0.992	0.935	0.790	4.25	0 to 550	4.28
Ucon LB-250-X	1.048	0.996	0.939	0.794	4.27	0 to 550	4.29
Ucon LB-550-X	1.037b	0.994	0.939	0.797	4.19	77 to 550	4.22
Poly(ethylene-propylene) Glycol Derivatives							
Ucon HB-100-X	1.070	1.017	0.958	0.805	4.47	-40 to 450	4.40
Ucon HB-260	1.086a	1.033	0.976	0.828	4.34	32 to 550	4.20
Ucon HB-260-X	1.090a	1.036	0.979	0.830	4.36	32 to 550	4.21
Ucon HB-600-X	1.095a	1.051	0.994	0.849	4.27	77 to 550	4.06
			PETROLEUM OILS				
Navy Symbol 2135	0.937b	0.909	0.861	0.736	3.64	0 to 500	4.00
Navy Symbol 2250	0.954c	0.937	0.890	0.765	3.61	32 to 500	3.85
Grade 1065	0.890c	0.874	0.828	0.709	3.49	32 to 550	3.99
Grade 1120	0.903c	0.887	0.841	0.725	3.44	32 to 700	3.88
			DIESTER OILS				
Di(n-butyl) sebacate	0.950c	0.932	0.874	0.722	4.35	32 to 450	4.67
Di(2-ethylhexyl) sebacate	0.962	0.913	0.860	0.719	4.09	-40 to 500	4.48
Di(undecvl) sebacate	0.942	0.896	0.844	0.708	3.92	-40 to 450	4.38
			HALOCARBONS				
Fluoro Lubricant FCD-331	2.083c	2.040	1.903	1.561f	11.15	(g)	5.47
Fluorolube - Standard	1.994c	1.953	1.832	1.550f	9.07	32 to 300	4.64
Fluorolube - Light Grease		1.975d	1.898	1.594	8.91	130 to 450	4.51

a - Density at -20°F.
b - Density at 0°F.
c - Density at 32°F.
d - Density at 130°F.

e - Density at 450°F.
f - Density at 500°F.
g - Average value; graph curves

Table III

Kinematic Viscosities of Fluids

Identification	Viscosity, Centistokes °F																	Kinematic V.I.
	-40	-20	0	32	100	130	210	250	300	350	400	450	500	550	600	650	700	
SILICONES																		
Polymethylsiloxanes																		
DC 500 "A"	119.8c	78.a	56.9	35.8	17.11	13.0a	7.16	5.54	4.16	3.20	2.52	2.028	1.641	1.358				207
DC 500 "B"	329. c	215.a	152.8	94. a	44.6	33.8a	18.21	13.98	10.40	7.93	6.19	4.90	3.96	3.22				169
DC 500 "C"	564. c	360.a	259.	160. a	74.7	56. a	30.2	23.28	17.20	13.07	10.15	8.09	6.48	5.26				155
DC 200 "D"	1320 c	840.a	608.	375. a	173.7	130. a	69.9	53.4	39.7	30.1	23.46	18.56	15.01	12.3				139
DC 200 "E"	2144. c	1380.a	980.	610. a	279.	208. a	111.8	85.5	63.1	47.9	36.9	29.0	23.19	17.7	14.			
Polyethylsiloxanes																		
DC 400 "A"	360. c	178.a	100.3	45.7	13.51	9.16	4.09	3.00	2.178	1.643	1.309	1.035						218
DC 400 "B"	5460. c	2100.a	960.	296.	51.7	30.7	11.52	7.92	5.35	3.78	2.80	2.15						159
DC 400 "C"	8180. c	3200.a	1482.	493.	98.6	62. a	22.95	15.56	10.26	7.05	5.28	3.84						152
Poly(methyl-phenyl)siloxanes																		
DC 702			657. c	113.8	17.29	10.2	4.08	2.90	2.046	1.522	1.176	0.940	0.765	0.630	0.532	0.446	0.38	159
DC 703			2600. c	308.	34.2	19.3	6.84	4.74	3.25	2.377	1.805	1.426	1.141	0.935	0.780	0.65	0.55	152
DC 710			18300. c	1555	122.0	66.9	21.05	14.30	9.56	6.84	5.17	3.97	3.15	2.6				144
DC 550			2960.	612	95.4	56.2	20.68	14.34	9.77	6.99	5.22	4.01	3.16	2.53	2.066	1.698	1.42	152
POLYALKYLENE GLYCOLS and DERIVATIVES																		
Polyethylene Glycols																		
Polyethylene Glycol 200	29600.	4780.	1164.	221.0	25.5	13.69	4.34	2.88	1.922	1.376	1.044	0.828	0.674	0.561	0.48			75
Carbowax 1000						60.4	18.43	12.14	7.99	5.66	4.36	3.46	3.0					
Polyprolylene Glycols																		
Polyglycol P-400		21920.	3780.	464.	33.5	16.30	4.64	2.99	1.985	1.431	1.084	0.862	0.701	0.581				26
Polyglycol P-750		32300.	5520.	681.	51.6	25.5	7.33	4.75	3.15	2.228	1.709	1.339	1.090	0.88				111
Polyglycol P-1200		41400.	7170.	930.	73.4	36.7	10.77	7.00	4.64	3.30	2.493	1.95	1.62	1.28				130
Polypropylene Glycol Derivatives																		
Ucon LB-100	12000.	2269.	623.	138.3	19.59	11.3a	4.16	2.91	2.040	1.545	1.191	0.99	0.80					134
Ucon LB-100-X	16570.	2910.	760.	158.3	20.87	12.1a	4.23	2.94	2.070	1.555	1.217	0.985	0.80	0.67				125
Ucon LB-250		10350.	2422.	456.	53.9	30.1a	9.97	6.78	4.69	3.41	2.63	2.08	1.68	1.4				148
Ucon LB-250-X		13670.	3010.	534.	57.5	30.8a	10.13	6.86	4.68	3.43	2.63	2.102	1.69	1.5				144
Ucon LB-550-X			9410.	1359.	121.7	63. a	18.90	12.53	8.35	5.85	4.50	3.53	2.87	2.3				140
Poly(ethylene-propylene) Glycol Derivatives																		
Ucon HB-100-X	9510.	1976.	554.	140.0	21.72	12.6a	4.77	3.36	2.381	1.784	1.411	1.140	0.948	0.799				156
Ucon HB-260		6500.	1667.	362.	49.7	29. a	10.00	6.93	4.75	3.53	2.74	2.21	1.79	1.55				154
Ucon HB-260-X		7800.	1966.	406.	52.3	29.5a	10.10	6.96	4.77	3.54	2.74	2.19	1.82	1.55				151
Ucon HB-600-X		31000.	6900.	1226.	134.2	71. a	23.14	15.61	10.41	7.58	5.73	4.54	3.67	3.2				143
PETROLEUM OILS																		
Navy Symbol 2135			15010.	1401.	68.5	28.8a	6.70	4.17	2.62	1.829	1.358	1.057	0.846	0.698	0.583	0.496	0.42	29
Navy Symbol 2250				8080.	169.1	62. a	9.77	5.52	3.25	2.166	1.586	1.207	0.953	0.775	0.643	0.542		19
Grade 1065				1748.	120.6	53. a	12.37	7.49	4.60	3.11	2.259	1.728	1.366	1.113	0.923	0.780	0.66	101
Grade 1120				8800.	369.	140. a	24.89	13.78	7.72	4.92	3.41	2.52	1.940	1.544	1.263	1.05	0.90	95
DIESTER OILS																		
Di(n-butyl)sebacate				19.63	6.10	4.27	2.085	1.593	1.213	0.953	0.773	0.640	0.543	0.461				151
Di(2-ethylhexyl)sebacate	1410.	445.a	187.	60.9	12.61	7.96	3.32	2.406	1.742	1.333	1.054	0.862	0.716	0.609	0.515			154
ndecyl)sebacate	8990.	2159.	706.	161.7	23.03	13.9	4.68	3.26	2.285	1.697	1.314	1.067	0.865					138
HALOCARBONS																		
Fluoro Lubricant FCD-331				5240. c	49.0	17.16	3.28	1.916	1.168	0.788	0.562	0.423	0.334					-694
Fluorolube - Standard				2690. c	86.9	31.7	5.61	3.20	1.886	1.221	0.869	0.650	0.51					-178
Fluorolube - Light Grease							72.0	26.6	10.53	5.30	3.11	2.059	1.446	1.074	0.83			

a Interpolated value
c Sample cloudy

value of water at 68°F (1.007 centistokes). At temperatures above 400°F the viscosities of some of the fluids were not reproducible with this precision as is indicated by the number of significant figures in the value reported.

Due to gel formation and pyrolysis within the 30 to 40 minutes required for measurements, the viscosities of the methyl silicones could not be determined accurately above 550°F. These samples became cloudy at 500°F, the turbidity increasing with a further rise in temperature. The phenomenon was not entirely reversible since a slight cloudiness remained after the samples had cooled to room temperature. Such turbidity effects are attributed to the precipitation of higher polymers formed at the high temperatures.[29] It was also of interest to note that the viscosity of these silicones at 250°F decreased about 1 percent after subjecting the samples to a temperature of 550°F for a short time, thereby indicating that cracking had occurred.[29] Polyethylsiloxanes "A" and "C" became cloudy at temperatures below zero apparently because of the precipitation of high polymers. Formation of gel in the viscometers became apparent at 450°F, while at 500°F the quantity was sufficient to foul the capillaries, preventing further measurements. The poly(methyl-phenyl) siloxanes became cloudy at 0°F, the turbidity increasing with the aromaticity. However, these fluids were the most heat-stable of the silicones, viscosity measurements being obtained through 700°F on all but the DC 710. No clouding at high temperatures was observed with any of these fluids, and only the DC 710 formed gel below 700°F.

The polyglycols and "Ucons" remained clear while measurements were made at low temperatures, but vaporlocking difficulties prevented viscosity determinations at temperatures above 550°F in most cases. From 300° to 350°F, the times of successive passes through the viscometers decreased 0.2 percent to 0.3 percent with the uninhibited "Ucon" fluids although the phenomenon disappeared at higher temperatures. The same effect was noted to a lesser degree with the inhibited fluids at temperatures of 50° to 100° higher. It was of interest that these inhibited fluids exhibited a reversible color change about 500°F.

The petroleum oils caused some lacquering above the liquid level in the viscometers at temperatures above 500°F, but it was possible to make measurements on all the oils at 700°F except Navy Symbol 2250 which vaporlocked at that temperature. These oils were not studied below the cloud point.

The butyl sebacate and 2-ethylhexyl sebacate diesters vaporlocked at 600° and 650°F respectively, while it was evident that the undecyl sebacate was changing chemically at 550°F. No difficulties were encountered with the diesters while making low-temperature measurements.

Methods of relating the change of viscosity with temperature of fluids, particularly petroleum oils and other hydrocarbons, has been a subject of controversy for many years. Evans[30] investigated a number of equations relating the change of viscosity with temperature as applied to hydrocarbons and petroleum oils and concluded that the three outstanding equations were the A.S.T.M. equation, a modification of the Andrade and Silverman equation, and a modification of Batschinski's equation. Though empirical, the A.S.T.M. equation fits the data for hydrocarbons with remarkable accuracy over a rather narrow temperature range (32° to 212°F) and has only two arbitrary constants. The other two equations, though having some theoretical justification, are tedious and unwieldy to use because each contains three arbitrary constants. As a large number of theoretical equations attempting to relate viscosity with temperature refer to the absolute viscosity and contain a term which is a function of the molecular weight, they are not readily adaptable for work with most lubricating fluids.

The A.S.T.M. equation in the chart form of Method D341-43[22] is used widely for estimating the viscosities of petroleum oils at temperatures from 300°F to the cloud point and has been used with success for such synthetic oils as silicones,[4] "Ucons,"[12] and diesters.[15] This well-known (Walther) equation is

$$\log \log (\mu + c) = A \log T + B$$

where

u = viscosity (centistokes),

c = a constant which Walther evaluated for petroleum oil as 0.95,

A and B = constants characteristic of each liquid, and

T = absolute temperature.

The A.S.T.M. equation and chart differ only in that c is a "constant" varying from 0.75 at 0.4 centistokes to 0.6 at 1.5 centistokes and above.[31] Use of this equation in chart form obviates the necessity of determining the constants A and B.

Other choices of c in the Walther equation have been made, values from 0.6 to 0.95 having been introduced to extend the viscosity range of the chart below 1.0 centistoke, while the particular value assigned was determined by the ability of the equation to predict the viscosity of the fluids of interest to the particular investigators. In general, the larger values of the constant c, tend to produce more linear graphs in the low-viscosity region. Objections to the choice of a varying term, c, in the A.S.T.M. chart (D341-39) have been raised. No difference in the dimensions of this chart and one based on a value of c equal to 0.6 can be observed above 1.5 centistokes, although below 1.0 centistoke the differences become increasingly great. At 0.4 centistokes the chart extends to minus infinity. A chart based on a value of 0.75 for c does not differ significantly from the A.S.T.M. chart above 3.0 centistokes, but it is approximately 16.5 percent shorter over the range 0.4 to 3.0 centistokes.

The A.S.T.M. chart was selected for this investigation although it was necessary to combine the C and D charts (to include the viscometric data) and to extend the range at both the high and low temperatures. These modified charts were printed on the same scale as the A.S.T.M. chart by the Nautical Chart Branch of the Coast and Geodetic Survey.

The data from Table III were plotted on these extended A.S.T.M. charts and the resulting curves will be found in Figures 1 through 4. Outstanding features of these graphs are listed and compared in Table IV, which also gives the approximate temperature limits of the essentially linear region of each graph. With the exception of Fluorolube-Standard, the graphs of all fluids are linear for a temperature interval varying from 140° to 450°F. Brief remarks are given in the last column of Table IV concerning the nature and amount of deviation from linearity at the extremes of the curves.

As noted in Figures 1 and 3, the polymethylsiloxane-, diester- and petroleum-oil graphs show no curvature in the low-temperature region but are convex at high temperatures. This behavior of the petroleum oils agrees with the only other available work.^{32} The polyglycols and low-viscosity "Ucon" fluid graphs in Figure 2 show both convexity at elevated and concavity at low temperatures. It is interesting to note that the graphs of the higher viscosity "Ucon" fluids are almost straight at the high-temperature end. The halocarbons are unique among the materials studied in that these curves (Figure 4) are convex at all temperatures. It is seen that in each homologous series of fluids increasing molecular weight or viscosity extends the linear portion of the graph and causes the convexity at high temperatures to decrease.

From the straight-line portion of each viscosity-temperature graph the tangent has been calculated and is given as the "slope" in the fifth column of Table IV. The uniquely low slopes of the polymethylsiloxanes are evident here, as is the increase in the slope from methyl to ethyl to phenyl side-chains, this being analogous to the rule for hydrocarbons that the slope increases with an increase in the ratio of the cross-sectional diameter of the molecule to its length. This relation also explains how the presence of side-chains in the polypropylene glycols causes the viscosity-temperature curves of these materials to have higher slopes than do those of the polyethylene glycols. As "Ucon" fluids are polymers of ethylene and/or propylene glycol, chain-stoppered at one end by a monohydric alcohol,^{10,11} comparisons with the analogous polyglycols of the same viscosities reveal they have much lower slopes than would be expected from the increase in chain-length caused by the chain-stopper. It is obvious to assume that this improvement is caused by the decrease in association or hydrogen bonding resulting from a blocking of one OH at the end of the polyglycol. The addition of the "Ucon" antioxidant had little effect on the slope of the viscosity-temperature graphs at the higher temperatures. The relations between the molecular structures and the slopes (or V.I.'s) of the diesters and petroleum oils have been discussed previously.^{15} Of the fluids considered here, the halocarbons had the lowest viscosity indices.

The viscoisty data presented in Table III, plotted using the Walther equation with c = 0.6, gave graphs essentially the same as those on the A.S.T.M. chart except that the convexity was greater in the low-viscosity region. When c was chosen as 0.75, the convexity at low viscosities was less than on the A.S.T.M. chart. The linear portion of some of the graphs was extended to higher temperatures (notably the fluorocarbons), but in no case was the convexity eliminated. By using the Walther equation as a three-constant equation it is evident that c can be selected for each liquid so as to increase the range of linearity of the graph. Continuously increasing the constant, c, to values considerably greater than the viscosity of the liquids under investigation would appear as an artificial means of obtaining linear graphs. Lack of theoretical justification also makes this inappropriate here. An attempt to correlate convexity at high temperature on the A.S.T.M. chart with the properties of the liquids studied is probably mathematically equivalent to correlating such properties with the values of c.

The absolute viscosity in centipoises of the fluids investigated were calculated ($\eta = \mu\rho$) and are listed in Table V. Graphs made by plotting some of this data on the modified A.S.T.M. viscosity-temperature chart are shown in Figure 5. No particularly new features are revealed by these graphs except that the linear region is shortened and the convexity at high temperatures is increased as the density of the fluid decreases from unity. Conversely, the graphs of the halocarbons, whose densities exceed unity, are straighter for longer temperature ranges and show less convexity at the high temperatures. Further study is being made of the applicability of other equations for predicting the viscosity-temperature characteristics of these fluids.

CONCLUSIONS

It is useful to treat the linear viscosity-temperature region of each fluid as a region of "more normal" or "more ideal" behavior and the regions of convexity or concavity as regions of "abnormal" behavior having their origin in the increasing prominence of some chemical or physical transformation peculiar to the particular class of liquids studied. But such an approach requires better acquaintance with other properties of the fluid in the extreme temperature regions and is justifiable only if it is thereby possible to collate a diverse group of phenomena. Because of the uniform gradation possible in all properties of the synthetic fluids like the silicones, "Ucons," and diesters, their comparative study is especially valuable.

The convexity of the graphs (Figures 1 to 4) at high temperatures cannot be explained by evaporation, cracking, or oxidation, since such behavior would cause much larger irreversible changes in the viscosities than were encountered. Convexity is thought to be due to a statistical uncoiling, as the temperature rises, of long-chain molecules because of the disorganizing effects of thermal agitation. In linear molecules with freedom of rotation about the chemical bonds in the main chain, coiling should be more pronounced the higher the molecular weight of the molecule or the higher the viscosity of the fluid. At high temperatures, the molecule exhausts its capacity to uncoil and a more random configuration results with a rapid divergence from the "normal" straight line graph on the viscosity-temperature chart.

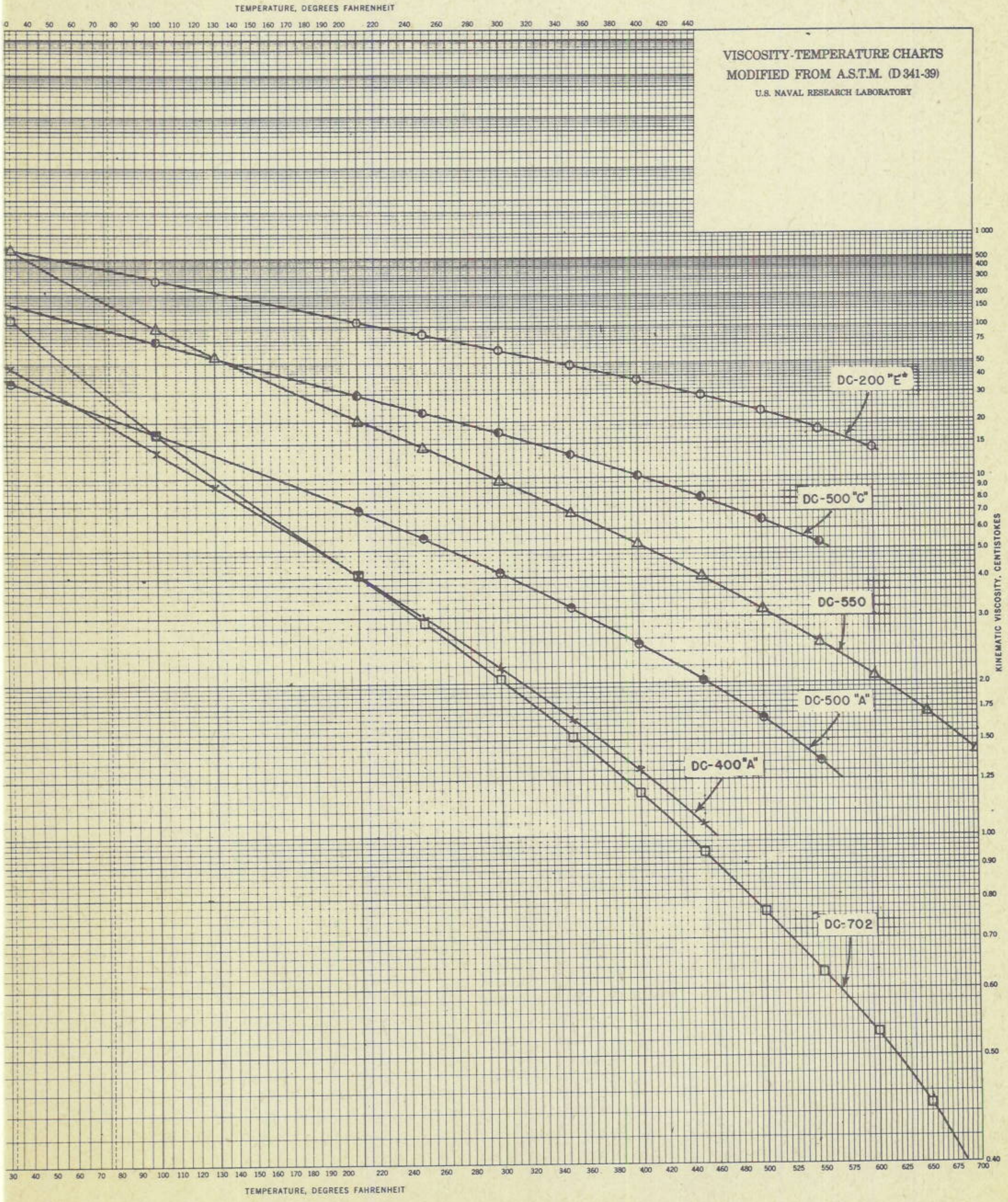
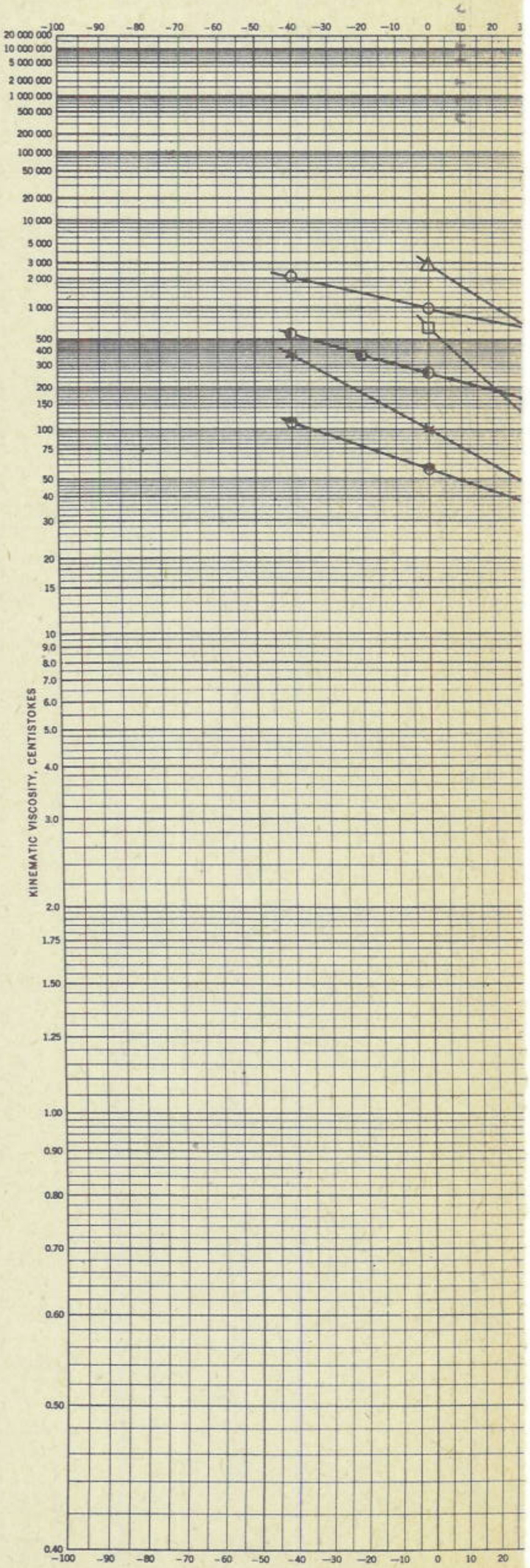


Figure 1- Silicones


KINEMATIC VISCOSITY, CENTISTOKES
20 000 000
10 000 000
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500 000
200 000
100 000
50 000
20 000
10 000
5 000
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2 000
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75
50
40
30
20
15
10
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.75
1.50
1.25
1.00
0.90
0.80
0.70
0.60
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−20
−10
0
10
20

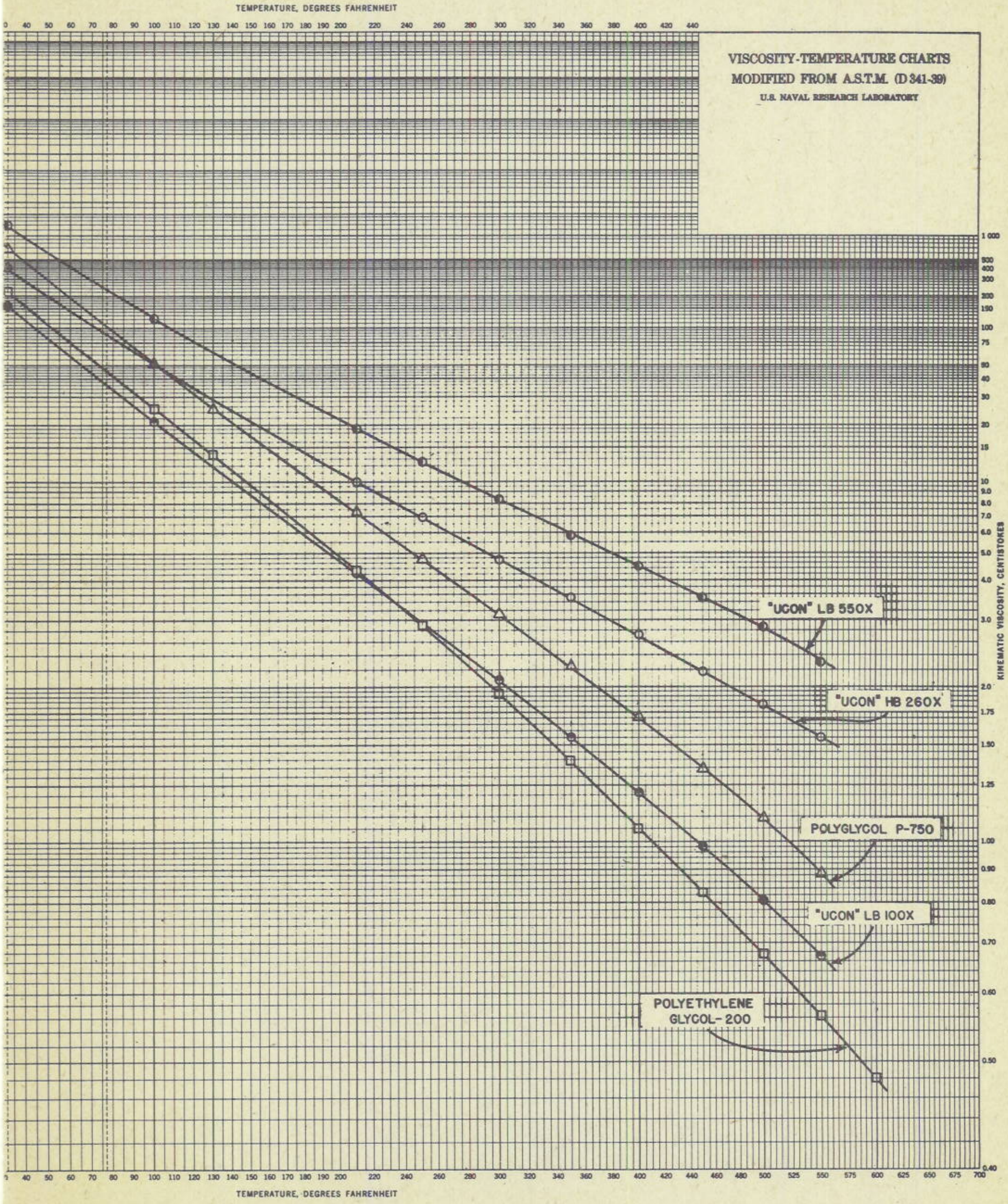
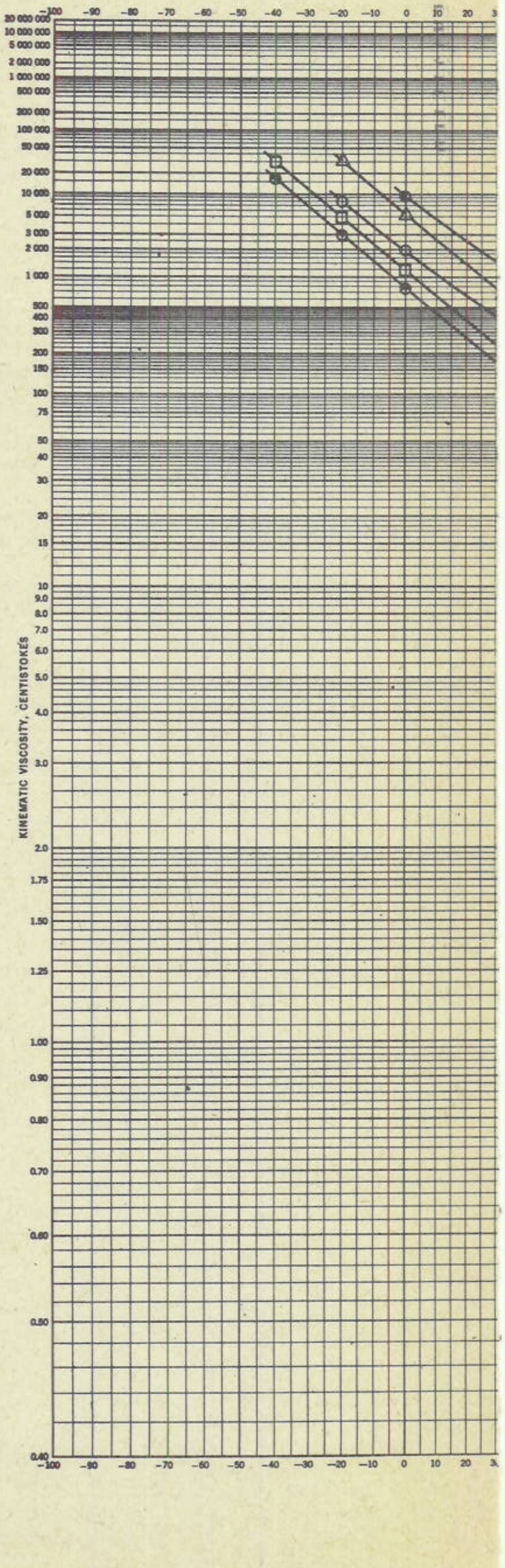


Figure 2- Polyglycols and Derivatives



KINEMATIC VISCOSITY, CENTISTOKES
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20 000
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75
50
40
30
20
15
10
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.75
1.50
1.25
1.00
0.90
0.80
0.70
0.60
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20

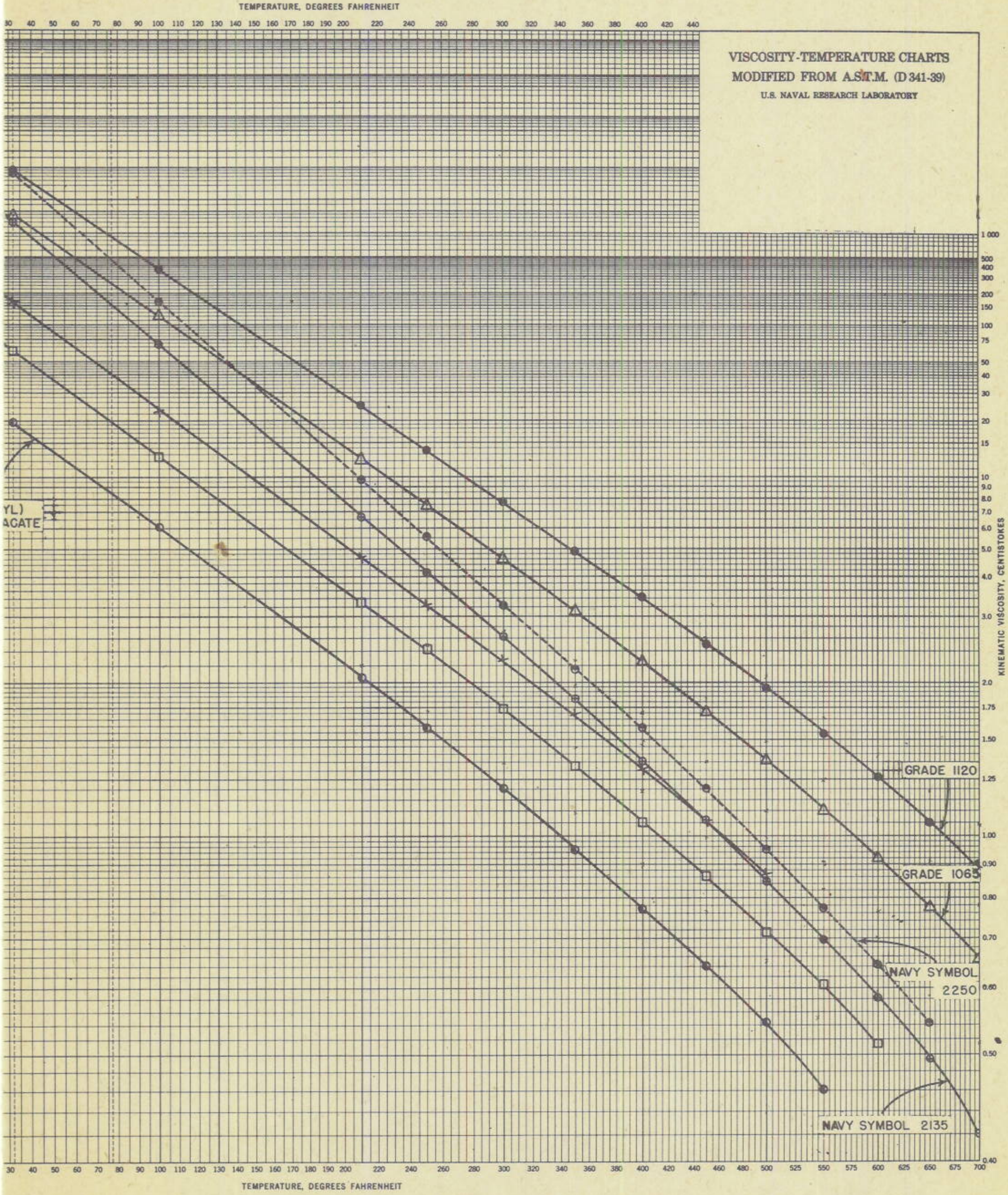
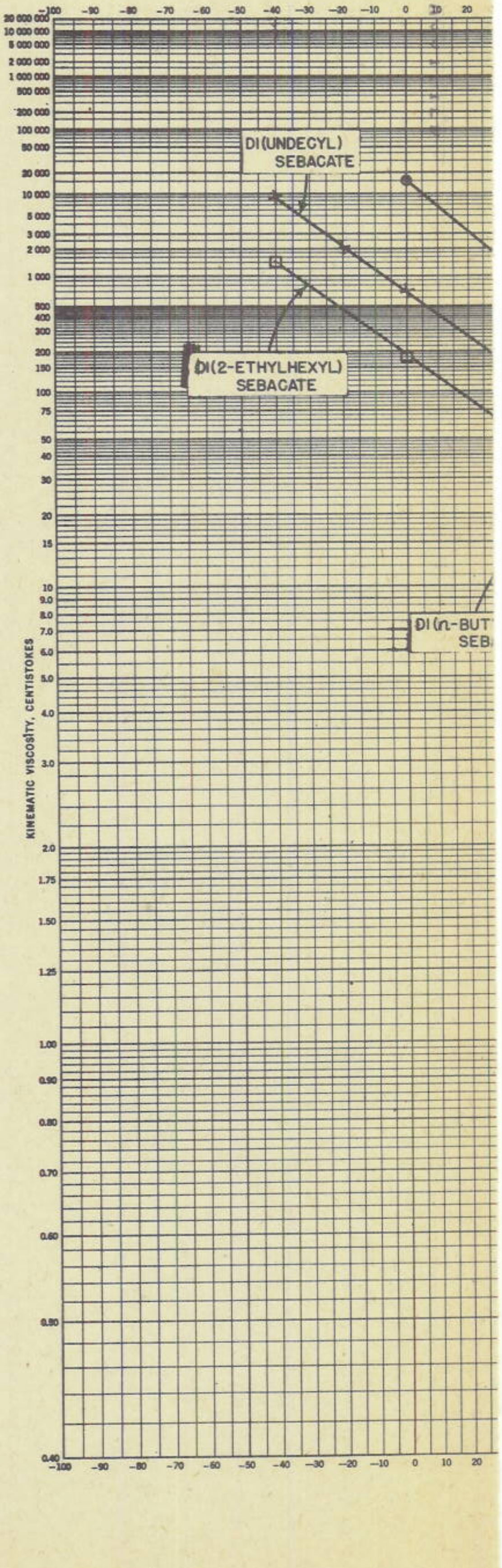


Figure 3- Petroleum Oils and Diesters


KINEMATIC VISCOSITY, CENTISTOKES
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7.0
6.0
5.0
4.0
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1.25
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0.40
−100 −90 −80 −70 −60 −50 −40 −30 −20 −10 0 10 20
DI(UNDECYL) SEBACATE
DI(2-ETHYLHEXYL) SEBACATE
DI(n-BUT
SEB

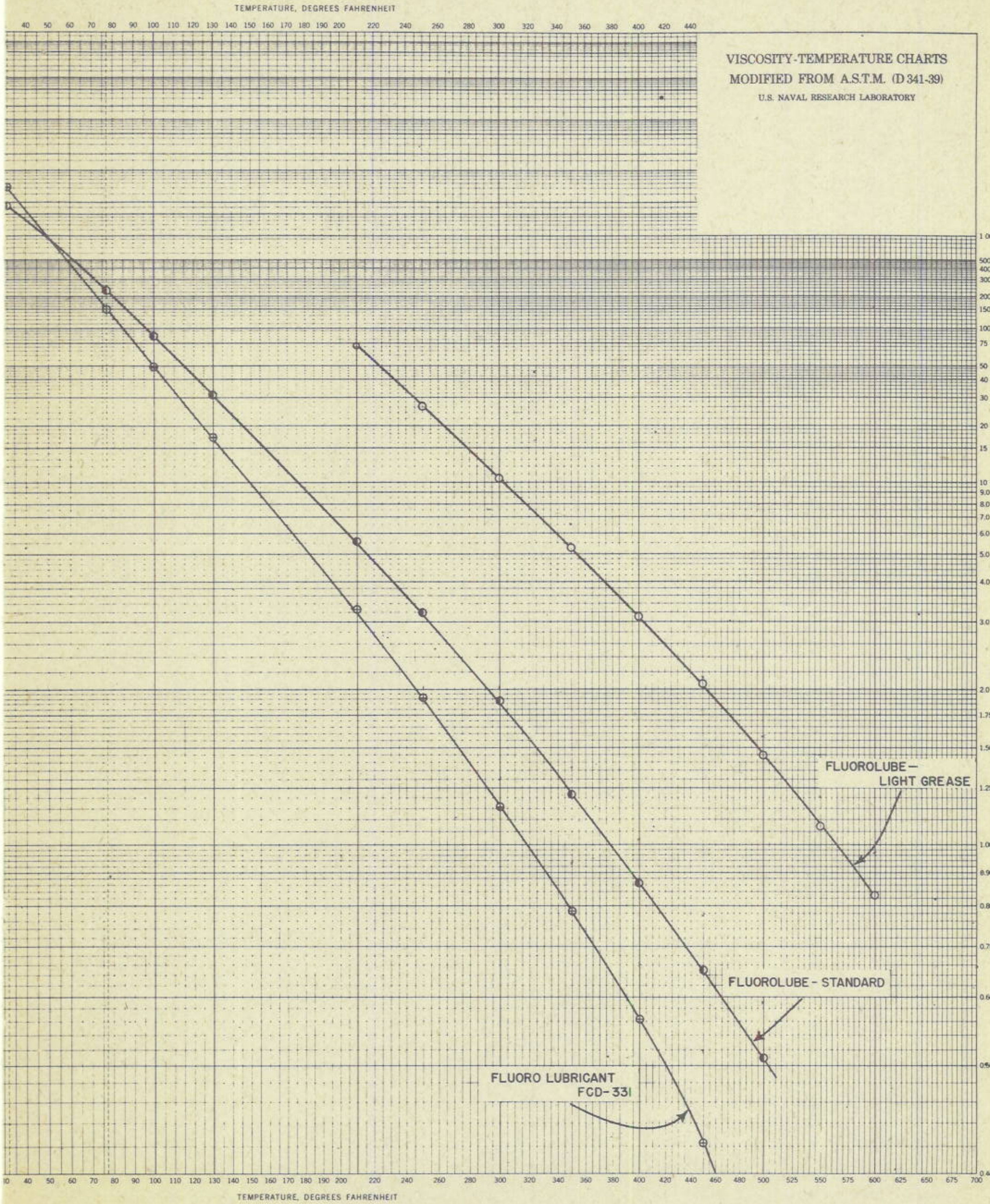
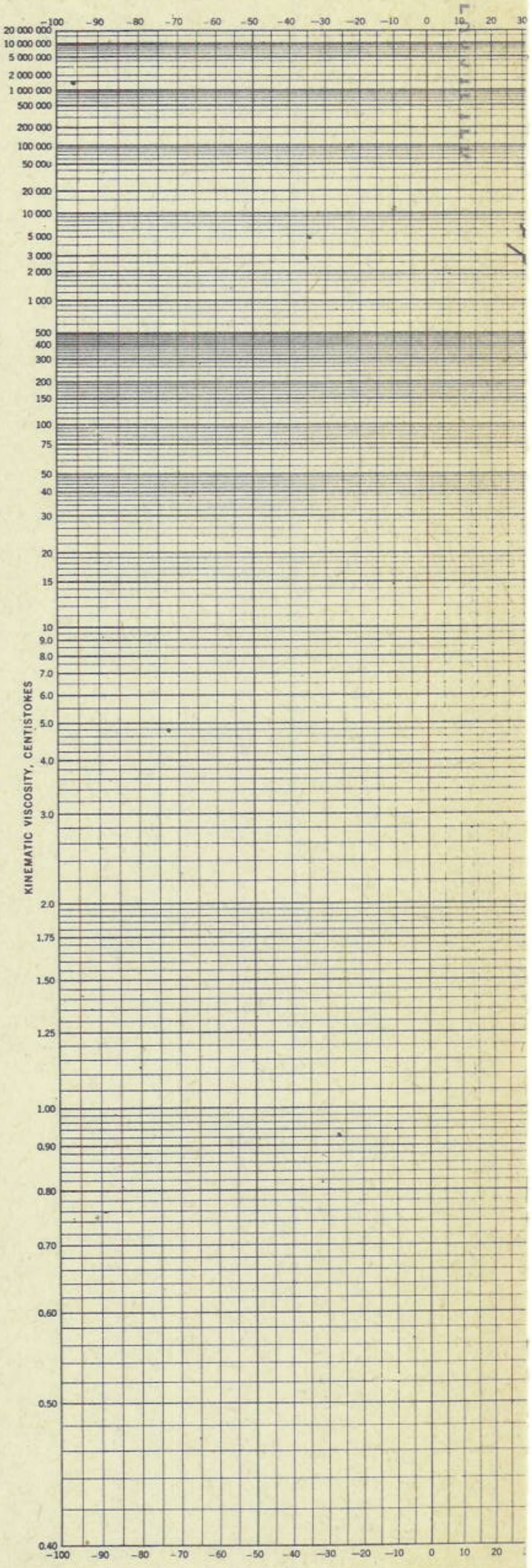


Figure 4- Halocarbons


KINEMATIC VISCOSITY, CENTISTOKES
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30
20
15
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9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.75
1.50
1.25
1.00
0.90
0.80
0.70
0.60
0.50
0.40
−100
−90
−80
−70
−60
−50
−40
−30
−20
−10
0
10
20
30

Table IV

Outstanding Features of Viscosity-Temperature Graphs

Identification	Viscosity cs. @ 100°F.	Straight Line Region			Curvature* At:	
		From	To	Slope	Low Temp. End	High Temp. End
SILICONES						
Polymethylsiloxanes						
DC 500 "A"	17.11	-40	100	0.374	None	Convex (vy)
DC 500 "B"	44.6	-40	210	0.288	None	Convex (vy)
DC 500 "C"	74.7	-40	300	0.264	None	Convex (med)
DC 200 "D"	173.7	-40	400	0.225	None	Convex (med)
DC 200 "E"	279.	-40	400	0.207	None	Convex (sl)
Polyethylsiloxanes						
DC 400 "A"	13.51	0	130	0.563	Convex (sl)	Convex (vy)
DC 400 "B"	51.7	-40	300	0.522	None	Convex (sl)
DC 400 "C"	98.6	0	350	0.449	Concave (sl)	Convex (sl)
Poly(methyl-phenyl)siloxanes						
DC 702	17.29	100	300	0.702	Concave (sl)	Convex (vy)
DC 703	34.2	100	350	0.629	Concave (vy)	Convex (vy)
DC 710	122.0	210	400	0.448	Concave (vy)	Convex (vy?)
DC 550	95.4	100	400	0.441	Concave (sl)	Convex (vy)
POLYALKYLENE GLYCOLS AND DERIVATIVES						
Polyethylene Glycols						
Polyethylene Glycol 200	25.5	-40	210	0.787	Concave(med)	Convex (sl)
Carbowax 1000	Solid	130	250	0.520		Convex (med)
Polypropylene Glycols						
Polyglycol P-400	33.5	-20	300	0.852	None	Convex (med)
Polyglycol P-750	51.6	100	350	0.715	Concave(med)	Convex (med)
Polyglycol P-1200	73.4	130	400	0.609	Concave(med)	Convex (sl)
Polypropylene Glycol Derivatives						
Ucon LB-100	19.59	32	350	0.744	Concave(sl)	Convex (sl)
Ucon LB-100-X	20.87	0	400	0.756	Concave(sl)	Convex (sl)
Ucon LB-250	53.9	100	450	0.570	Concave(med)	Convex (med)
Ucon LB-250-X	57.5	100	500	0.582	Concave(med)	Convex (sl)
Ucon LB-550-X	121.7	210	500	0.476	Concave(vy)	Convex (sl)
Poly(ethylene-propylene)Glycol Derivatives						
Ucon HB-100-X	21.72	100	400	0.687	Concave(sl)	Convex (sl)
Ucon HB-260	49.7	100	550	0.520	Concave(med)	None
Ucon HB-260-X	52.3	100	550	0.552	Concave(med)	None
Ucon HB-600-X	134.2	210	500	0.449	Concave(vy)	None
PETROLEUM OILS						
Navy Symbol 2135	68.5	0	300	0.830	None	Convex (med)
Navy Symbol 2250	169.1	32	300	0.865	None	Convex (med)
Grade 1065	120.6	32	300	0.685	None	Convex (med)
Grade 1120	369	32	350	0.661	None	Convex (med)
DIESTER OILS						
Di(n-butyl)sebacate	6.10	32	210	0.713	None	Convex (vy)
Di(2-ethylhexyl) sebacate	12.61	-40	300	0.713	None	Convex (med)
Di(undecyl) sebacate	23.03	-40	300	0.719	None	Convex (med)
HALOCARBONS						
Fluoro Lubricant FCD-331	49.0	32	210(?)	1.184	Convex (sl)	Convex (vy)
Fluorolube-Standard	86.9	None	--	None	Convex(med)	Convex (vy)
Fluorolube-Light Grease	Solid	210	400(?)	0.939	Convex(med)	Convex (vy)

* Vy = Very; Med = Medium; Sl = Slight

Table V

Absolute Viscosities of Fluids

Identification	Viscosity, centipoises at °F																
	-40	-20	0	32	100	130	210	250	300	350	400	450	500	550	600	650	700
						SILICONES											
Polymethylsiloxanes																	
DC 500 "A"	121.1		56.3	34.8	16.07		6.34	4.79	3.50	2.62	2.00	1.560	1.223	0.978			
DC 500 "B"	336.		152.8		42.4		16.35	12.29	8.90	6.59	5.00	3.84	3.01	2.37			
DC 500 "C"	578.		260.		71.2		27.2	20.58	14.79	10.94	8.25	6.39	4.97	3.91			
DC 200 "D"	1360.		613.		166.4		63.3	50.1	34.3	25.3	19.19	14.77	11.60	9.21			
DC 200 "E"	2210.		989.		267		101.5	76.1	54.7	40.4	30.3	23.15	17.95	13.3	10.		
Polyethylsiloxanes																	
DC 400 "A"	361.		98.9	44.5	12.74	8.52	3.66	2.64	1.867	1.372	1.066	0.820					
DC 400 "B"																	
DC 400 "C"	8520.		1519.	500.	97.2		21.60	14.39	9.29	6.24	4.57	3.25					
Poly(methyl-phenyl)siloxanes																	
DC 702			727.	124.3	18.33		4.12	2.87	1.976	1.434	1.081	0.841	0.666	0.532	0.436	0.353	0.29
DC 703			2904.	340.0	36.6		6.99	4.75	3.19	2.280	1.691	1.305	1.017	0.813	0.658	0.53	0.44
DC 710			20600.	1728.	132.0	71.6	21.83	14.59	9.56	6.70	4.96	3.73	2.89	2.4			
DC 550			3270.	667.	101.2	59.0	21.01	14.33	9.56	6.70	4.89	3.68	2.84	2.22	1.768	1.416	1.15
					POLYALKYLENE GLYCOLS and DERIVATIVES												
Polyethylene Glycols																	
Polyethylene Glycol 200	34800.	5570.	1347.	252.4	28.3	15.0	4.61	3.01	1.964	1.372	1.016	0.785	0.621	0.502	0.42		
Carbowax 1000						66.3	19.61	12.70	8.19	5.68	4.27	3.32	2.8				
Polypropylene Glycols																	
Polyglycol P-400		23080.	3940.	477.	33.4	16.02	4.38	2.78	1.792	1.259	0.928	0.718	0.567	0.456			
Polyglycol P-750		33800.	5730.	697.	51.3	25.0	6.93	4.40	2.85	1.967	1.471	1.122	0.889	0.70			
Polyglycol P-1200		43300.	7430.	951.	72.8	35.9	10.17	6.49	4.20	2.91	2.151	1.64	1.32	1.02			
Polypropylene Glycol Derivatives																	
Ucon LB-100	12300.	2298.	626.	136.9	18.81		3.79	2.60	1.777	1.312	0.986	0.80	0.63				
Ucon LB-100-X	17020.	2960.	767.	157.5	20.14		3.88	2.65	1.615	1.330	1.014	0.799	0.64	0.52			
Ucon LB-250		10700.	2480.	461.	52.9		9.32	6.22	4.20	2.98	2.24	1.74	1.36	1.1			
Ucon LB-250-X		14190.	3097.	542.	56.7		9.51	6.32	4.21	3.01	2.26	1.759	1.38	1.2			
Ucon LB-550-X			9670	1378.	119.8		17.75	11.55	7.53	5.15	3.87	2.96	2.35	1.8			
Poly(ethylene-propylene) Glycol Derivatives																	
Ucon HB-100-X	10180.	2095.	582.	145.2	21.87		4.56	3.16	2.188	1.600	1.233	0.970	0.785	0.643			
Ucon HB-260		7000.	1780.	382.	50.9		9.76	6.64	4.45	3.23	2.45	1.92	1.52	1.28			
Ucon HB-260-X		8430.	2108.	429.	53.8		9.89	6.69	4.48	3.25	2.44	1.92	1.55	1.28			
Ucon HB-600-X		33900.	7490.	1313.	139.7		23.00	15.25	9.95	7.09	5.24	4.05	3.20	2.7			
						PETROLEUM OILS											
Navy Symbol 2135			14060.	1296.	61.7		5.77	3.55	2.17	1.481	1.076	0.818	0.639	0.514	0.418	0.346	0.29
Navy Symbol 2250				7710.	157.1		8.70	4.83	2.79	1.819	1.304	0.970	0.748	0.593	0.480	0.394	
Grade 1065				1556.	104.4		10.24	6.10	3.66	2.42	1.721	1.286	0.993	0.789	0.637	0.524	0.43
Grade 1120				7950.	324.		20.93	11.41	6.26	3.91	2.65	1.91	1.439	1.119	0.894	0.726	0.61
						DIESTER OILS											
Di(n-butyl)sebacate				18.65	5.62		1.822	1.364	1.012	0.774	0.611	0.492	0.405	0.333			
Di(2-ethylhexyl)sebacate	1360.		176.	56.8	11.40		2.86	2.031	1.435	1.070	0.825	0.657	0.531	0.438	0.359		
Di(undecyl)sebacate	8470.	2017.	654.	147.8	20.52		3.95	2.73	1.849	1.339	1.012	0.800	0.631				
						HALOCARBONS											
Fluoro Lubricant FCD-331				10910.	98.9	34.27	6.24	3.56	2.108	1.377	0.949	0.687	0.521				
Fluorolube - Standard				5360.	167.9	60.6	10.27	5.74	3.30	2.081	1.437	1.042	0.791				
Fluorolube - Light Grease							136.6	49.5	19.16	9.42	5.38	3.48	2.376	1.712	1.282		

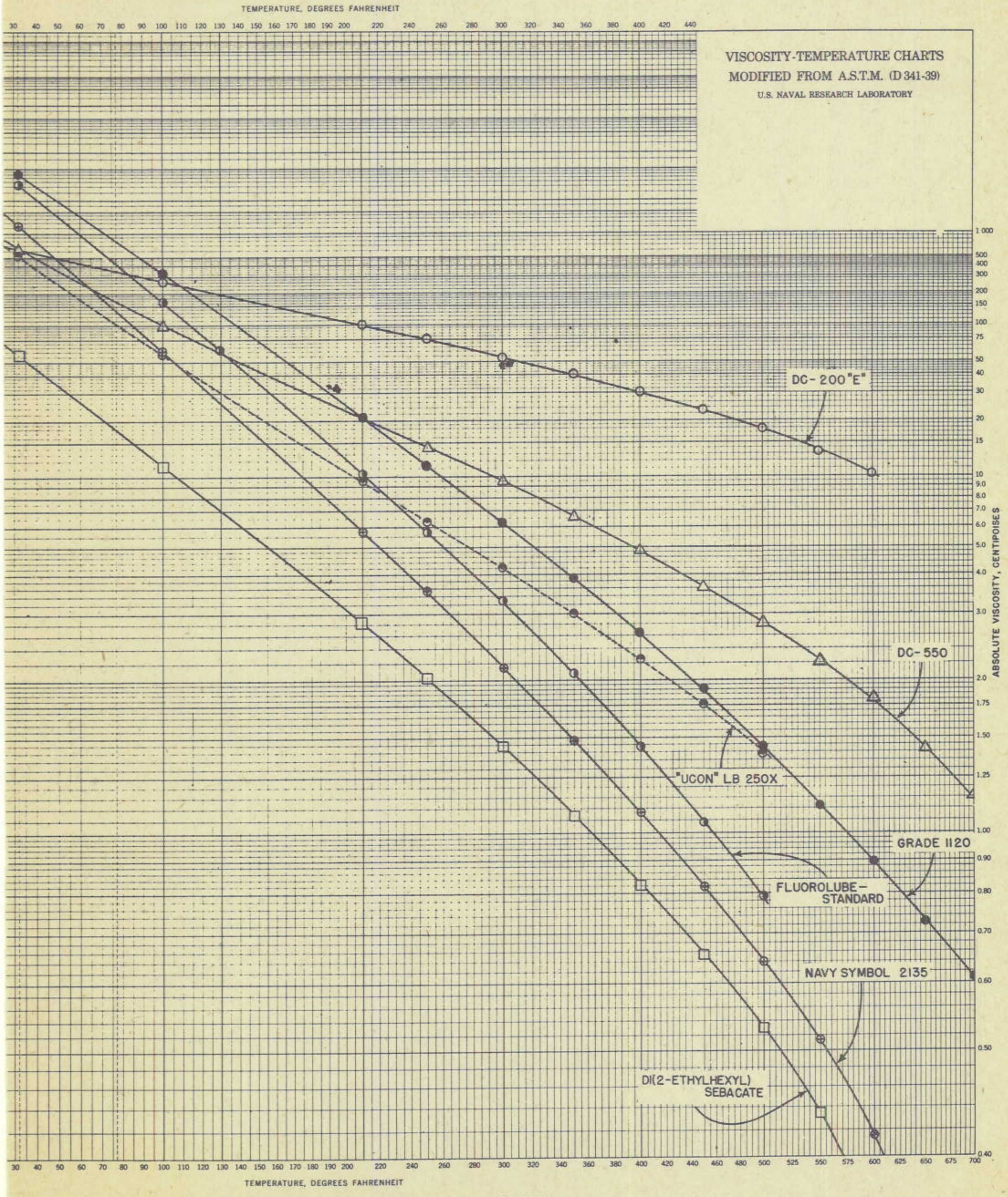
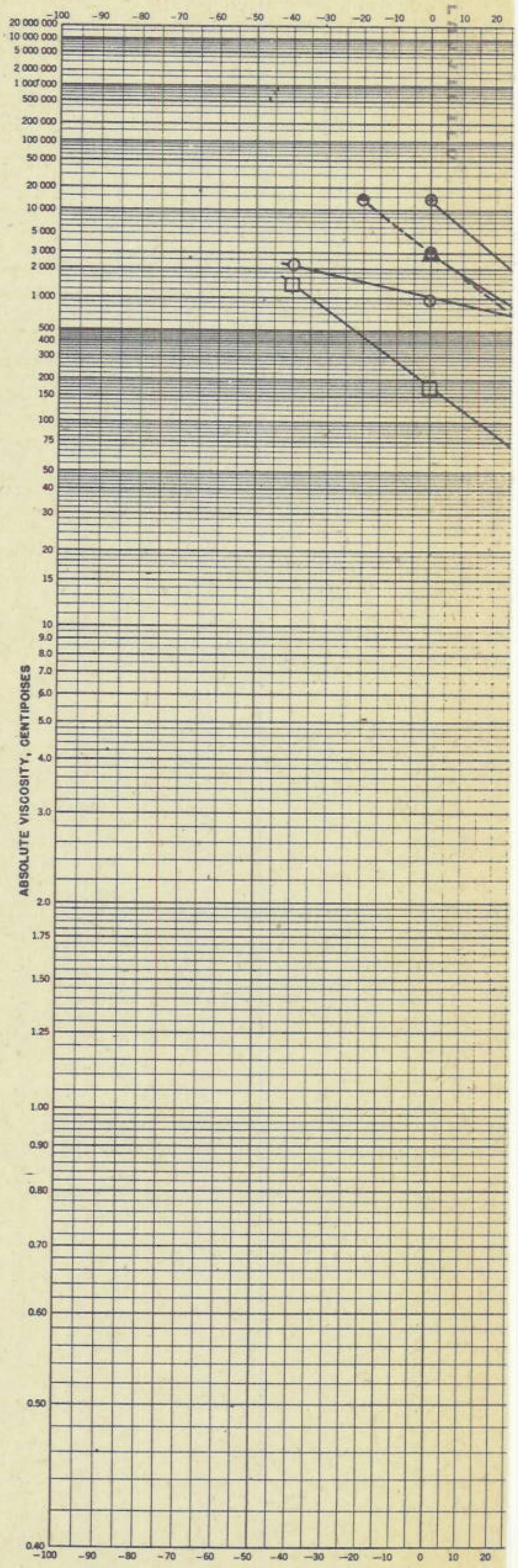


Figure 5- Absolute Viscosity Various Fluids


-100
-90
-80
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500
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200
150
100
75
50
40
30
20
15
10
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.75
1.50
1.25
1.00
0.90
0.80
0.70
0.60
0.50
0.40
ABSOLUTE VISCOSITY, CENTIPOISES

The ability to coil is pronounced in the polymethylsiloxanes, high-VI petroleum oils, and aliphatic diesters, and may be attributed to essentially straight-chain and short-branched structure. At high temperatures the graphs of the aromatic silicones are very convex, probably because of the great hindrance offered to coiling by large phenyl groups. Similar behavior is observed in the halocarbons, but here the cause is the presence of the larger-diameter fluorine or chlorine atoms and the slightly shorter carbon-carbon bond distance,[33] both of which hinder free rotation. Needing further study is the exceptional behavior of the "Ucon" fluids at high temperatures, possibly caused by loss of water and consequent increase in association between the polymer molecules.

At low temperatures the lack of concavity in the viscosity-temperature graphs of the polymethylsiloxanes, petroleum oils, and aliphatic diesters may be considered evidence that no new phenomena are occurring such as precipitation, crystallization, or association. The slight curvature of the polyethylsiloxanes can be associated with the precipitation of an insoluble fraction as reported earlier. Similarly, the concavity of the graphs of the poly(methyl-phenyl) siloxanes may in part be due to the precipitation of an insoluble fraction. The higher the aromaticity the more pronounced the concavity, possibly because of the van der Waal's forces developing at low temperatures between adjacent phenyl groups of different polymer molecules. A rapid increase in association due to hydrogen bonding between hydroxyl groups may be the cause of the concavity of the graphs of the polyglycols and "Ucons" at low temperatures.

Many of the fluids investigated show considerable promise as lubricants where extreme temperatures are encountered. The limitations, however, of the A.S.T.M. viscosity-temperature chart can be seen. Obviously, there is need for developing equations capable of predicting more accurately the viscosity-temperature relationship of lubricants, particularly at higher temperatures. There is also need for additional study of the manner in which molecular structure and behavior influences viscosity and the viscosity-temperature relationship.

SUMMARY

Comparative data have been presented on the kinematic and absolute viscosities, densities, and cubical coefficients of expansion as functions of temperature over the entire useful range of a variety of petroleum-base and synthetic lubricants. Data have been presented permitting better definition of the regions for which linearity can be assumed safely on the extended A.S.T.M. viscosity-temperature chart. The deviations from linearity on these charts can be accounted for reasonably in the light of other physical and chemical properties of the fluids. It is believed that, to be capable of predicting the change of viscosity with temperature of a lubricant over a wide temperature range, an equation must take into account other physical and chemical changes in the material. Convexity of the curves appears general, and it has been found possible to present a qualitative explanation based on the idea of coiling and uncoiling of linear molecules under changing conditions of temperature. It is pointed out that hindrances to rotation about carbon-carbon bonds may be responsible for (1) the increase in convexity of the high-temperature graphs of some of the more complex materials and (2) for the large decrease in V.I. with the halogenation of hydrocarbons.

RECOMMENDATIONS

The increasing demand for more satisfactory lubricants for use at extreme temperatures makes further investigation of other high-temperature-resistant liquids very desirable. A clear understanding of the relationship of viscosity to structure is prerequisite to the development of new materials having unusual properties as lubricants under severe conditions. The present means of predicting the viscosity-temperature characteristics of lubricants leaves much to be desired. As the fluorine- and chlorine-containing compounds show unusual high-temperature stability, these materials merit further study particularly with respect to the influence of atomic size on free rotation, helical coiling, and V.I.

ACKNOWLEDGMENT

The authors wish to express their appreciation to Chester E. Cox for his valuable work in the construction and calibration of the density apparatus and for taking all of the measurements of Table II. Much of the data on the viscosity of silicones was obtained by Miss Lorraine S. Arkin.

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