

# REPORT No. 398

## INVESTIGATION OF DAMPING LIQUIDS FOR AIRCRAFT INSTRUMENTS—II

By M. R. HOUSEMAN and G. H. KEULEGAN

## SUMMARY

*Data are presented on the kinematic viscosity, in the temperature range  $-50^{\circ}$  to  $+30^{\circ}$  C, of pure liquids and of solutions of animal oils, vegetable oils, mineral oils, glycerine, and ethylene glycol in various low freezing point solvents. It is shown that the thermal coefficient of kinematic viscosity as a function of the kinematic viscosity of the solutions of glycerine and ethylene glycol in alcohols is practically independent of the temperature and the chemical composition of the individual liquids. This is similarly true for the mineral oil group and, for a limited temperature interval, for the pure animal and vegetable oils.*

The efficiency of  $\beta$ -naphthol, hydroquinone, and diphenylamine to inhibit the change of viscosity of poppy-seed and linseed oils was also investigated.

## I. INTRODUCTION

This investigation was undertaken at the request and with the financial assistance of the National Advisory Committee for Aeronautics, with the object of finding liquids suitable for damping aircraft instruments. It is an extension and expansion of the work reported in Technical Report No. 299. (Reference 6.)

An ideal damping liquid for aircraft instruments would be transparent, homogeneous, noncorrosive, colorless, and stable in composition. It would not solidify above  $-50^{\circ}\text{C.}$ , its vapor pressure would be low, and above all, the change in viscosity with temperature would be small. While the above properties were considered in choosing the liquids to be investigated, our measurements were confined mainly to the kinematic viscosity (ratio of viscosity to density) and to the change of kinematic viscosity with temperature. The determination of the absolute viscosities of these liquids would have required additional experiments to determine the change of the density of the liquids with temperature. Such additional data were not considered essential because the resistance experienced by a body moving in a liquid depends upon the kinematic viscosity of the liquid rather than the absolute viscosity.

The liquids chosen for the tests were solutions of selected animal oils, vegetable oils, and mineral oils in m-xylene, toluene and mineral spirits, and solutions of glycerine, and ethylene glycol in various alcohols.

Data were obtained through the temperature range  $+30^{\circ}\text{C.}$  to  $-50^{\circ}\text{C.}$

The kinematic viscosity data for the above liquids and solutions are shown by curves,  $\log_{10} \frac{\nu_\theta}{\nu_0}$  being plotted against the temperature ( $\theta$ ) of the liquid;  $\nu_\theta$  and  $\nu_0$  are respectively the kinematic viscosities at temperatures  $\theta^\circ$  and  $0^\circ$  C. A study of the data shows that a single curve represents the thermal coefficient of kinematic viscosity when plotted against the kinematic viscosity of all of the solutions of the alcohol group. That is, the thermal coefficient as a function of the kinematic viscosity is practically independent of the temperature and of the chemical composition of liquids of this group. This is also true for the mineral oil group and, in a limited temperature interval, for the pure animal and vegetable oils.

The effect of several chemicals in inhibiting the change of viscosity due to the oxidation of poppy-seed oil and linseed oil, upon exposure to air and light for 590 days, was also investigated.

## II. APPARATUS AND EXPERIMENTAL PROCEDURE

## METHOD

The kinematic viscosity was measured by means of viscometers of the Ostwald type, the design of which is shown in Figure 1. The viscometer is initially filled so that one of the free surfaces of the liquid is at mark  $m$ . The time of discharge  $t$  is the time necessary for the surface of the liquid to fall from marks  $M_1$  to  $M_2$ . The volume  $Q$  of the liquid discharged through the capillary tube is then the volume of the bulb included between these marks. The important geometrical features of these viscometers are as follows: First, the discharging bulb consists of two cones and a cylinder, all of the same altitude; second, the base of the

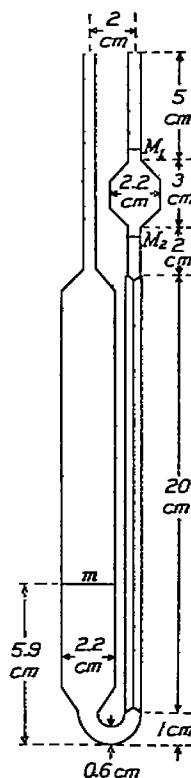


FIGURE 1.—Modified Ostwald type viscometer. The time is measured for the free surface of the liquid to pass from  $M_1$  to  $M_2$ . The tube is initially filled to the level  $m$ .

cones, the cylindrical portion of the discharging bulb, and the cylindrical receiving tube are all of the same radius.

#### THEORY AND CALIBRATION OF VISCOMETERS

The theory and method of calibration of the viscometers have been further developed and considerably simplified over that given in the previous report. (Reference 6.) This is given briefly. The discharge of a liquid through a capillary tube may be expressed by:

$$Q = \frac{\pi r^4 P t}{8 \nu \rho l_e} \quad (1)$$

where  $Q$  = volume of liquid in  $\text{cm}^3$  discharged in  $t$  seconds,

$r$  = radius of the capillary tube in cm,

$P$  = effective pressure applied to the liquid to produce the flow, in dynes/ $\text{cm}^2$ ,

$\rho$  = density of the liquid in gram/ $\text{cm}^3$ ,

$\nu$  = kinematic viscosity in c. g. s. units,

$l_e$  = the effective length of the capillary in cm.

It follows from equation (1) that

$$\nu = \frac{\pi r^4 P t}{8 Q l_e \rho} \quad (2)$$

The effective pressure  $P$  in general will be the sum of an external pressure  $p_e$  and the pressure  $p$  arising from the head of the liquid in the viscometer. If we define  $P$  by the equation

$$P = H \rho g$$

where  $H$  is the effective head, and  $\rho$  the density of the liquid, equation (2) will be written as

$$\nu = \frac{\pi r^4 g H t}{8 Q l_e}$$

then if

$$\frac{\pi r^4 g}{8 Q l_e} = A_1$$

$$\nu = A_1 H t \quad (3)$$

The effective head  $H$  can be evaluated on the basis of Poiseuille's law for the Ostwald type viscometers with discharging and receiving bulbs of geometrically known forms. The effective head  $H$ , for the type of viscometer used in this investigation (see fig. 1) proves to be of the form:

$$H = \frac{h_e + h}{1 + 0.373 \left( \frac{h_r}{h_e + h} \right)^2 + 0.270 \left( \frac{h_r}{h_e + h} \right)^4} \quad (4)$$

where  $h_e$  is the head due to the external pressure defined by the relation  $p_e = \rho g h_e$ ,  $p_e$  being the externally applied pressure,  $h$  is  $\left(1 - \frac{\sigma}{\rho}\right)$  times the head of the liquid in the viscometer when half, by volume, of the discharge has taken place,  $h_r$  is the change in the level

of the liquid in the receiving bulb or tube during the discharge. Here,  $\sigma$  is the density of the atmosphere at the level of the viscometer; for our purposes, the factor  $\left(1 - \frac{\sigma}{\rho}\right)$  may be regarded as equal to unity. The derivation and the application of equation (4) will be discussed in a separate paper.

The expression

$$\nu = A_1 H t \quad (3a)$$

holds only for slow rates of flow, that is for values of  $t$  larger than  $t_c$ . The quantity  $t_c$  is affected by the form of the viscometer and must be determined experimentally. For higher rates of flow, that is for  $t$  smaller than  $t_c$ , experience shows that equation (3a) must be replaced by

$$\nu = A_2 H t - \frac{B}{t} \quad (5)$$

It is to be remarked that  $A_2$  in formula (5) differs from  $A_1$  in formula (3a).

It is evident from the above that the calibration of a given viscometer involves the determination of  $t_c$  and of the constants  $A_1$ ,  $A_2$ , and  $B$ . In carrying out the calibration, the discharge time  $t$  for various values of  $H$  is noted for a liquid of known kinematic viscosity.

Then  $\frac{Ht}{\nu}$  is plotted as the ordinate against  $\frac{1}{\nu t}$  as the abscissa. The graph thus obtained will be composed of two straight lines, one of zero slope in accordance with equation (3a) and another of slope  $\frac{B}{A_2}$  in accordance with equation (5). The intersection of these lines gives the value of  $\frac{1}{\nu t_c}$ ; since  $\nu$  is known,  $t_c$  follows.  $A_1$  and  $A_2$  are then the reciprocals of the intercepts of the two lines, the horizontal and the inclined, with the axis of the ordinates.

In this investigation 10 viscometers were used, all similar in design to the one shown in Figure 1, except for the diameter of the capillary tube. The calibration constants of these in c. g. s. units are given in Table 1. The constants of the viscometers of smaller bore, that is  $V_5$ ,  $V_6$ , and  $V_7$ , were determined using the viscosity of water at 20° C. and 4° C. as standards. The calibration of the remaining viscometers were made to depend on  $V_5$ ,  $V_6$ , and  $V_7$ .

TABLE I.—CALIBRATION CONSTANTS OF VISCOMETERS

Viscometer	Critical time of discharge $t_c$ , seconds	$A_1 H$	$A_2 H$	$B$
$V_1$	50.1	$1.990 \times 10^{-4}$	$2.044 \times 10^{-4}$	$1.338 \times 10^{-3}$
$V_2$	60.2	$2.147 \times 10^{-4}$	$2.211 \times 10^{-4}$	$2.182 \times 10^{-3}$
$V_3$	50.2	$2.130 \times 10^{-4}$	$2.197 \times 10^{-4}$	$1.653 \times 10^{-3}$
$V_4$	40.9	$4.081 \times 10^{-4}$	$4.141 \times 10^{-4}$	$1.330 \times 10^{-3}$
$V_5$	27.9	$1.047 \times 10^{-3}$	$1.066 \times 10^{-3}$	$1.484 \times 10^{-3}$
$V_6$	23.2	$1.277 \times 10^{-3}$	$1.300 \times 10^{-3}$	$1.228 \times 10^{-3}$
$V_7$	8.7	$7.163 \times 10^{-3}$	$7.394 \times 10^{-3}$	$1.844 \times 10^{-3}$
$V_8$		$1.834 \times 10^{-4}$		
$V_9$		$1.566 \times 10^{-4}$		
$V_{10}$		$2.581 \times 10^{-4}$		

## TEMPERATURE CONTROL

The apparatus used for the control of temperature is shown in Figure 3 and diagrammatically in Figure 2. It consists of a metal box sufficiently large to contain three viscometers and the stirring apparatus. The design was such that if the upper surface of the box was level the viscometers were held in a vertical position. The liquid bath came well above the discharging bulb of the viscometer. This metal box was placed within a wooden container sufficiently large to allow about one and one-half inches thickness of insulating material between the two boxes. To observe the flow of the liquid in the viscometers, rectangular openings of such size and position as permitted the timing marks ( $M_1$  and  $M_2$  of fig. 1) of the viscometer to be seen were placed in the boxes. The openings in the metal box were covered by heavy plate glass, properly sealed to the box to prevent any leakage of the bath liquid. In the openings of the outer box were placed holders containing four glass plates, separated by strips of insulation. This arrangement proved sufficient to allow clear vision, with but little frosting of the glass even at a bath temperature of  $-50^\circ\text{C}$ .

Ethyl alcohol was used for the bath liquid for temperatures below  $0^\circ\text{C}$ ., solid carbon dioxide being used to cool the liquid. For temperatures above  $0^\circ\text{C}$ ., water and ice were used. Equalization of the temperature was obtained by means of an electrically driven agitator. The temperature was measured by a liquid-in-glass thermometer, its bulb placed about on a level with the mid-point of the capillary. The temperature at this point was found to give within  $0.1^\circ$  the same reading as the average of those of two thermometers measuring, respectively, the temperature of the upper and of the lower portions of the bath.

This method of temperature control was an improvement in two ways over that described in Technical Report No. 299. It enabled the temperature of the bath liquid to be lowered more rapidly and made possible lower temperatures.

## EXPERIMENTAL ERRORS

The several sources of experimental error are the uncertainty in the calibration, in the observation of the time of flow, in the measurement of temperature, and in the drainage. Errors in the calibration of the viscometers probably do not exceed 0.5 per cent. It is necessary to consider the errors in the measurement of the time of flow only for small values of the time. The smallest was about 10 seconds. To reduce the error in these cases, three or more measurements of time were made at each temperature and the average noted; for a time of flow of about 10 seconds, the values usually agreed, to within 0.1 second. Hence, it follows that in no case do errors in the measurement of the time cause the viscosity determinations to be in error by more than 1 per cent.

Temperature errors may arise in two ways: A temperature gradient may exist along the capillary, and the average temperature of the bath may not be constant during the measurement of the time of flow. Above  $0^\circ\text{C}$ . the temperatures at the upper and the lower portions of the bath did not differ by more than  $1^\circ\text{C}$ . and efforts were made to keep the average temperature constant to  $0.5^\circ\text{C}$ . Below  $0^\circ\text{C}$ . this was more difficult, and then the temperature was taken as the average of those read immediately before and after the flow. In most cases the average did not differ from either reading by more than  $1^\circ$  centigrade.

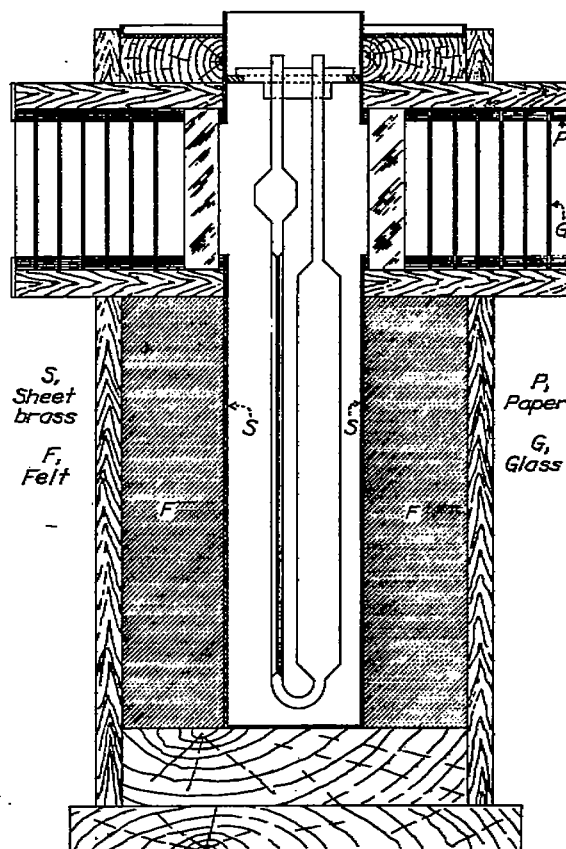


FIGURE 2.—Cross section of the apparatus for controlling the temperature of the viscometers and liquids

Considerable error due to drainage is to be expected with very viscous liquids. All solutions having a high viscosity at ordinary temperatures become extremely viscous at low temperatures. This being the case, the accuracy of the measurements at high temperatures exceeds that of the measurements at low temperatures. If  $\Delta Q$  is the amount of liquid remaining on the walls of the discharging bulb when the meniscus of the liquid reaches the lower timing mark, the fractional error of the measurement of the time of discharge of volume  $Q$  will be  $\frac{\Delta Q}{Q}$  if we disregard the change in effective head  $H$ . The latter will be small compared with  $\frac{\Delta Q}{Q}$ , since the effective head was about 19 cm. No estimate has been made of the value of  $\frac{\Delta Q}{Q}$ .

Another source of error is due to the separation of the components of some of the liquids at low temperature. In solutions of poppy-seed oil and of neat's-foot oil, in xylene and in toluene, there was evidence of a partial separation at low temperatures. This separation caused the kinematic viscosity to increase with the length of time the solutions were kept at these temperatures.

### III. DESCRIPTION OF THE LIQUIDS

The following data are available concerning the source and properties of the samples of the individual liquids:

Color.....	Light straw.
Odor.....	Normal animal oil.
Condition.....	Clear.
Specific gravity at 15.6° C.....	0.9232.
Saponification No.....	193.8.
Acid No.....	4.5.
Free acid (oleic), per cent.....	2.3.

#### POPPY-SEED OIL

A sample was purchased without specifications from a wholesale dealer. This froze at  $-15^{\circ}\text{C}.$  to  $-18^{\circ}\text{C}.$  The kinematic viscosity at  $30^{\circ}\text{C}.$  was 0.499 c. g. s. units.

The chemistry division furnished the following analysis:

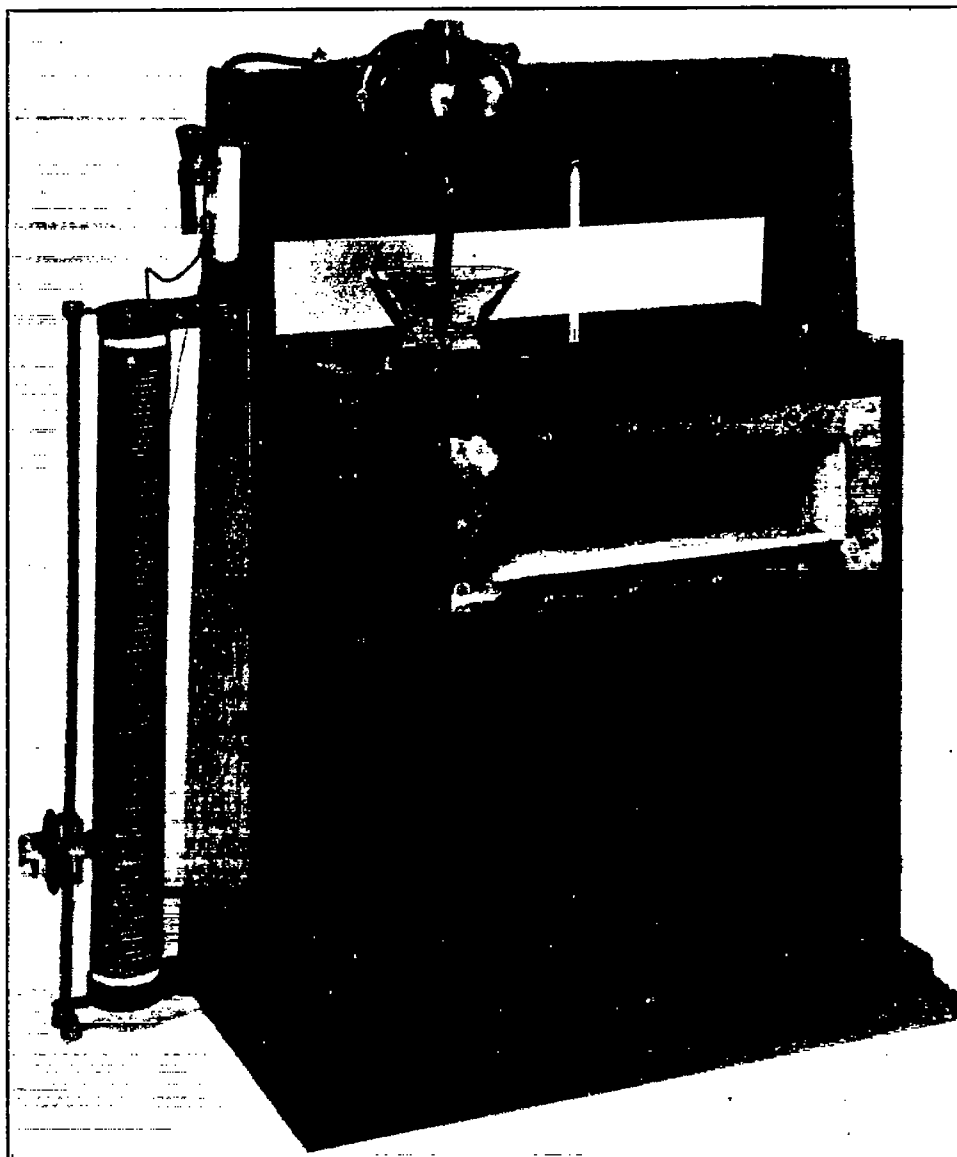


FIGURE 3.—Temperature control apparatus

#### NEAT'S-FOOT OIL

The neat's-foot oil was purchased from Morris & Co. The sample is a "wintered" product known as  $20^{\circ}\text{F}.$  ( $-6.7^{\circ}\text{C}.$ ) cold or flow-test neat's-foot oil. The sample froze at about  $-10^{\circ}\text{C}.$  and had a kinematic viscosity at  $30^{\circ}\text{C}.$  of 0.632 c. g. s. units. A sample of the oil was analyzed by the chemistry division of the Bureau of Standards. Their report follows:

Color.....	Light amber.
Odor.....	Normal vegetable oil.
Condition.....	Clear.
Specific gravity at 15.6° C.....	0.9253.
Saponification No.....	184.8.
Acid No.....	1.3.
Free acid (oleic), per cent.....	0.7.
Iodine No.....	142.9.

To this oil 1 per cent, by weight of hydroquinone was added to reduce the oxidation (Cf. section on Secular Variations), and this mixture was used as a unit in making up the solutions studied. Data obtained show that the addition of hydroquinone did not noticeably change the kinematic viscosity or its rate of change with temperature.

## WILKINS' OIL

This sample was a mineral oil purchased from the Pioneer Instrument Co., and manufactured by the Standard Oil Co. This oil is being used as a lubricant on aircraft instruments and a solution with mineral spirits is being used as a damping liquid in ball-type inclinometers. It was stated to have a pour point of  $-40^{\circ}\text{C}$ . At a temperature of  $-32^{\circ}\text{C}$ . its kinematic viscosity approached an infinite value. At  $30^{\circ}\text{C}$ . it had a kinematic viscosity of 0.185 c. g. s. units.

## "SUPERLA" CLOCK OIL

This mineral oil was furnished by the Aircraft Control Corporation with the statement that it was manufactured by the Standard Oil Co. of Indiana and had a pour point of about  $-20^{\circ}\text{C}$ . Its kinematic viscosity was 0.342 c. g. s. units at  $30^{\circ}\text{C}$ . and its kinematic viscosity approached infinity at  $-28^{\circ}\text{C}$ .

A solution of Superla clock oil and mineral spirits is being used by one manufacturer as a damping liquid in ball-type inclinometers.

GLYCERINE ( $\text{C}_3\text{H}_8(\text{OH})_3$ )

The density of the sample used was 1.244 at  $25^{\circ}\text{C}$ . According to the International Critical Tables (Vol. III) this density corresponds to that of a sample containing about 5.5 per cent water. Shöttner's value of the viscosity of glycerol, as given in the Physico-Chemical Tables (Vol. II), is 4.939 poises at  $26.5^{\circ}\text{C}$ . Our determination of this quantity gives 3.82 poises. The considerable difference between these two values is undoubtedly due to the water content of the sample. The kinematic viscosity at  $30^{\circ}\text{C}$ . was found to be 2.38 c. g. s. units.

ETHYLENE GLYCOL ( $(\text{CH}_2\text{OH})_2$ )

The sample used is a commercial product sold under the trade name "Eveready Prestone." This sample is believed to be free from the antileak compound now being added to Prestone. Its kinematic viscosity at  $30^{\circ}\text{C}$ . was found to be 0.107 c. g. s. units.

## MINERAL SPIRITS

Two different samples of mineral spirits were used. One sample is a petroleum product known commercially as Varnolene. It was used with Wilkins' oil and with neat's-foot oil, and had a kinematic viscosity of 0.0112 c. g. s. units and a density of 0.769 grams per  $\text{cm}^3$  at  $30^{\circ}\text{C}$ . and infinite viscosity at a temperature below  $-60^{\circ}\text{C}$ . This sample darkened on exposure to light, indicating the presence of unsaturated compounds.

The other sample, known as mineral spirits No. 9, was manufactured by the Standard Oil Co. of Indiana. It was used only as a solvent for Superla clock oil. At  $30^{\circ}\text{C}$ . its kinematic viscosity was 0.0166 c. g. s. units and its density 0.783 grams per  $\text{cm}^3$ . Its viscosity approached an infinite value below  $-60^{\circ}\text{C}$ .; during reduction to this temperature it remained clear. It remained clear upon exposure to light for a period of more than 12 months.

TOLUENE ( $\text{C}_6\text{H}_5\text{CH}_3$ )

The sample was manufactured by the J. T. Baker Chemical Co. The manufacturer's label gave the following:

Specific gravity.....	0.87.
Nonvolatile material.....	0.001 per cent.
Boiling point.....	$111^{\circ}\text{C}$ .
CS <sub>2</sub> .....	None.

The kinematic viscosity at  $30^{\circ}\text{C}$ . was 0.00615 c. g. s. units. The International Critical Tables (Vol. III and V) give a value of 0.00628 c. g. s. units for the kinematic viscosity at  $25^{\circ}\text{C}$ . as compared to our result of 0.00651 c. g. s. units at the same temperature.

XYLENE (META) ( $\text{C}_6\text{H}_4(\text{CH}_3)_2$ )

The following data were obtained from the label of the container:

Molecular weight.....	106.12.
Specific gravity.....	0.86.
Boiling point.....	$138^{\circ}\text{--}139^{\circ}\text{C}$ .

At  $30^{\circ}\text{C}$ . it had a kinematic viscosity of 0.00670 c. g. s. units and, at  $25^{\circ}\text{C}$ ., 0.00707 c. g. s. units, while the value at  $25^{\circ}\text{C}$ ., given in the International Critical Tables (Vol. III, 1928, and V, 1929), is 0.00700 c. g. s. units. It froze at  $-54^{\circ}\text{C}$ . and became cloudy at about  $-20^{\circ}\text{C}$ .

METHYL ALCOHOL ( $\text{CH}_3\text{OH}$ )

The sample was of reagent quality. The manufacturer's label gave the following:

Reaction.....	Neutral.
Nonvolatile material.....	0.002 per cent.
Chloroform ( $\text{CHCl}_3$ ).....	0.01 per cent.
Aldehydes.....	0.000 per cent.
Empyreumatic substances.....	0.000 per cent.
Reducing substances.....	0.000 per cent.
Acetone (ketones).....	0.000 per cent.
Specific gravity $25^{\circ}/25^{\circ}\text{C}$ .....	Not over 0.790.

It was found to have a kinematic viscosity of 0.00667 at  $30^{\circ}\text{C}$ . The International Critical Tables (Vol. I, 1926) gives the melting point as  $-97.8^{\circ}\text{C}$ .

ETHYL ALCOHOL ( $\text{C}_2\text{H}_5\text{OH}$ )

The alcohol used had a kinematic viscosity at  $30^{\circ}\text{C}$ . of 0.0149 c. g. s. units; at  $0^{\circ}\text{C}$ . of 0.0290 c. g. s. units. Comparing these results with the values given for the viscosity in the Smithsonian Physical Tables (1927), we conclude that this sample must have contained about 6 per cent water.

n-PROPYL ALCOHOL ( $C_3H_7OH$ )

The sample was purchased from the Eastman Kodak Laboratories as of the chemically pure grade. From the International Critical Tables (Vols. III, 1928, and V, 1929) we obtain the following: Specific gravity at 25° C., 0.8060; kinematic viscosity at 25° C., 0.0245 c. g. s. units. Our value for the kinematic viscosity at 25° C. is 0.0244 c. g. s. units. The same tables (Vol. I, 1926) give the melting point as -127° C.

n-BUTYL ALCOHOL ( $C_4H_9OH$ )

The sample was purchased from the Eastman Kodak Laboratories. Two grades of the chemical are available; one is known as technical and has a boiling point of 114° to 118° C.; the other is the purer product and has a boiling point of 116° to 118° C. The technical grade was used in the tests.

The density of the sample at 20° C. was 0.810 grams per  $cm^3$ ; its kinematic viscosity at 30° C. was 0.0269 c. g. s. units; at 25° C. was 0.0304 c. g. s. units. The International Critical Tables (Vols. III, 1928, and IV, 1929) gives data for the absolute viscosity and density from which we obtain the value of 0.0310 c. g. s. units for the kinematic viscosity at 25° C.

## IV. EXPERIMENTAL RESULTS

## KINEMATIC VISCOSITY

The kinematic viscosity of the following solutions was determined in the temperature range +30° to -50° C:

Neat's-foot oil.....	Mineral spirits. Toluene.
Poppy-seed oil.....	Xylene (meta). Toluene.
Superla clock oil...	Mineral spirits No. 9.
Wilkins' oil.....	Mineral spirits. Xylene (meta).
Glycerine.....	Methyl alcohol. n-Propyl alcohol.
Ethylene glycol....	Methyl alcohol. Ethyl alcohol. n-Propyl alcohol. n-Butyl alcohol.

In most cases five different concentrations of each were investigated, namely, 0, 25, 50, 75, and 100 per cent of one of the components.

The experimental data on the kinematic viscosity of these liquids and solutions are presented in Table II and in Figures 4 to 16, inclusive,  $\log_{10} \frac{\nu_\theta}{\nu_0}$  being plotted against temperature;  $\nu_\theta$  and  $\nu_0$  are, respectively, the kinematic viscosities at  $\theta^\circ$  and  $0^\circ$  C. The composition of each solution and the kinematic viscosity at  $0^\circ$  are stated in each of the figures. The data are thus sufficient to compute the kinematic viscosity at any temperature within the range. In computing the ratio,  $\frac{\nu_\theta}{\nu_0}$ , the values of  $\nu_\theta$  were computed from the

observed values of the time of flow ( $t_\theta$ ) at the temperature  $\theta$ , by means either of formula (3a) or (5), depending upon whether  $t_\theta$  was larger or smaller than  $t_0$ . The time of discharge for  $\theta = 0^\circ$  C. was not usually observed but was determined graphically from the values of  $t$  in the neighborhood of  $0^\circ$  C.; similarly for  $t_{30}$ .

It will be noted that the kinematic viscosity is given in "c. g. s. units," which means that the units used in the calculation are the centimeter, the gram of mass, and the second. Viscosity in poises is obtained by multiplying the kinematic viscosity in c. g. s. units by the density in grams per cubic centimeter.

A comparison of the solutions as regards the relative variations of their kinematic viscosities with the temperature may be made thus: Select an appropriate value for the kinematic viscosity at some one temperature, say  $30^\circ$  C., and determine for each solution the concentration at which its kinematic viscosity has this value. This can be done by a graphical interpolation between the values given in Table II,  $\log_{10} \nu_{30}$  being plotted against the concentration. From Figures 4 to 16 determine the values of  $n_\theta = \log_{10} \frac{\nu_\theta}{\nu_0}$ , corresponding to these concentrations and to each of a selected series of temperatures, including  $30^\circ$  C. This generally requires interpolation. In some cases the interpolation can be made directly from the figures; in others it will be more convenient to plot  $\log_{10} \frac{\nu_\theta}{\nu_0}$  against the concentration for each solution and for each of the selected temperatures, the proper values being read from Figures 4 to 16, and to use these new curves for determining the values of  $n_\theta$  for the desired concentrations. From the values of  $n_\theta$  those of  $\nu_\theta$  can be determined by means of the relation  $\log_{10} \frac{\nu_\theta}{\nu_{30}} = n_\theta - n_{30}$ ,  $\nu_{30}$  being known. This procedure may be repeated for each of the selected values of  $\nu_{30}$ .

Having selected a value for  $\nu_{30}$  and determined the corresponding concentrations, the value of the temperature at which the kinematic viscosity of any one solution is a stated multiple ( $x$ ) of  $\nu_{30}$  may be determined thus: From the proper curves of Figures 4 to 16 read the value of  $\log_{10} \frac{\nu_{30}}{\nu_0}$  for each concentration; increase each by  $\log_{10} x$ , obtaining the value of  $\log_{10} \frac{x\nu_{30}}{\nu_0}$ , seek on each curve the temperature corresponding to the value of  $\log_{10} \frac{\nu_\theta}{\nu_0} = \log_{10} \frac{x\nu_{30}}{\nu_0}$ ; plot these temperatures against the concentration, and from the curve so obtained read the temperature corresponding to the concentration defined by the value selected for  $\nu_{30}$ . Repeat for other values of  $x$ , for other solutions, and for other values selected for  $\nu_{30}$ .

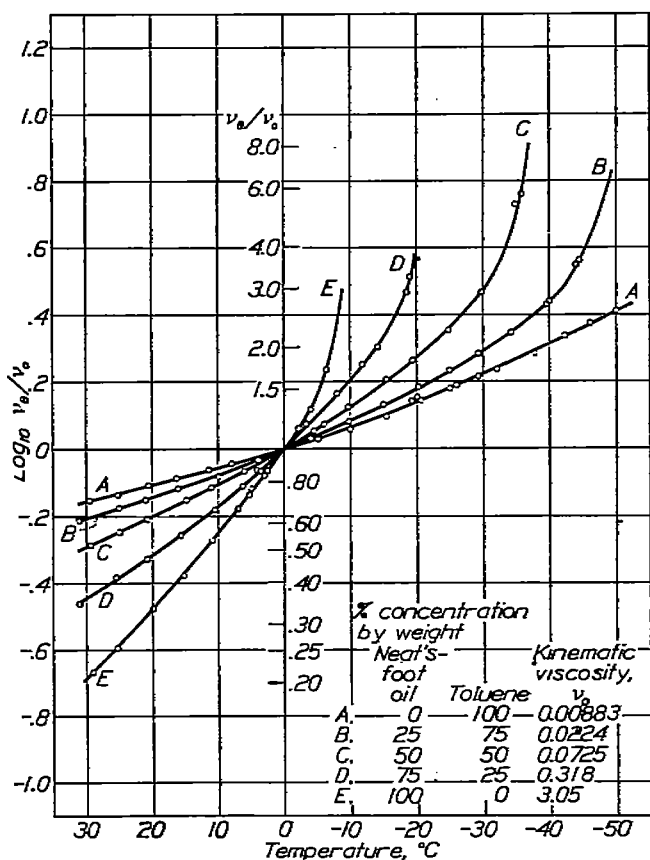


FIGURE 4.—Effect of temperature on the kinematic viscosity of solutions of neat's-foot oil (20° F.) and toluene.  $v_{\theta}$  and  $v_0$  are the kinematic viscosities of the liquid at a given temperature (designated by  $\theta$ ) and at 0° C.

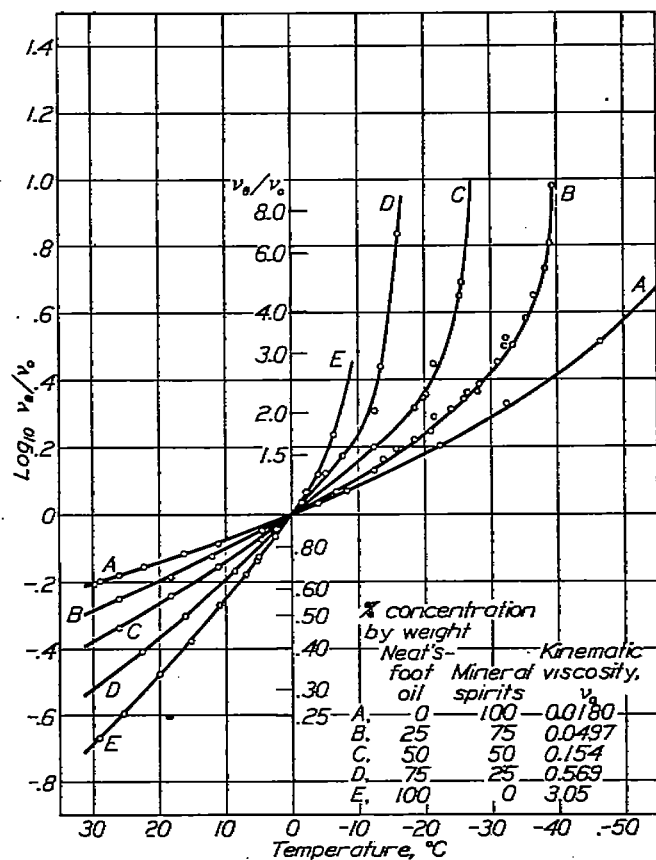


FIGURE 5.—Effect of temperature on the kinematic viscosity of solutions of neat's-foot oil (20° F.) and mineral spirits.  $v_{\theta}$  and  $v_0$  are the kinematic viscosities of the liquid at a given temperature (designated by  $\theta$ ) and at 0° C.

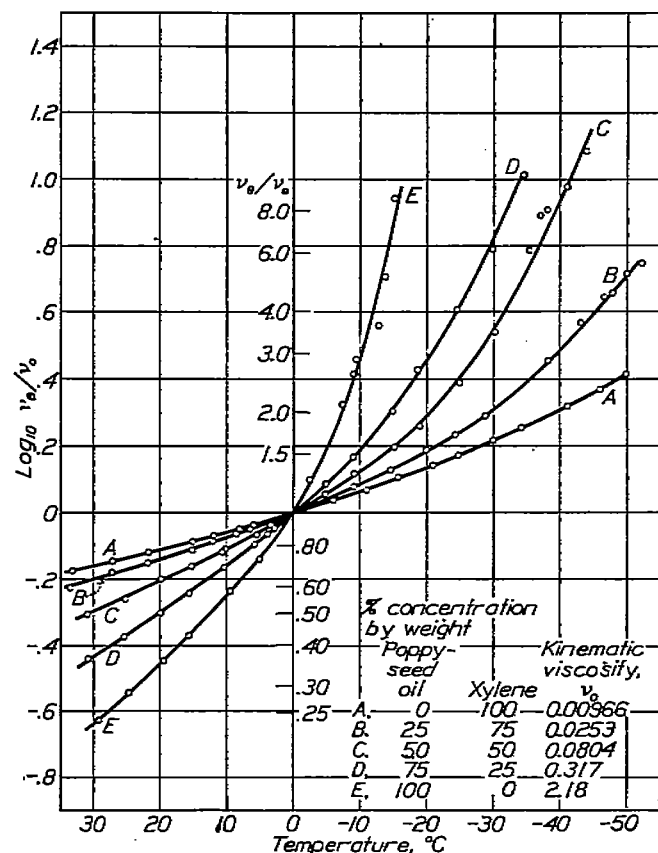


FIGURE 6.—Effect of temperature on the kinematic viscosity of solutions of poppy-seed oil and xylene.  $v_{\theta}$  and  $v_0$  are the kinematic viscosities of the liquid at a given temperature (designated by  $\theta$ ) and at 0° C.

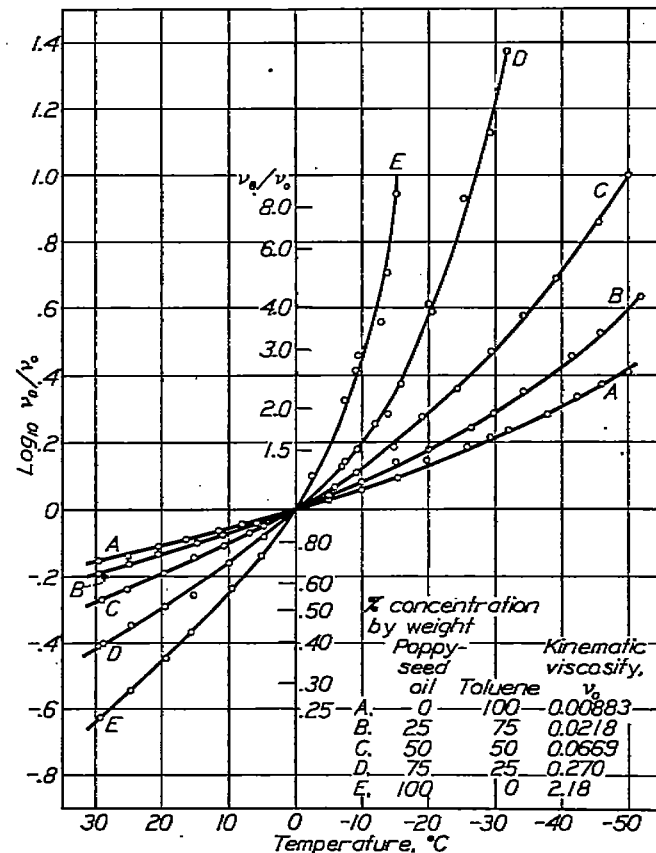


FIGURE 7.—Effect of temperature on the kinematic viscosity of solutions of poppy-seed oil and toluene.  $v_{\theta}$  and  $v_0$  are the kinematic viscosities of the liquid at a given temperature (designated by  $\theta$ ) and at 0° C.

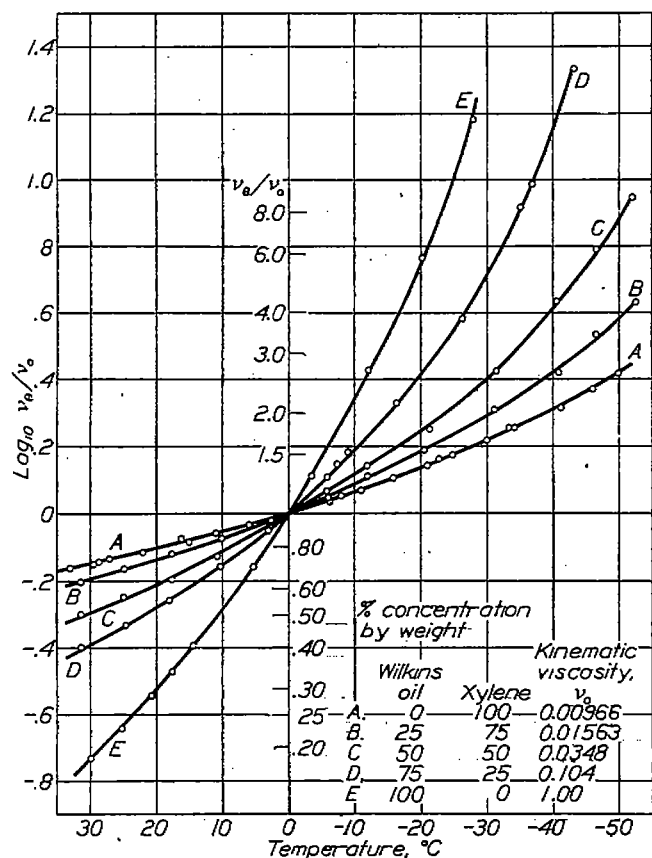


FIGURE 8.—Effect of temperature on the kinematic viscosity of solutions of Wilkins' oil and xylene.  $v_{\theta}$  and  $v_0$  are the kinematic viscosities of the liquid at a given temperature (designated by  $\theta$ ) and at  $0^{\circ}\text{C}$ .

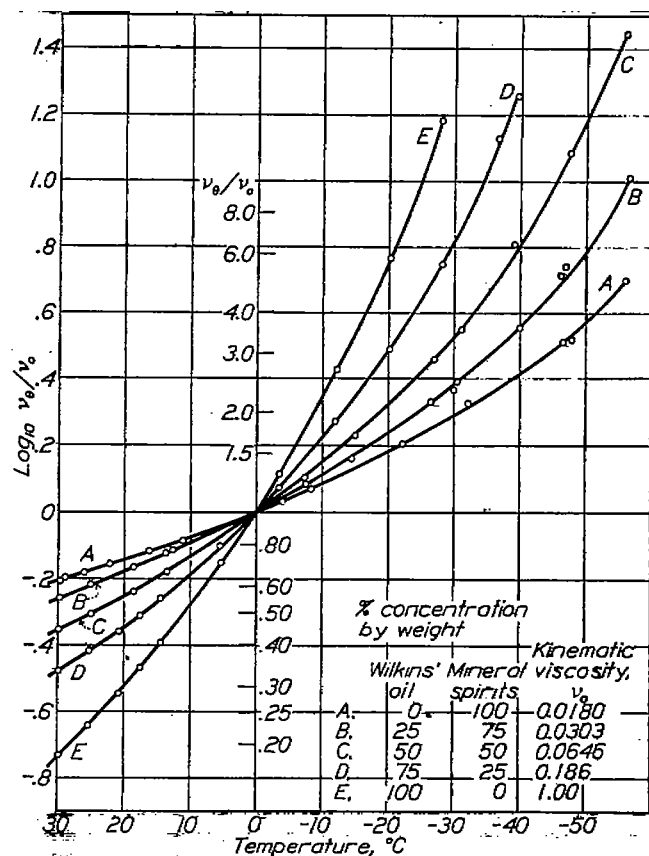


FIGURE 9.—Effect of temperature on the kinematic viscosity of solutions of Wilkins' oil and mineral spirits.  $v_{\theta}$  and  $v_0$  are the kinematic viscosities of the liquid at a given temperature (designated by  $\theta$ ) and at  $0^{\circ}\text{C}$ .

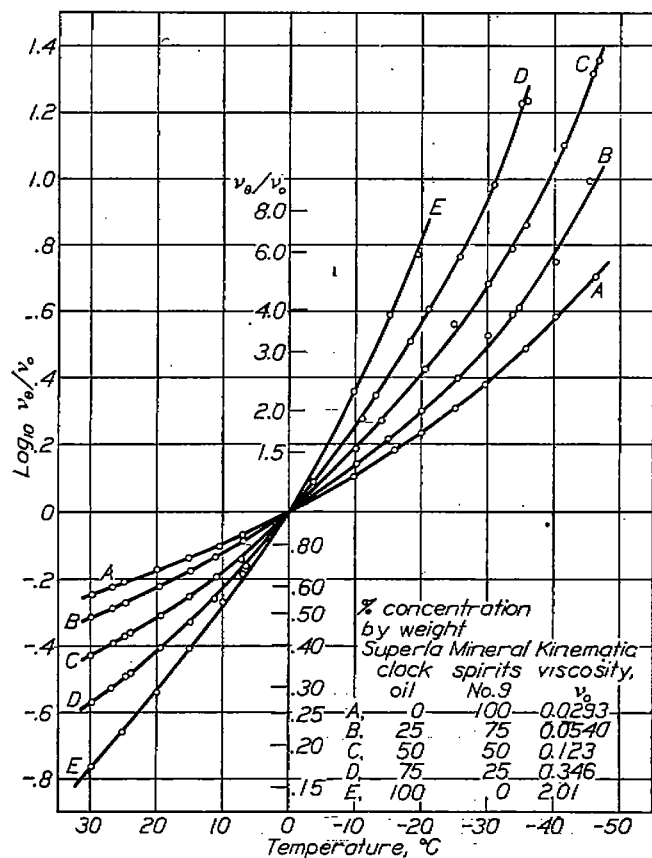


FIGURE 10.—Effect of temperature on the kinematic viscosity of solutions of Superia clock oil and mineral spirits No. 9.  $v_{\theta}$  and  $v_0$  are the kinematic viscosities of the liquid at a given temperature (designated by  $\theta$ ) and at  $0^{\circ}\text{C}$ .

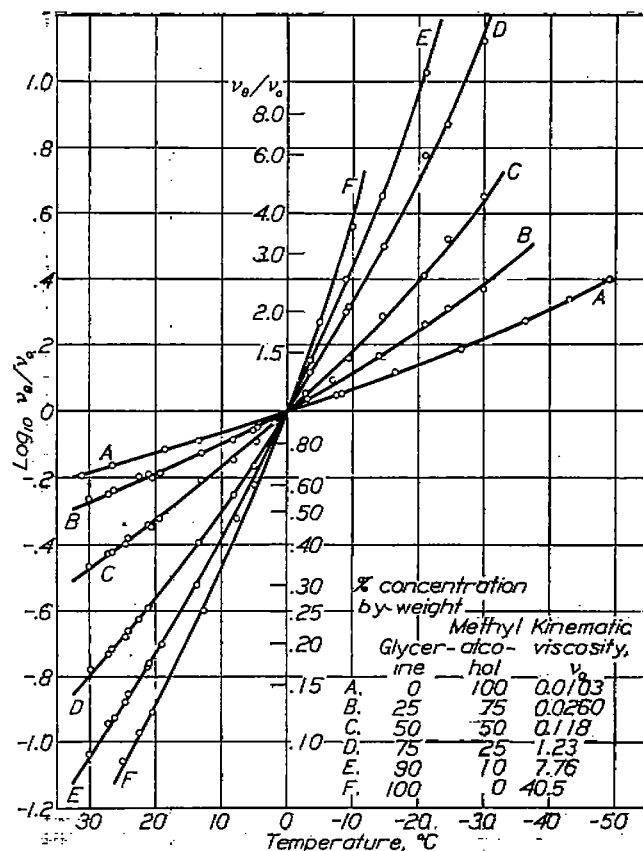


FIGURE 11.—Effect of temperature on the kinematic viscosity of solutions of glycerine and methyl alcohol.  $v_{\theta}$  and  $v_0$  are the kinematic viscosities of the liquid at a given temperature (designated by  $\theta$ ) and at  $0^{\circ}\text{C}$ .

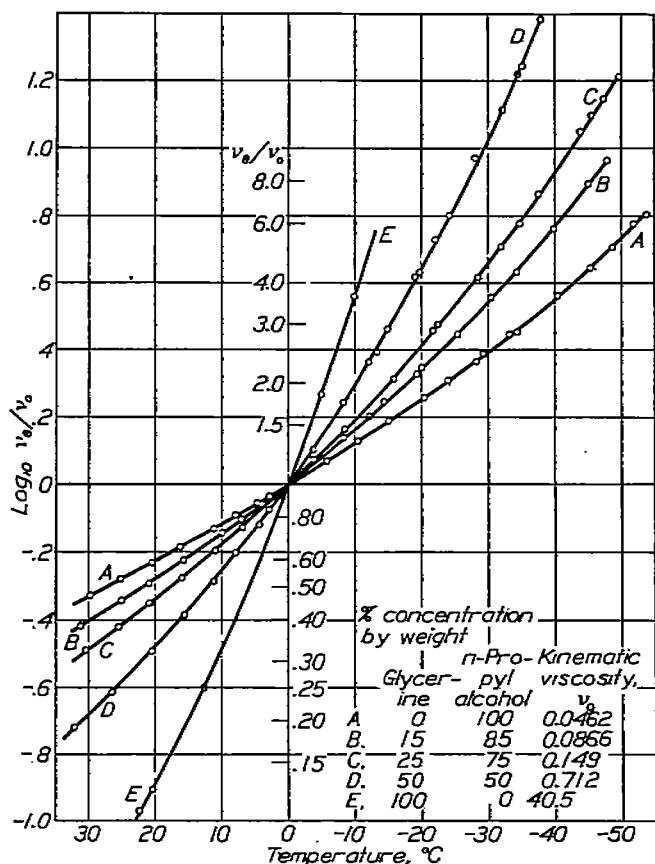


FIGURE 12.—Effect of temperature on the kinematic viscosity of solutions of glycerine and n-propyl alcohol.  $v_\theta$  and  $v_0$  are the kinematic viscosities of the liquid at a given temperature (designated by  $\theta$ ) and at 0° C.

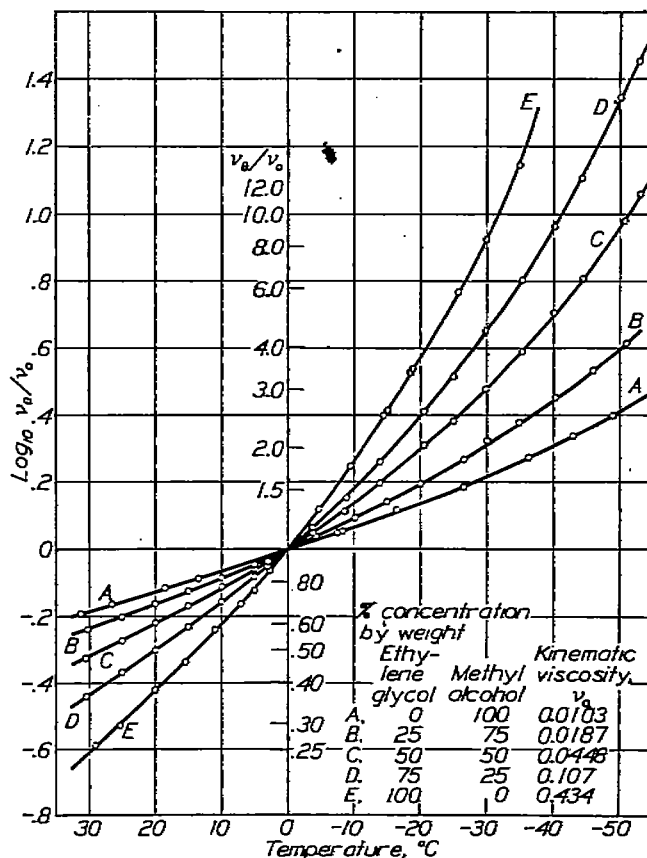


FIGURE 13.—Effect of temperature on the kinematic viscosity of solutions of ethylene glycol and methyl alcohol.  $v_\theta$  and  $v_0$  are the kinematic viscosities of the liquid at a given temperature (designated by  $\theta$ ) and at 0° C.

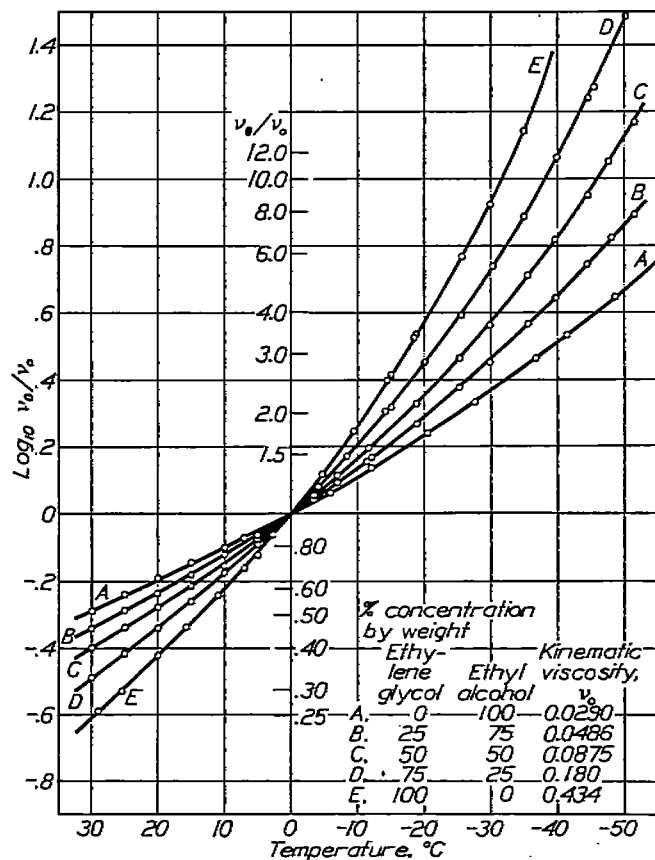


FIGURE 14.—Effect of temperature on the kinematic viscosity of solutions of ethylene glycol and ethyl alcohol.  $v_\theta$  and  $v_0$  are the kinematic viscosities of the liquid at a given temperature (designated by  $\theta$ ) and at 0° C.

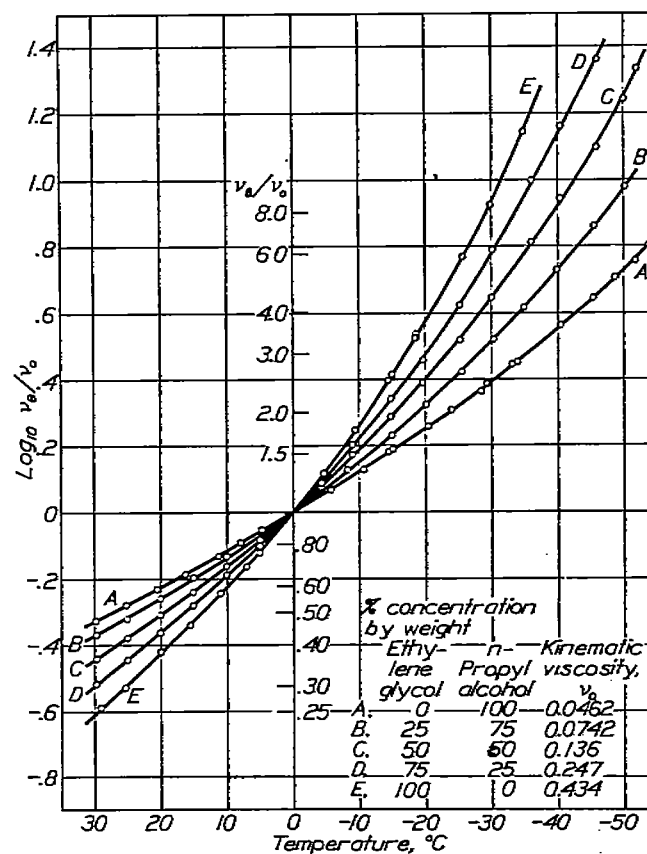


FIGURE 15.—Effect of temperature on the kinematic viscosity of solutions of ethylene glycol and n-propyl alcohol.  $v_\theta$  and  $v_0$  are the kinematic viscosities of the liquid at a given temperature (designated by  $\theta$ ) and at 0° C.

The data of Table III were obtained by this method. In Table III the solutions have been divided into three groups as indicated by the braces: (a) Alcoholic solutions; (b) mixtures containing mineral oils; (c) mixtures containing animal or vegetable oil. It will be noticed that if a series of mixtures within a single group (a)

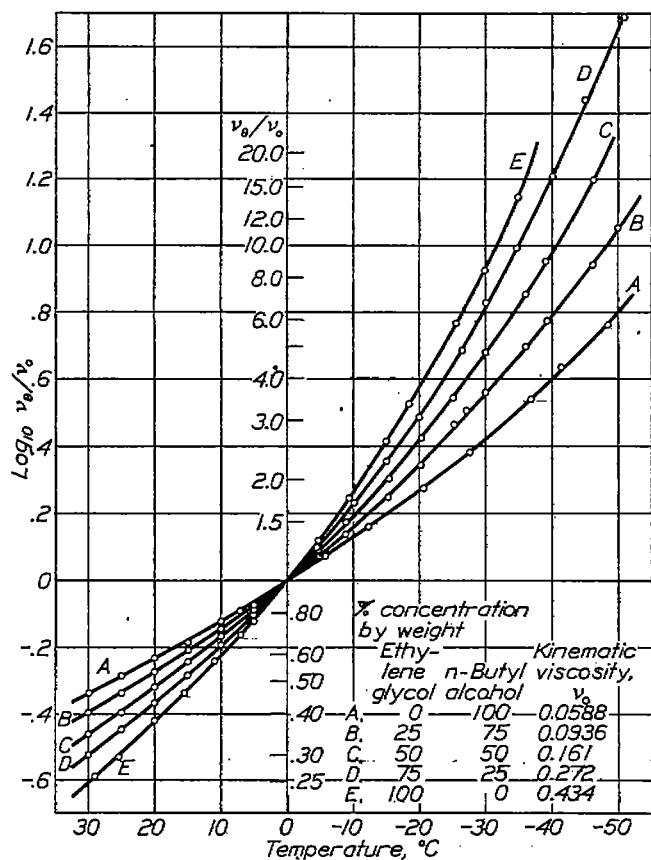


FIGURE 16.—Effect of temperature on the kinematic viscosity of solutions of ethylene glycol and n-butyl alcohol.  $\nu_\theta$  and  $\nu_0$  are the kinematic viscosities of the liquid at a given temperature (designated by  $\theta$ ) and at  $0^\circ\text{C}$ .

and (b) all have the same value for  $\nu_{30}$ , they will also all have essentially the same value for  $\nu_\theta$ , whatever value  $\theta$  may have within the range  $+30^\circ$  to  $-\theta_s^\circ\text{C}$ , where the value of  $-\theta_s$  depends upon the solidifying point of the mixture. Less exactly, the same holds true for group (c). Furthermore, the differences between groups (a) and (b) are slight, while that between them and group (c) is large at the higher temperatures, but at low temperatures is small.

TABLE II.—KINEMATIC VISCOSITY OF LIQUIDS AT  $30^\circ\text{C}$  AND  $0^\circ\text{C}$ .

Temperature		30° C.			0° C.		
Per cent by weight		Viscometer No.	Time of flow, seconds	Kinematic viscosity, c. g. s. units	Viscometer No.	Time of flow, seconds	Kinematic viscosity, c. g. s. units
A	B						
A=neat's-foot oil; B=toluene							
100 75 50 25	0 25 50 75	V <sub>10</sub> V <sub>2</sub> V <sub>3</sub> V <sub>1</sub>	24.4 18.1 35.8 33.8	0.632 .1160 .0870 .0136	V <sub>10</sub> V <sub>2</sub> V <sub>3</sub> V <sub>1</sub>	117.7 44.8 69.2 55.1	3.05 .318 .0725 .0224
A=neat's-foot oil; B=mineral spirits							
100 75 50 25	0 25 50 75	V <sub>10</sub> V <sub>2</sub> V <sub>3</sub> V <sub>1</sub>	24.4 23.9 61.1 63.8	0.632 .171 .0640 .0257	V <sub>10</sub> V <sub>2</sub> V <sub>3</sub> V <sub>1</sub>	117.7 79.4 147.1 122.4	3.05 .569 .154 .0497
A=poppy-seed oil; B=m-xylene							
100 75 50 25	0 25 50 75	V <sub>10</sub> V <sub>2</sub> V <sub>3</sub> V <sub>1</sub>	69.7 90.8 83.8 74.5	0.499 .116 .0406 .0180	V <sub>10</sub> V <sub>2</sub> V <sub>3</sub> V <sub>1</sub>	304.3 248.2 78.8 117.9	2.18 .317 .0804 .0263
A=poppy-seed oil; B=toluene							
100 75 50 25	0 25 50 75	V <sub>10</sub> V <sub>2</sub> V <sub>3</sub> V <sub>1</sub>	69.7 97.4 83.6 34.6	0.499 .102 .0352 .0140	V <sub>10</sub> V <sub>2</sub> V <sub>3</sub> V <sub>1</sub>	304.3 267.9 63.9 53.7	2.18 .370 .0629 .0218
A=Wilkins' oil; B=m-xylene							
100 75 50 25	0 25 50 75	V <sub>10</sub> V <sub>2</sub> V <sub>3</sub> V <sub>1</sub>	11.8 8.1 17.5 25.6	0.185 .0421 .0177 .0100	V <sub>10</sub> V <sub>2</sub> V <sub>3</sub> V <sub>1</sub>	63.8 14.5 33.3 35.4	1.00 .104 .0343 .0156
A=Wilkins' oil; B=mineral spirits							
100 75 50 25	0 25 50 75	V <sub>10</sub> V <sub>2</sub> V <sub>3</sub> V <sub>1</sub>	11.8 8.6 27.2 40.9	0.185 .0617 .0235 .0166	V <sub>10</sub> V <sub>2</sub> V <sub>3</sub> V <sub>1</sub>	63.8 28.0 9.0 23.9	1.00 .186 .0646 .0303
A=Superia clock oil; B=mineral spirits							
100 75 50 25	0 25 50 75	V <sub>10</sub> V <sub>2</sub> V <sub>3</sub> V <sub>7</sub>	21.8 13.0 43.7 122.5	0.342 .0931 .0453 .0281	V <sub>10</sub> V <sub>2</sub> V <sub>3</sub> V <sub>1</sub>	123.3 32.1 9.2 42.3	2.01 .546 .123 .0540

TABLE II.—KINEMATIC VISCOSITY OF LIQUIDS AT 30° C. AND 0° C.—Continued

Temperature		30° C.			0° C.		
Per cent by weight		Vis-com-eter No.	Time of flow, sec-onds	Kine-matic viscos-ity, c. g. s. units	Vis-com-eter No.	Time of flow, sec-onds	Kine-matic viscos-ity, c. g. s. units
A	B						
A=glycerine; B=methyl alcohol							
100	0	V <sub>1</sub>	151.9	2.38	V <sub>1</sub>	2,535	40.5
90	10	V <sub>1</sub>	44.6	.698	V <sub>1</sub>	496.6	7.76
75	25	V <sub>1</sub>	27.4	.196	V <sub>1</sub>	171.7	1.23
50	50	V <sub>1</sub>	33.1	.0399	V <sub>1</sub>	112.7	.118
25	75	V <sub>1</sub>	34.5	.0139	V <sub>1</sub>	64.0	.0260
A=glycerine; B=n-propyl alcohol							
100	0	V <sub>1</sub>	152.9	2.38	V <sub>1</sub>	2,585	40.5
50	50	V <sub>1</sub>	115.9	.149	V <sub>1</sub>	63.4	.712
25	75	V <sub>1</sub>	34.4	.0465	V <sub>1</sub>	116.7	.149
15	85	V <sub>1</sub>	28.7	.0341	V <sub>1</sub>	67.8	.0866
A=ethylene glycol; B=methyl alcohol							
100	0	V <sub>1</sub>	14.9	0.107	V <sub>1</sub>	60.6	0.434
75	25	V <sub>1</sub>	30.6	.0391	V <sub>1</sub>	54.5	.107
50	50	V <sub>1</sub>	20.8	.0213	V <sub>1</sub>	42.8	.0448
25	75	V <sub>1</sub>	27.8	.0108	V <sub>1</sub>	46.0	.0187
A=ethylene glycol; B=ethyl alcohol							
100	0	V <sub>1</sub>	14.9	0.107	V <sub>1</sub>	60.6	0.434
75	25	V <sub>1</sub>	45.9	.0536	V <sub>1</sub>	141.0	.190
50	50	V <sub>1</sub>	33.2	.0343	V <sub>1</sub>	83.6	.0875
25	75	V <sub>1</sub>	54.7	.0222	V <sub>1</sub>	119.7	.0456
A=ethylene glycol; B=n-propyl alcohol							
100	0	V <sub>1</sub>	14.9	0.107	V <sub>1</sub>	60.6	0.434
75	25	V <sub>1</sub>	10.4	.0745	V <sub>1</sub>	34.5	.247
50	50	V <sub>1</sub>	38.4	.0490	V <sub>1</sub>	106.5	.136
25	75	V <sub>1</sub>	30.1	.0315	V <sub>1</sub>	70.9	.0742
A=ethylene glycol; B=n-butyl alcohol							
100	0	V <sub>1</sub>	14.9	0.107	V <sub>1</sub>	60.6	0.434
75	25	V <sub>1</sub>	11.4	.0813	V <sub>1</sub>	33.0	.272
50	50	V <sub>1</sub>	43.6	.0557	V <sub>1</sub>	126.1	.161
25	75	V <sub>1</sub>	36.1	.0378	V <sub>1</sub>	93.4	.0936
Solvents							
Toluene.....	V <sub>1</sub>	32.3	0.00615	V <sub>1</sub>	44.7	0.00683	
m-Xylene.....	V <sub>1</sub>	34.8	.00670	V <sub>1</sub>	43.6	.00966	
Mineral spirits.....	V <sub>1</sub>	11.8	.0112	V <sub>1</sub>	17.7	.0180	
Mineral spirits No. 9.....	V <sub>1</sub>	83.4	.0166	V <sub>1</sub>	73.3	.0293	
Methyl alcohol.....	V <sub>1</sub>	18.1	.00668	V <sub>1</sub>	26.1	.0103	
Ethyl alcohol.....	V <sub>1</sub>	36.9	.0149	V <sub>1</sub>	71.4	.0290	
n-Propyl alcohol.....	V <sub>1</sub>	52.9	.0215	V <sub>1</sub>	113.7	.0462	
n-Butyl alcohol.....	V <sub>1</sub>	25.7	.0269	V <sub>1</sub>	56.2	.0588	

TABLE III.—EFFECT OF TEMPERATURE ON KINEMATIC VISCOSITY

Kinematic viscosity at 30° C., c. g. s. units	Solutions, <sup>1</sup> per cent by weight	Temperature in °C. at which the relative kinematic viscosity $\frac{v_1}{v_m}$ is—				
		2	5	10	20	30
0.6	a 83 G+12 M.....	20	8	0	-7	-11
	b 79 G+21 Pr.....	19	6	-3	-11	-15
	c 93 N+1 S.....	16	-1	-8	-9	
	d 98 N+1 T.....	16	-1	-8		
	e 95 P+5 X.....	13	-3	-11	-16	-18
.4	a 84 G+16 M.....	19	7	-2	-10	-13
	b 71 G+29 Pr.....	18	4	-5	-13	-17
	c 92 N+8 S.....	15	-2	-8	-9	
	d 94 N+6 T.....	14	-4	-11		
	e 89 P+11 X.....	12	-6	-14	-20	-23
.2	a 80 G+43 Pr.....	16	2	-9	-18	-22
	b 93 Su+7 S.....	16	1	-9	-17	-21
	c 78 N+22 S.....	12	-7	-13	-15	
	d 85 N+15 T.....	11	-10	-18		
	e 80 P+20 X.....	10	-10	-20	-17	-30
.1	a 87 P+13 T.....	12	-7	-14	-19	-21
	b 66 G+34 M.....	16	-3	-12	-21	-27
	c 41 G+59 Pr.....	12	-4	-16	-25	-31
	d 99 E+1 M.....	14	-4	-15	-24	-29
	e 97 E+3 EA.....	14	-4	-15	-24	-30
.05	a 96 E+4 Pr.....	12	-5	-16	-24	-30
	b 92 E+8 B.....	13	-5	-16	-24	-30
	c 77 Su+23 S.....	17	-4	-16	-23	-27
	d 87 W+13 S.....	13	-4	-13	-22	-27
	e 90 W+10 X.....	14	-4	-14	-23	-29
.0269	a 62 N+33 S.....	8	-14	-20	-25	
	b 73 N+27 T.....	7	-14	-22		
	c 68 P+32 X.....	7	-16	-26	-33	-38
	d 74 P+26 T.....	8	-14	-21	-26	-29
	e 54 G+46 M.....	12	-10	-23	-32	-37
.026	a 24 G+76 Pr.....	10	-11	-24	-36	-42
	b 82 E+18 M.....	10	-11	-23	-33	-42
	c 68 E+32 EA.....	9	-13	-26	-36	-41
	d 62 E+48 Pr.....	9	-13	-26	-37	-43
	e 44 E+56 B.....	9	-13	-26	-38	-44
.0215	a 83 Su+47 S.....	8	-12	-25	-34	-39
	b 69 W+31 S.....	8	-12	-24	-33	-38
	c 78 W+22 X.....	8	-14	-24	-32	-36
	d 43 N+57 S.....	4	-23	-26		
	e 53 N+42 T.....	2	-22	-30		
.0166	a 55 P+45 X.....	1	-24	-33	-41	-43
	b 59 P+41 T.....	2	-21	-33	-40	-45
	c 40 G+60 M.....	6	-20	-43	-50	
	d 5 G+95 Pr.....	3	-25	-42	-55	-55
	e 61 E+39 M.....	5	-20	-34	-51	-55
.0149	a 32 E+63 EA.....	3	-22	-37	-51	-55
	b 9 E+91 Pr.....	3	-26	-43	-56	-55
	c 45 W+55 S.....	3	-26	-37	-47	-50
	d 61 W+39 X.....	2	-23	-38	-47	-51
	e 23 Su+77 S.....	1	-26	-38	-43	-60
.0112	a 26 N+75 S.....	-1	-30	-38	-39	
	b 41 N+59 T.....	-4	-32	-40		
	c 37 P+63 X.....	-5	-32	-43	-50	-50
	d 41 P+59 T.....	-5	-33	-48	-50	-50
	e 15 G+85 M.....	-6	-42	-45		
.00670	a 24 E+76 M.....	-8	-42	-55		
	b 25 W+75 X.....	-12	-45	-55		
	c 15 N+85 T.....	-15	-50	-50		
	d 12 P+83 X.....	-19	-50	-55	-55	
	e 15 P+85 T.....	-15				
.00683	a m-Xylene.....	-21	-50			
	b Methyl alcohol.....	-16	-50			
	c Toluene.....	-20	-50			

<sup>1</sup> B=n-Butyl alcohol, E=ethylene glycol, EA=ethyl alcohol, G=glycerine, M=methyl alcohol, N=neat's-foot oil, P=poppyseed oil, Pr=n-Propyl alcohol, S=mineral spirits, Su=Superia clock oil, T=toluene, W=Wilkins' oil, and X=m-Xylene.

<sup>2</sup> Indicates that the temperature is lower than that given.

## SECULAR VARIATIONS

Certain oils, notably poppy-seed and linseed, oxidize comparatively rapidly when exposed to the air, and this oxidation is accompanied by a progressive increase in the kinematic viscosity. The addition of small amounts of certain substances, such as  $\beta$ -naphthol, hydroquinone, and diphenylamine, called antioxidants, are known to retard the oxidation in many cases. Consequently it seemed desirable to study the secular variation in the kinematic viscosity of solutions of these oils containing a small amount of antioxidant. Hydroquinone is insoluble in linseed oil (reference 4), but can be dissolved in poppy-seed oil by first dissolving it in ether, adding that solution to the oil, and then removing the ether by heating to about 60° C. The other two antioxidants can be mixed readily with either oil.

One per cent of antioxidant was added to the oil, and the mixture was dissolved in m-xylene in various proportions.

About 100 cm.<sup>3</sup> of each solution was kept for 590 days in a bottle open to the air and exposed to daylight, but protected from dust. The liquids were not agitated. The kinematic viscosity of each of the solutions was measured at intervals during the exposure. As a certain amount of the xylene evaporated during the exposure, the weight of each of the solutions containing xylene was brought up to its original weight by the addition of xylene before determining the kinematic viscosity. This procedure does not take account of the change in weight through oxidation, but the error so introduced in the viscosity measurements is in all probability small in comparison with the effect due to oxidation.

The quotients of the kinematic viscosity of each of these solutions after various intervals of time divided by its initial value are given in Table IV. It is evident that in all cases the kinematic viscosity changes more slowly at the beginning than at the end of the exposure. Owing to the induction period, the same is true of the oxidation. (Cf. section on Oxidation.) It is also evident that only for the solutions of poppy-seed oil containing hydroquinone is the viscosity sufficiently constant for practical purposes. The color of the poppy-seed oil solutions was initially a light amber; during exposure it changed to a deep red brown, making the solution unsatisfactory when high visibility is required.

Analyses of the mixture of poppy-seed oil and hydroquinone that had been exposed for 590 days and of the untreated oil that had been stored in a closed, opaque container were made by the chemistry division. The iodine number for the unexposed sample was found to be 142.9; that for the exposed sample 141.0; the acid content for the unexposed was 1.3 per cent, for the exposed 1.8 per cent. These values indicate that the oxidation was small. This comparison is justified

since Lewkowitsch (reference 5) states that an oil protected from moisture and light is stable.

TABLE IV.—CHANGE OF KINEMATIC VISCOSITY WITH TIME OF LIQUIDS CONTAINING ANTIOXIDANTS

Liquids	Relative kinematic viscosity			
	Time (days)			
	0	93	385	590
<i>Solutions with <math>\beta</math>-naphthol</i>				
Linseed oil, 100 per cent; xylene, 0 per cent.....	1.00	1.15	1.72	4.22
Linseed oil, 75 per cent; xylene, 25 per cent.....	1.00	1.25	1.72	3.45
Linseed oil, 50 per cent; xylene, 50 per cent.....	1.00	1.47	3.33	10.30
Poppy-seed oil, 100 per cent; xylene, 0 per cent.....	1.00	1.17	1.49	2.06
Poppy-seed oil, 75 per cent; xylene, 25 per cent.....	1.00	1.18	1.43	1.83
Poppy-seed oil, 50 per cent; xylene, 50 per cent.....	1.00	1.03	1.72	1.16
<i>Solutions with hydroquinone</i>				
Poppy-seed oil, 100 per cent; xylene, 0 per cent.....	1.00	1.01	1.07	1.14
Poppy-seed oil, 75 per cent; xylene, 25 per cent.....	1.00	1.01	1.02	1.07
Poppy-seed oil, 50 per cent; xylene, 50 per cent.....	1.00	.994	.970	1.05
<i>Solutions with diphenylamine</i>				
Linseed oil, 100 per cent; xylene, 0 per cent.....	1.00	1.09	1.73	2.39
Linseed oil, 75 per cent; xylene, 25 per cent.....	1.00	.97	2.39	3.48
Linseed oil, 50 per cent; xylene, 50 per cent.....	1.00	1.28	3.58	9.04
Poppy-seed oil, 100 per cent; xylene, 0 per cent.....	1.00	1.00	1.27	1.95
Poppy-seed oil, 75 per cent; xylene, 25 per cent.....	1.00	1.23	2.62	6.10
Poppy-seed oil, 50 per cent; xylene, 50 per cent.....	1.00	1.29	7.06	9.28

## THERMAL COEFFICIENT

The thermal coefficient  $R$  of the kinematic viscosity is defined by expression (7)

$$R = \frac{1}{\nu} \frac{d\nu}{d\theta} \quad (7)$$

which is equivalent to (8)

$$R = \frac{d}{d\theta} \log_e \frac{\nu_\theta}{\nu_0} \quad (8)$$

That is, for each point of the curves of Figures 4 to 16,  $R$  is the product of the slope of the curve at that point multiplied by 2.303, the factor required to convert common to Napierian logarithms.

 $R$ - $\nu$  RELATION

The slopes at the points corresponding to various temperatures were determined graphically. When  $R$  was plotted against  $\theta$  the points did not deviate from a smooth curve by more than 2 per cent. Values of  $\log_{10} R$  were plotted against associated values of  $\log_{10} \nu$ .

It was found that all points so determined for the alcoholic solutions (of glycerine and ethylene glycol) lie closely along a single smooth curve. Figure 17 and GE of Figure 19 show this curve for values determined at 0° and 30° C. Values for temperatures from 0° to -40° C. fall on this same curve. These values were not included in the figure.

The points determined for the mineral oil group at 0° and 30° C. lie along a second smooth curve. (GM of figs. 18 and 19.) For temperatures below 0° C. the curve for this group of liquids shifts to the right; that is,  $R$  increases with decrease in temperature. Curve CD of Figure 18 gives its position for -40° C.

The points determined for the animal and vegetable oils, including those derived from data given in the Smithsonian Physical Tables (1927), for soya-bean oil at 30° C., olive oil at 10°, 15°, 20°, 30°, and 40° C., and castor oil at 15°, 30°, and 40° C. lie along a third curve; and those for m-xylene, toluene, and mineral spirits at +30° C., 0° and -15° C. lie along a fourth curve differing but little from GM. (Fig. 19.) The points for the 50-50 solutions of animal and vegetable oils are much more scattered, but suggest a curve that is flatter than any of the others. Excepting these solutions, the individual points do not ordinarily depart from the curve by more than 10 per cent in  $R$ , an amount that is negligible for all practical purposes.

Thus within an error of 10 per cent in  $R$ , there is, for the range 30° to -40° C., for each of the groups of substances—(a) the alcohol group and (e) the solvents m-xylene, toluene, and mineral spirits—and for the range 30° to 0° C., for each of the groups—(b) mineral oils group and (d) the pure animal and vegetable oils—a definite relation between  $R$  and  $\nu$ ; a relation which is independent both of the chemical constituents of the various substances and solutions

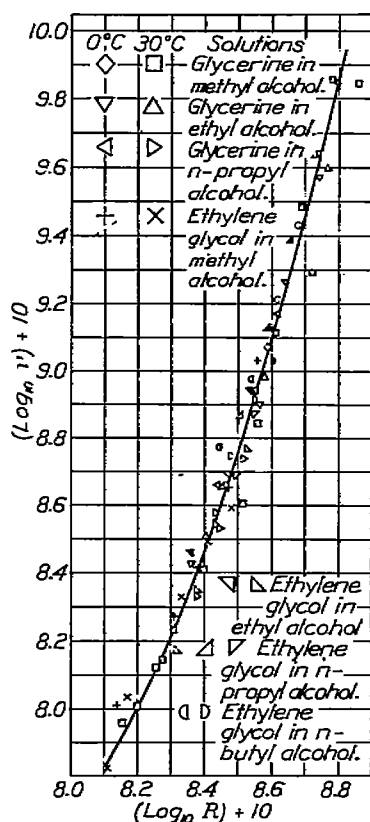


FIGURE 17.—Relation of the thermal coefficient  $R$  of kinematic viscosity and the kinematic viscosity  $\nu$  for the alcohol group of liquids.  $R$  is the relative change in kinematic viscosity per degree centigrade and  $\nu$  is in c. g. s. units

included in each group and also of the temperature. That is, within the limitations stated, the complete curve showing the relation between  $\nu$  and  $\theta$  can be constructed for any of the liquids when its value of  $\nu$  is known at any temperature; or, in other words, for

a given group, all solutions that have the same value of  $\nu$  at any one temperature will also have the same value at any other common temperature. This may also be seen by inspection of Table III. For the mineral oil group in the range of temperature from 0° to -40° C.

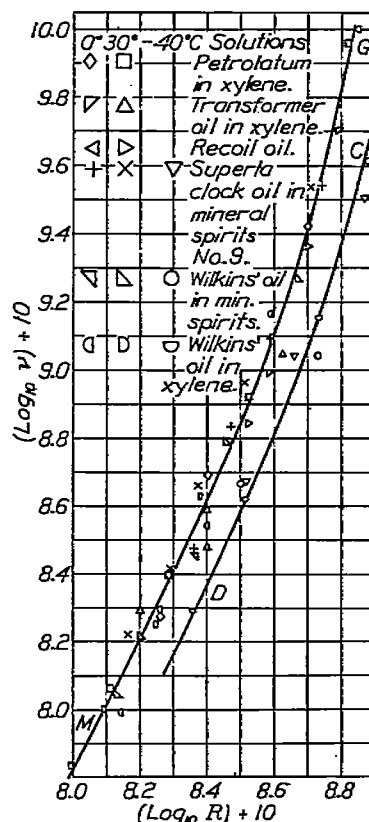


FIGURE 18.—Relation of thermal coefficient  $R$  of kinematic viscosity and the kinematic viscosity  $\nu$  for the mineral oil group of liquids.  $R$  is the relative change in kinematic viscosity per degree centigrade and  $\nu$  is in c. g. s. units

the fact that at any particular temperature  $R$  is a function only of  $\nu$  leads to the same conclusion that all solutions of this group having the same value of  $\nu$  at any one temperature will also have the same value at any other common temperature.

From the curves of Figure 19 it is evident that at temperatures above 0° C. the value of  $R$  for a given kinematic viscosity is smallest for the pure animal and vegetable oils group (d), and that for solutions of mineral oils group (b), it is somewhat less than for the alcoholic solutions group (a). For some of the pure animal and vegetable oils  $R$  remains less than for solutions of groups a and b even when the temperature has been reduced to -15° C.

#### $R$ - $\theta$ RELATION

The variation of  $R$  with the temperature  $\theta$  is shown by typical curves in Figures 20 to 23. Those of Figure 20 are typical of solutions of the alcohol group (a); those of Figure 21, of the mineral oil group (b); those of Figure 22, of solutions of animal and vegetable oils in m-xylene, toluene, or in mineral spirits; and in Figure 23 are several curves pertaining to the three groups,

the liquids being so chosen that for each of the curves A, B, and C, and also for each of the curves D, E, and F, the kinematic viscosity at 30° C. is the same.

All these curves are, as should be expected, characterized by a rapid increase in  $R$  as the solidification

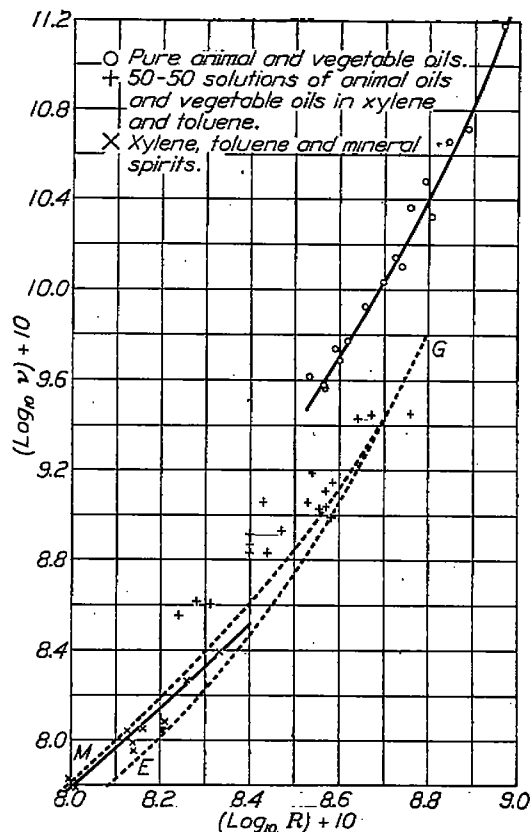


FIGURE 19.—Relation of the thermal coefficient  $R$  of kinematic viscosity and the kinematic viscosity  $\nu$  for the animal oil and vegetable oil group of liquids.  $R$  is the relative change in kinematic viscosity per degree centigrade and  $\nu$  is in c. g. s. units. The range of temperatures represented is from 0° to 40° C. for the pure oils and from -15° to +30° C. for the solutions and solvents. The dotted line GE is for the alcohol group from Figure 17, GM for the mineral oil group from Figure 18

point is approached, but the change in slope of the curves is particularly abrupt in the case of solutions of the animal and vegetable oils (figs. 22 and 23, curve F) which, when pure, solidify not far below 0° C. The temperature at which this abrupt change occurs may be called a critical temperature ( $\theta_c$ ). Though, of course, rather indefinite, it varies quite regularly with the concentration of the solution. In Figure 22, the several values of  $\theta_c$  lie in the neighborhood of the points E, F, G, H. Below that temperature the solution becomes more or less opaque, indicating the separation of something from the solution. That this change is progressive is shown by the gradual increase in the kinematic viscosity at constant temperature, the rate of change depending upon the temperature.

## V. SELECTION OF LIQUIDS

### KINEMATIC VISCOSITY

#### IDEAL REQUIREMENTS

In so far as the kinematic viscosity is concerned, that damping liquid is the best for a given aircraft use which has a suitable value of  $\nu_{30}$  and for which  $\log \frac{\nu_{\theta}}{\nu_{30}}$  remains the smallest throughout the temperature range +30° to -30° or -40° C.

The most suitable value for  $\nu_{30}$  will depend upon the mechanical characteristics of the particular instrument with which the liquid is to be used. Its determination lies beyond the scope of this paper.

From expression (8), (9) follows at once

$$\log_s \frac{\nu_{\theta}}{\nu_{30}} = \int_{30}^{\theta} R d\theta = n_1 \quad (9)$$

where  $n_1$  is the area inclosed by the axis of temperature, the ordinates at 30° and  $\theta$ , and some one of such curves as are given in Figures 20 to 23. Since the numerical value of  $R$  increases as the temperature decreases, the requirement that  $n_1$  shall be as small as possible for a given value of  $\nu_{30}$  demands that the

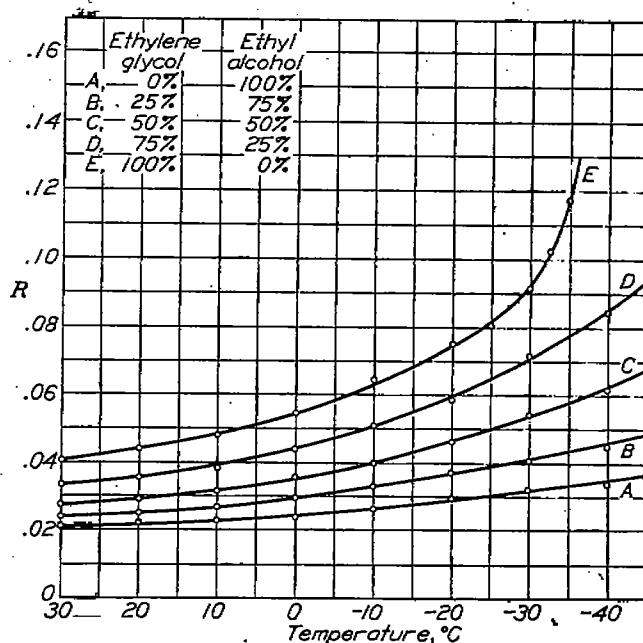


FIGURE 20.—Effect of temperature on the thermal coefficient  $R$  of kinematic viscosity of ethylene glycol-ethyl alcohol solutions.  $R$  is the relative change in kinematic viscosity per degree centigrade. Similar curves are obtained for the other liquids of the alcohol group

( $\theta$ ,  $R$ ) curve shall be reasonably flat throughout the range 30° to  $\theta$ , and that  $R$  be small at 30° C.; that is, that  $R$  be reasonably small throughout the range. But it has been shown (Cf. section on Thermal Coefficient, that within a given group (a, b, d, e, and,

less exactly, c) the value of  $R$  for a wide range of temperature is very closely determined by the value

under certain conditions be worth considering. The values of  $R$  for the various groups have already been compared.

#### SPECIFIED KINEMATIC VISCOSITY

The concentrations of mixtures having a specified kinematic viscosity at 30° C. may be found from Table III, which also gives an indication of the way  $\nu$  varies with the temperature.

In order to find the concentrations of mixtures having a specified kinematic viscosity at some specified

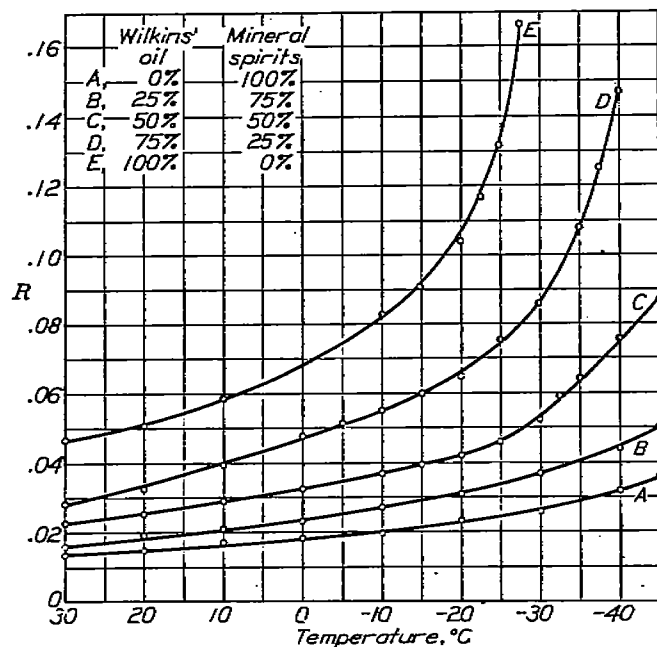


FIGURE 21.—Effect of temperature on the thermal coefficient  $R$  of kinematic viscosity of Wilkins' oil-mineral spirits solutions.  $R$  is the relative change in kinematic viscosity per degree centigrade. Similar curves are obtained for the other liquids of the mineral oil group

of  $\nu$  alone; hence all members of the group that have the same value for  $\nu_{30}$  will have nearly the same value of  $n_1$ . The choice, therefore, rests between the groups

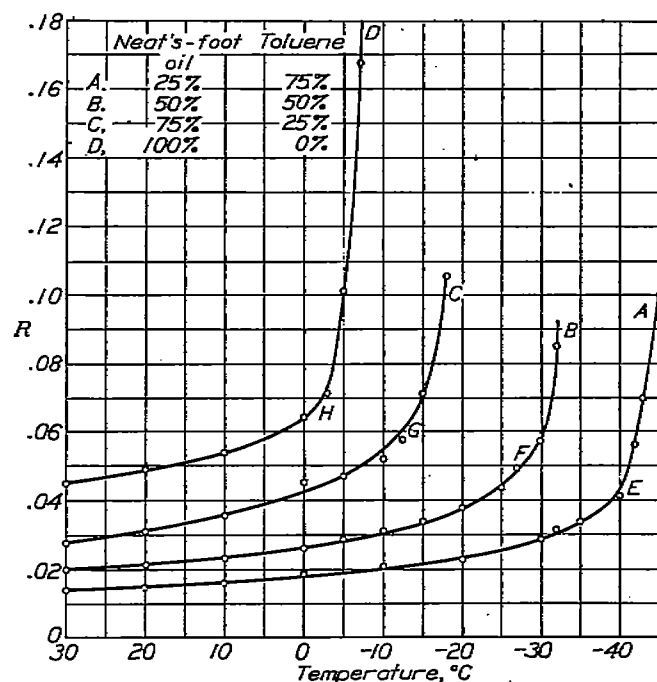


FIGURE 22.—Effect of temperature on the thermal coefficient  $R$  of kinematic viscosity of neat's-foot oil-toluene solutions.  $R$  is the relative change in kinematic viscosity per degree centigrade. Note the inflection in the curves at the points marked E, F, G, and H. This behavior is characteristic of the animal and vegetable oil solutions

rather than between the individual members of a group, although the small differences between the latter, as illustrated in Table III and in Figure 23, may

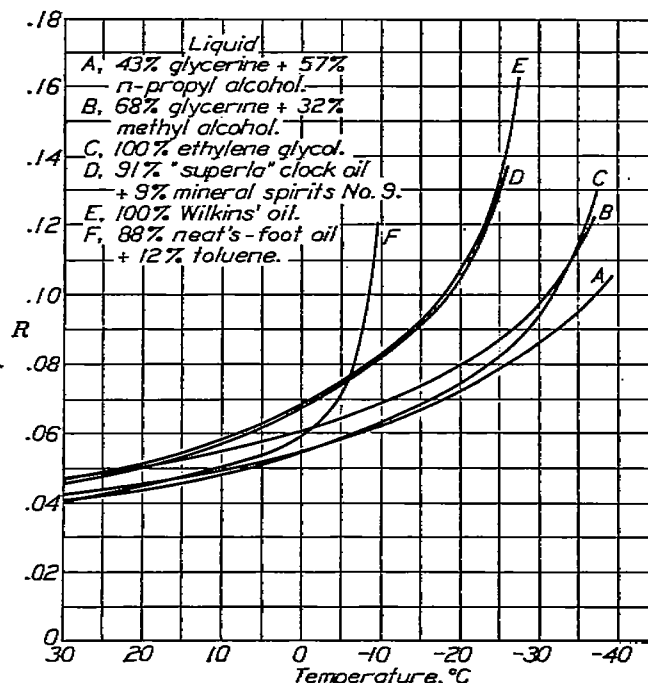


FIGURE 23.—Curves showing the variation in the effect of temperature on the thermal coefficient  $R$  of kinematic viscosity of two groups of liquids the kinematic viscosity of which is the same at 30° C. The latter quantity is 0.107 c. g. s. units for curves A, B, and C and 0.185 c. g. s. units for curves D, E, and F.  $R$  is the relative change in kinematic viscosity per degree centigrade.

temperature other than 30° C, proceed thus. From the appropriate figure (17, 18, or 19), depending upon the group of mixtures in which you are interested, find the value of  $R$  corresponding to the specified value of  $\nu$ . With this value of  $R$  and the specified temperature enter that figure (20, 21, or 22) in which is given data for a liquid of your group and, by interpolation, determine the concentration. Then from Table II or Table III determine the value of  $\nu_{30}$  for the concentration of this special mixture, and then from the same tables find the concentrations of other mixtures for which  $\nu_{30}$  has the same value. (Cf. Section on Experimental Results.) These, having all the same value at 30° C., will all have practically the same value (that specified) at the specified temperature. If the specified temperature is below 0° C.,  $R$  should be determined from Figure 18 by interpolation.

#### SPECIFIED CONCENTRATION

The value of  $\nu$  for a solution of specified concentration can often be obtained by interpolation be-

tween the values of Table III. In other cases obtain the appropriate value of  $\nu_0$  from Table II and the appropriate  $n_0 = \log_{10} \frac{\nu_0}{\nu_0}$  from Figures 4 to 16, interpolating in each case, as may be necessary. Then  $\nu_0$  is determined by means of (10)

$$\nu_0 = \nu_0 \text{ antilog}_{10} n_0 \quad (10)$$

#### OTHER FACTORS

Besides the kinematic viscosity, to which the present investigation has been mainly restricted, other factors must be considered in choosing a damping liquid. These factors may in some cases be of sufficient importance to cause the rejection of a liquid that would be ideal from the standpoint of its kinematic viscosity alone. Thus, solutions of glycerine and of ethylene glycol are relatively unsuitable for instruments that have to be sealed by means of gaskets, but are quite suitable for those using an all-glass container.

In the following paragraphs some of the more important of these factors are considered, in many cases together with their pertinence to the solutions studied in this work.

#### TRANSPARENCY

It is known that the lighter mineral oil products will darken in time upon exposure to light if unsaturated compounds are present. Two samples of mineral spirits were used in this work. One darkened in color so as to become nearly opaque; the other remained clear in color after over 12 months' exposure, a good portion of the time in sunlight.

#### HOMOGENEITY

In selecting the solutions to be studied in this work, considerable weight was given to the miscibility of their constituents at low temperatures. The kinematic viscosity was measured only of those mixtures which remained homogeneous solutions down to  $-10^\circ \text{C}$ .

Those solutions of glycerine and of ethylene glycol of which the kinematic viscosity was measured remained miscible from  $+30^\circ$  to  $-50^\circ \text{C}$ . or until freezing occurred. This was also true for the solutions of mineral oil in mineral spirits, but not for the solutions of mineral oil in toluene or in xylene, which showed a gradual crystallization of the solvent at low temperatures. As the temperature was lowered the animal oil and the vegetable oil solutions all showed a gradual separation and freezing of some of the components of the oil, the amount of separation at any temperature being dependent on the length of time it was kept at that temperature.

The following solutions were miscible at room temperature, but separation took place at a tempera-

ture above  $-10^\circ \text{C}$ ., and no determination of the viscosity was made:

Neat's-foot oil in...	n-propyl alcohol.
	n-butyl alcohol.
	acetone.
Poppy-seed oil in...	n-propyl alcohol.
	n-butyl alcohol.
	acetone.
Glycerine in.....	acetone.
	toluene.
	n-butyl alcohol.

#### CORROSION

In order that a liquid may be satisfactory as a damping liquid it must not corrode metals with which it may come in contact. The corrosion is usually due to acids present in the liquid. In general, both animal and vegetable oils contain acids, which increase in amount with age if the oils are exposed to the air and light. The factors affecting the change in acid content are discussed in connection with oxidation in another paragraph. It was found that brass was corroded in a few hours by a mixture of neat's-foot oil and xylene though neither the neat's-foot oil nor the xylene alone caused corrosion. Steel balls corroded when sealed in glass tubes nearly filled with this solution. Evidently the xylene acted as a catalyst and hastened the formation of acid.

#### VAPOR PRESSURE

In choosing a damping liquid to be used in open containers consideration should be given to its vapor pressure; other factors being equal, the liquid with the lowest vapor pressure will evaporate the slowest.

#### OXIDATION AND ANTIOXIDANTS

The unsaturated fatty oils, of which poppy-seed oil and linseed oil are typical, are subject to oxidation upon exposure to the air, with an accompanying increase in viscosity and acidity. The unsaturated fatty oil is primarily oxidized into a peroxide  $\begin{pmatrix} -\text{CH}-\text{O} \\ -\text{CH}-\text{O} \end{pmatrix}$  which is decomposed by heat into aldehydes which are further transformed into acids by the absorption of oxygen. (Reference 1.)

The oxidation usually shows two stages—the induction or incubation period, during which the rate of oxidation is very slow, and a second stage in which the rate is much more rapid. Several factors influence the duration of the first stage. Yamaguchi (reference 2) in his report of the action of antioxidants in the oxidation of unsaturated fatty oils, using olive oil and castor oil, gives data which indicates that the logarithm of the period of induction is nearly linear with the temperature. The rate of oxidation is affected by light, moisture, increase in oxygen concentration, temperature, catalysts, acids, electrolytes, and is usually accompanied by a darkening, a change in color, in odor, and in taste, the appearance of waxes,

hardening, and other changes in physical and chemical properties. (Reference 3.)

The determination of both the decrease in the iodine value and the increase in the acid content appears to be the best method for measuring the rate of oxidation. The iodine value is a measure of the amount of double bonds present in the unsaturated compounds. (Reference 1.) The primary oxidation into the peroxide results in a decrease in the iodine value. The decomposition products absorb oxygen and form acids, with a resultant increase in acid content.

The addition of an inhibitor or antioxidant to the oil retards the rate of oxidation, or even stays it for a period. From the results of Yamaguchi there appear to be two kinds of inhibitors. (References 2 and 7.) He finds diphenylhydrazine and hydroquinone inhibit oxidation in such a way as to increase the induction period by an amount which depends both on the amount of antioxidant used and the temperature of the oil. After this period, oxidation proceeds as if no antioxidant were present. This leads to the conclusion that these antioxidants, diphenylhydrazine and hydroquinone, must be entirely absent from the oil before the oxidation can start and that the presence of even a very small amount of them can inhibit the oxidation very effectively. Yamaguchi found hydroquinone to have an inhibitory power superior to that of the other. A mere trace of hydroquinone is sufficient to lengthen the period of induction greatly.

The inhibitive action of  $\alpha$ -naphthylamine and diphenylamine is different in that they do not alter the period of induction but do lower the rate of oxidation considerably. The lowered rate of oxidation gradually increases with time until it finally becomes that of the untreated oil.

In the present work it was found that the addition of one per cent of hydroquinone to a *m*-xylene solution of poppy-seed oil inhibits its oxidation to such an extent that its viscosity changed only a few per cent in the course of 590 days. (See Table IV.)

## VI. CONCLUSIONS

In choosing a damping liquid for use in aircraft instruments the following factors must be considered in addition to the proper value of the kinematic viscosity: (a) Useful temperature range, (b) transparency, (c) homogeneity, (d) corrosion, (e) vapor pressure, and (f) chemical stability. In this investigation data were secured principally on the kinematic viscosity of selected liquids and solutions in the range  $-50^{\circ}$  to  $+30^{\circ}$  C. The range of temperature in which a given liquid may be useful is thus determined. Data on the other factors were obtained only incidentally except that the effect of certain antioxidants on the kinematic viscosity of solutions of poppy-seed oil and of linseed oil were investigated. One, hydroquinone, was found to be effective.

The results on kinematic viscosity may be summarized as follows:

(1) For each of the alcohol and mineral oil groups of the liquids tested, a single curve represents the relation of the thermal coefficient of kinematic viscosity to the kinematic viscosity. (Figs. 17 and 18.) This relation is independent of the composition of the individual liquids and mixtures and, within the range  $+30^{\circ}$  to  $0^{\circ}$  C. for the mineral oil group, and  $+30^{\circ}$  to  $-40^{\circ}$  C. for the alcohol group, of the temperature of the liquid. This relation is also true for the group of pure animal and vegetable oils within the range  $30^{\circ}$  to  $0^{\circ}$  C.

(2) For the three groups of liquids tested no one liquid or solution in a particular group had a thermal coefficient at a given kinematic viscosity which varied more than 10 per cent from that defined by the curve for the group.

(3) At the higher temperatures the pure animal and vegetable oils have, relatively, the smallest thermal coefficient of kinematic viscosity. The coefficient of the mineral oil group is less than that of the alcohol group but the difference is slight.

## ACKNOWLEDGMENTS

It is desired to acknowledge the kindly interest and valuable assistance of Dr. W. G. Brombacher and Dr. N. E. Dorsey, and the suggestions of Mr. J. B. Peterson for improving the design of the apparatus for the control of temperature.

BUREAU OF STANDARDS,

WASHINGTON, D. C., March 28, 1931

## REFERENCES

1. Ingle, H.: Preliminary Notes on the Oxidation of Oils. *Jour. Soc. Chem. Ind.*, Vol. 32, p. 639, 1913.
2. Yamaguchi, B.: Action of Antioxidants in Oxidation of Unsaturated Fatty Oils. Part I: Mechanism of inhibitory action of diphenylhydrazine and  $\alpha$ -naphthylamine. Report of the Aeronautical Research Institute, Tokyo Imperial University, Vol. 5, p. 195, 1930.
3. Smith, O. M. and Wood, E. R.: Inhibiting Agents in the Oxidation of Unsaturated Organic Compounds. *Journal of Industrial & Engineering Chemistry*, Vol. 18, p. 691, 1926.
4. Rogers, W., and Taylor, H. S.: The Rate of Oxidation of Linseed Oil. *Jour. Phys. Chem.*, Vol. 30, p. 1334, 1926.
5. Lewkowitsch, J.: Chemical Technology and Analysis of Oils, Fats and Waxes, Vol. 1, p. 34, 4th Edition, 1909.
6. Keulegan, G. H.: Investigation of Damping Liquids for Aircraft Instruments. N. A. C. A. Technical Report No. 299, 1929.
7. Yamaguchi, B.: Action of Antioxygens in the Oxidation of Fatty Oils. Part II: Inhibitory effect of diphenylamine, diphenylguanidine and hydroquinone. Report of the Aeronautical Research Institute, Tokyo Imperial University, Vol. 5, p. 287, 1930.