STUDY OF THE PRESENT METHODS FOR THE MEASUREMENT OF VISCOSITY AND THE DESIGN AND CONSTRUCTION OF VISCOSIMETERS

by

Walter Webb

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Approved:

Head of Department

Professor in Charge

Dean of the College

Chairman, Graduate Committee

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I. Introduction

The property of a liquid whereby it resists the relative motion of its parts is called viscosity.

In the study of the flow of viscous fluids, complete solutions to problems may be obtained only when the viscosity of the fluid is known. The subject of the measurement of viscosity is known as viscometry, or viscosimetry, and the instruments employed for this purpose are called viscometers, or viscosimeters.

The viscosity of liquids is of great importance in the paint, pyroxlin, silicate, starch and other industries as well as in the lubrication of machinery.

The purpose of this study is the preparation of a digest of the literature on the present methods of measuring viscosity, and the construction and the calibration of a viscosimeter of the Stormer type for the Department of Physics.

II. Newton's Hypothesis

Newton was the first to formulate a hypothesis regarding the magnitude of the force required to overcome viscous resistance andto treat a case of motion in a viscous fluid.

> " On the Circular Motion of Liquids
>
> Hypothesis
>
> That the resistance which arises from the lack of slipperiness of the parts of the liquid, other things being equal, is proportional to the velocity with which the parts of the liquid are separated from one another." [1]

Newton's fundamental assumption amounts to the following: If two laminae having an area of contact A move with constant velocities v_1 and v_2, the force required to maintain the constant difference of velocity is

$$F = nA \frac{(v_1 - v_2)}{(z_1 - z_2)}$$

where the z's (thickness of liquid) are measured in the direction perpendicular to the laminae. Since the velocity in the liquid changes continuously the differences should be replaced by differentials:

$$F = nA \frac{dv}{dz}$$

n is a characteristic constant for each liquid and is called the coefficient of viscosity. It decreases with temperature.

The fundamental unit (cgs) of absolute viscosity is the poise, and its hundreth part, the centipoise (the practical unit). If a liquid placed between two parallel plates one centimeter a part, introduces a resistance of one dyne per square centimeter when one plate is moved one centimeter per second, its viscosity is said to be one poise. The unit is called a poise in honor of Poiseuille.[*]

The reciprocal of the viscosity is called the fluidity and it is usually expressed, in rhes, as one divided by the viscosity in poises, $1/n$ in poises.

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[*] French physicist, 1799 - 1869

III. Absolute Viscosity and the Flow of a Viscous Fluid In a Capillary

The most widely used method for determining viscosity coefficients is still in principle that of Poiseuille.[2] The liquid is forced through a capillary tube, and n is deduced from the volume discharged in unit time, the pressure and the dimensions of the apparatus. The advantages of the apparatus are: the simplicity and cheapness of the equipment, the small quanity of liquid required for examination, the ease with which it can be maintained at constant temperature, and finally that the mathematical theory can be readily developed.

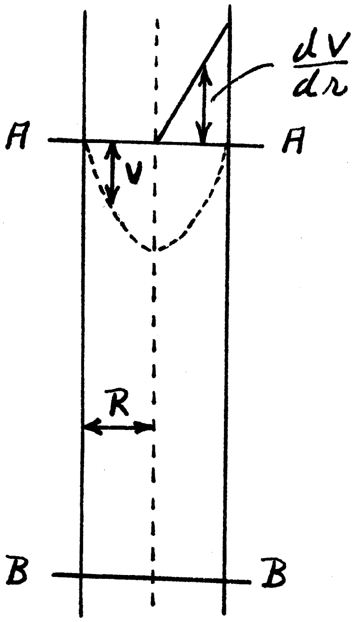

Figure 1

Consider a portion AB of a cylindrical tube having a circular cross section of radius R (Fig. 1). The distance AB = L, and a difference of pressure = P is maintained between A and B, which causes the liquid to flow through the tube. Assume the flow to be such that every particle of liquid moves parallel to the axis of the cylinder with constant velocity v. For reasons of symmetry this velocity will be the same for all points lying on the same circle, so that we may consider the liquid composed of cylindrical laminae moving with velocities which are functions of their radii.

The force exerted by the pressure P on a cylinder of radius r is

$$F_p = \pi r^2 P$$

the resistance around the surface of the cylinder caused by the viscosity of the liquid will, according to the fundamental assumption, be given by the product: area x viscosity coefficient x velocity gradient,

$$F_v = 2\pi rLn\frac{dv}{dr}$$

If the cylinder is not being accelerated, i.e., if v remains constant, the forces acting on the cylinder must be equal and opposite, $F_p = -F_v$, and

$$\pi r^2 P = -2\pi rLn\,\frac{dv}{dr}$$

$$rP = -\,2Ln\,\frac{dv}{dr} \qquad (1)$$

the velocity gradient is

$$\frac{dv}{dr} = -\frac{rP}{2Ln} \qquad (2)$$

By integration we find:

$$v = -\frac{r^2P}{4Ln} + C \qquad (3)$$

It now remains to determine the integration constant C. The usual assumption is that the lamina in contact with the wall of the tube adheres to it, that is,

$$v = 0, \text{ for } r = R$$

The integration constant then becomes

$$C = \frac{R^2P}{4Ln}$$

and the velocity

$$v = -\frac{r^2P}{4Ln} + \frac{R^2P}{4Ln}$$

$$v = \frac{P}{4Ln}(R^2 - r^2) \tag{4}$$

This is the equation of a parabola (Fig.1), the axis of which is the axis of v, while the axis r is at the distance $R^2P/4Ln$ from the apex of the curve, Since v is the distance traveled in unit time, the particles of liquid which were in the plane AA at zero time will be on the surface of the paraboloid, the profile of which is given by equation (4) after unit time; the volume of this paraboloid is the volume of liquid V_1 which passes in unit time. The volume of this solid of revolution is

$$V_1 = 2\pi \int_0^R vrdr$$

introducing the value of v,

$$V_1 = \frac{2\pi}{2Ln}\int_0^R (R^2 - r^2)r\,dr$$

$$V_1 = \frac{\pi PR^4}{8Ln} \tag{5}$$

As the rate of flow is constant, it follows that the volume V_t discharged in time t is

$$V_t = \frac{\pi PR^4}{8Ln}\ t \tag{6}$$

Osbourne Reynolds[3] found that Poiseuille's law holds with great exactness when the rate of flow is slow, yet it breaks down when the mean velocity exceeds a certain value depending on the size of the tube and the velocity of the liquid.

The most accurate method for measuring viscosity appears to consist in measuring the rate of flow of a liquid through a long narrow tube. If the dimensions of the tube are known, it has been found from much experiment that the time of flow is directly proportional to the absolute viscosity, to the length of the tube, and to the volume of liquid that flows through it, and is inversely proportional to the pressure forcing the liquid through the tube, to the fourth power of the radius of the tube, and to the force of gravity, that is

$$t = \frac{8\ LVn}{\pi gPR^4} \tag{7}$$

which is Poiseuille's law (usually solved for n instead of t).

It is very difficult to construct a capillary of exactly uniform and known bore, several investigators[4] have attempted this, and have used their best tubes to measure the absolute viscosity of water. Their results are in very good agreement and the best of these give an average value of 1.005 centipoises at 20.0°C (68.00°F), which is now generally accepted as correct for the absolute viscosity of water.

IV. Kinematic Viscosity

In an instrument of the so called Saybolt or Ostwald type[5] wherein the force driving the oil through the capillary is the pressure produced by the column of oil above the outlet, gravatation, as well as the viscosity of the oil, determines the time of flow. In such a case the time of flow is proportional to the absolute viscosity, n, (in poises) divided by the density, d, (in grams per cubic centimeter). This ratio is called the kinematic viscosity, **KV**, the unit being called the stoke and its hundreth part the centistoke. This unit is very convenient, because in instruments of the Saybolt type the time of flow is directly proportional to the kinematic viscosity, which can be determined without knowing the density. It is scientifically precise, since multiplying it by the density gives the absolute viscosity: **KV** x d = n.

In calibrating a viscosimeter with water or any other standard liquid it is convenient to transfer Poiseuille's law into the form

$$\frac{n}{t} = \frac{\pi gHdR^4}{8\ LV} \qquad (8)$$

where the force driving the liquid through the capillary is due to the difference in level of the liquid in the two arms of the viscosimeter, the pressure P, being equal to the average head, H, times the density, d, of the liquid. If the kinematic viscosity is used instead of the absolute viscosity, this equation becomes

$$\frac{KV}{t} = \frac{\pi gHR^4}{8\ LV} = C \qquad (9)$$

$$KV = Ct$$

For a given viscosimeter, all the terms on the right-hand side of equation (9) are constant, so that the entire expression can be set equal to a constant C. This calibration constant, C, is evaluated by measuring the time of flow, t, at the desired temperature for the standard liquid of known kinematic viscosity, KV; C = KV/t. If the viscosimeter has been so constructed that all errors can be avoided, or corrected this calibration constant remains the same regardless of the viscosity of the liquid that is being examined. Hence, the kinematic viscosity, KV, of any liquid can be determined simply by observing its time of flow, t, and multiplying this time by the viscosimeter constant, C : KV = Ct. Once an Ostwald viscosimeter has been calibrated it is easy to calculate the kinematic viscosity of any liquid from its time of flow.

The U. S. Bureau of Standards and the American Society for Testing Materials have adopted the Saybolt and Ostwald Viscosimeters as two of the official instruments for measuring kinematic viscosity.

Saybolt viscosity is expressed in Saybolt Universal (Furol) seconds which is the time for 60 ml. of oil to be delivered through the universal outlet tube. The relation between Saybolt and kinematic viscosity is given by the following table:

Table I. Values for Converting Kinematic Viscosity to Saybolt Universal Viscosity.[6]

Kinematic Viscosity (Centistokes)	Equivalent Saybolt Universal Viscosity in Seconds at Temperatures of:		
	100°F Basic Values*	130°F	210°F
2	32.6	32.7	32.8
5	42.3	42.4	42.6
10	58.8	58.9	59.2
15	77.2	77.3	77.7
20	97.5	97.7	98.2
25	118.9	119.1	119.7
30	140.9	141.2	141.9
35	163.2	163.5	164.3
40	185.7	186.1	187.0
45	208.4	208.8	209.9
50	231.4	231.8	233.0
55	254.4	254.9	256.2
60	277.4	277.9	279.3
65	300.4	301.0	302.5
70	323.4	324.0	325.7
over 70	Saybolt sec. = centistoke x 4.620	Say. sec. = centistk. x 4.629	Say. sec = centistk x 4.652

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*To obtain the Saybolt Universal Viscosity equivalent to a kinematic viscosity determined at t° F, multiply the equivalent Saybolt Universal Viscosity at 100° F by $1 + (t - 100) \cdot 0.000064$.

V. Description of Different Viscosimeters

Capillary viscosimeters fall into two classes: (1) instruments for determining absolute viscosities directly from the dimensions of the instruments and from the experimental data, and (2) instruments for determining relative viscosities by reference to suitable standard liquids.

The measurement of relative viscosities is comparitively easy. It is customary to determine accurately how the viscosity of any given liquid compares with that of water, and then calculate its absolute viscosity from the known absolute viscosity of water. This means that instead of constructing standard viscosity tubes, any tube of approximately the right dimensions can be chosen and calibrated by means of water as a standard liquid, and can then be used for determining the absolute viscosity of other liquids.

A. Stokes' Falling Sphere Type

One of the simplest viscosimeters is that in which a small sphere is allowed to fall through a column of liquid.[7] The rate at which it falls is inversely proportional to the viscosity, which can be calculated with the aid of Stokes' law. The volume of liquid required is inconveniently large; and the experimental errors are such that the method is not highly accurate.

Stokes[*] shows that a sphere impelled by a constant force, F, in a viscous liquid eventually assumes a constant velocity V, and that the following linear relation holds:

$$F = 6 \pi n r V$$

The most important special case, as far as the determination of

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[*] English mathematical physicist, 1819 - 1903

viscosity coefficients is concerned, is that in which the sphere falls(or rises) through the liquid owing to its weight (or buoyancy). The force then becomes

$$F = \frac{4}{3}\pi r^3 g(p - p')$$

Introducing this value into the previous expression the equation known generally as Stokes' formula is obtained:

$$V = \frac{2 r^2 g(p - p')}{9n}$$

r = radius of sphere
p = density of sphere
p' = density of liquid.

This equation enables us to deduce the viscosity coefficient from the observed velocity of fall of a sphere of known mass and radius in a liquid of known density, provided a number of conditions assumed in deducing the formula are satisfied. These are:

(1) The velocity is so small that higher powers of it may be neglected.

(2) There is no slip between the liquid and the surface of the sphere.

(3) The liquid is infinitely extended.

B. Mac Michael

Mac Michael[8] has described a viscosimeter of the torsional type (see Fig. 2), in which a disk is suspended by a wire in a rotating cup containing the liquid to be examined. When the temperature and speed of rotation are controlled, the angular deflection is proportional to the viscosity of the liquid. It is claimed that the results are accurate to within ± 0.5 per cent. The determination is more rapid than with capillary tube viscosimeters and the presence of small particles

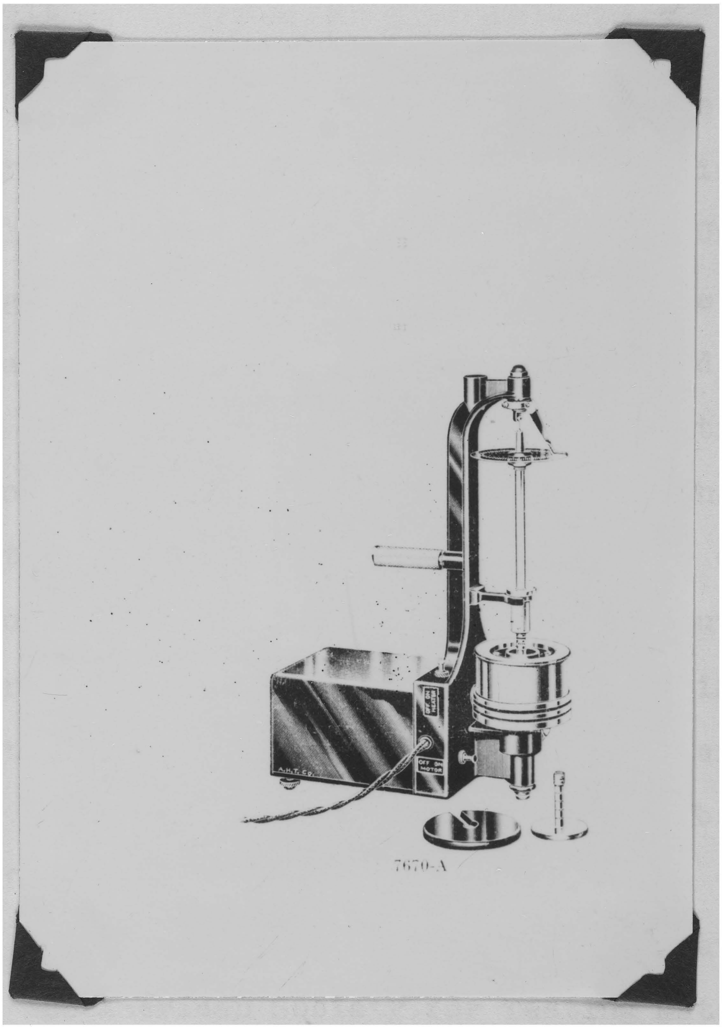


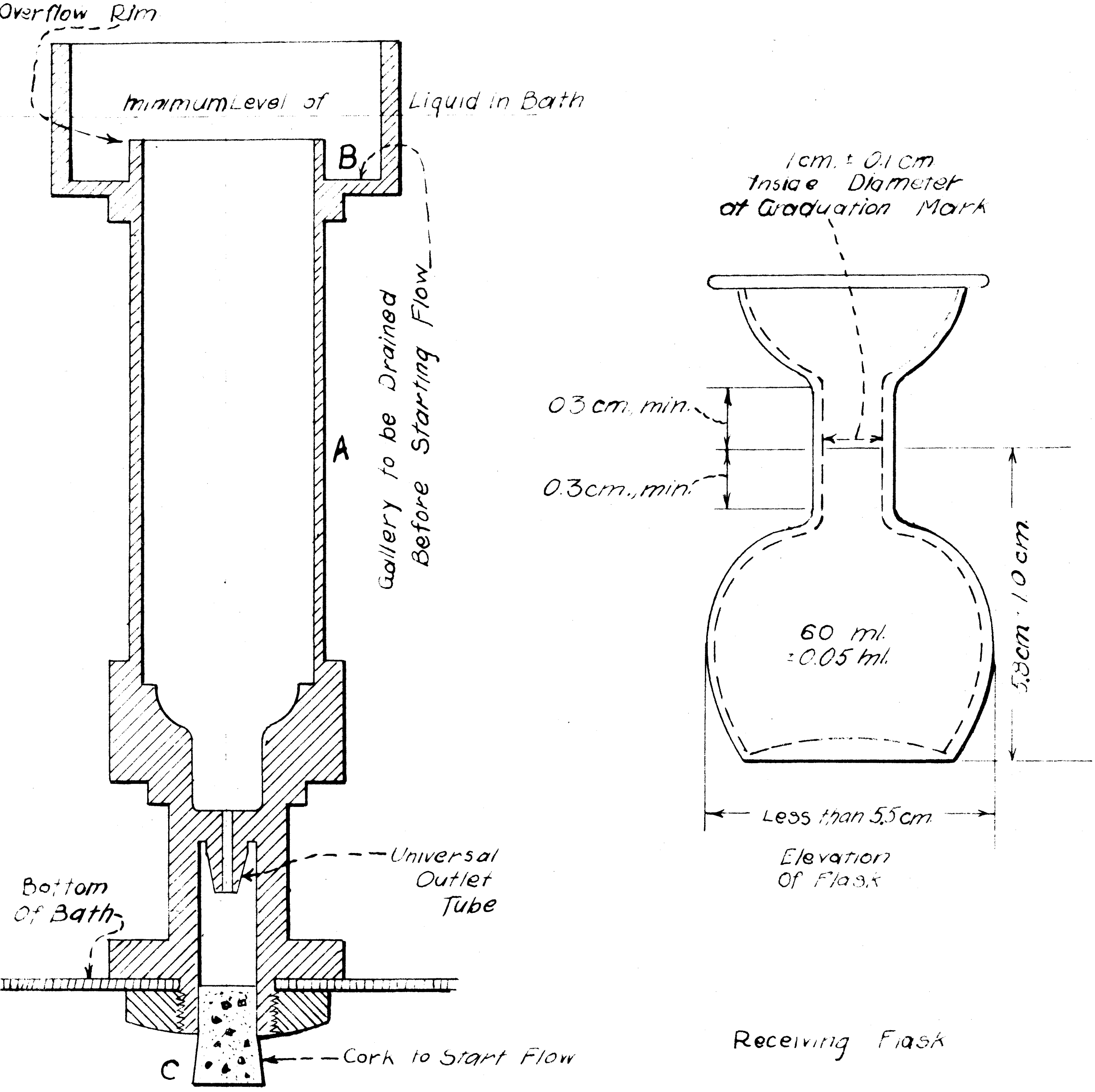
Fig. 2. MacMichael Viscosimeter.

of foreign materials in the liquid does not affect the accuracy. This instrument has been used to determine the apparent viscosity of drilling muds. The results are obtained in entirely arbitrary units unless the scale is calibrated with fluids of known viscosity. About 100 cc. of liquid is required for a determination.

C. Saybolt

The [9] viscosimeter best known in the oil industry is that officially adopted by the American Society for Testing Materials in 1926 and called the " Saybolt Universal Viscosimeter (see Fig. 3). It is about the only viscosimeter that is commercially available in this country, calibrated and ready to use. It is a convenient viscosimeter for the testing of most lubricating oils, consisting of a chamber A in which the oil is held at constant temperature(usually 100°, 130°, or 210°F) while a given volume, 60 ml, is permitted to flow out through a small metal orifice in the bottom of the tube during a measured time. Viscosities measured with this instrument are expressed in Saybolt Universal seconds, which is the number of seconds required for 60 ml. ofthe oil to be delivered through a Master Saybolt tube kept at the United States Bureau of Standards.

The American Society for Testing Materials Specifications (1930) state that the time of flow for a commercial Saybolt shall be within ±1 percent of the time with the master tube. One reason why the experimental errors become considerable in the low viscosity range is the difficulty of measuring the time with sufficient accuracy. If 60 cc. of a light motor oil are delivered in 50 seconds (at 210°F), the volume of oil in the receiver is



Elevation Of Flask

Receiving Flask

Sectional View Of Standard Oil Tube

(SAYBOLT)

Fig. 3.

changing by more than 1 cc. per second, and if a stopwatch graduated to 0.2 second is used, the oberservation for the time of 60 cc. delivery may be in error by as much as 0.4 second, which corresponds to an error of 0.8%.

It has been shown that an even greater lack of precision in the Saybolt instruments is introduced by the tables or equations for converting Saybolt seconds to kinematic viscosity. The viscosity-temperature chart arranged by a committee of the American Society for Testing Materials has recommended the use of two equations for converting kinematic viscosity to Saybolt seconds, the first being used when the Saybolt viscosity is less than 100 seconds and the second being used when the Saybolt viscosity is greater than 100 seconds.

$$(1) \quad KV = 0.00226t - 1.95/t$$

$$(2) \quad KV = 0.00220t - 1.35/t$$

After much experience with the Saybolt and other viscosimeters, W. H. Herschel[10] of the Bureau of Standards has stated that only in a few cases do the data with Saybolt instruments warrant a precision greater than about 5 per cent.

A few objections to the Saybolt instrument from a scientific standpoint may well be listed: (1) It requires about 75 cc of a liquid for a viscosity measurement. Frequently oil samples of 10 cc. or less are obtained and it is inconvenient and expensive to run the experiment on a scale large enough to obtain 75 cc. (2) It gives results in units which are used only in the United States, and at present they cannot be changed, with perfect accuracy, into absolute or other units.

In the determination of the viscosity of heavy fuel oils and asphaltic road materials a larger instruments known as the

Saybolt-Furol viscosimeter is generally used. For the Furol instrument,measurements are generally made at 122°F, although 77°, 100°, and 210°F are used, and for liquid asphaltic materials also 140° and 180° F.

Saybolt-Furol seconds (S. F. S.) are the number of seconds required for 60 ml. of oil to flow through the orifice of the Saybolt-Furol viscosimeter at a specified temperature.

D. Ostwald

In the Ostwald type of viscosimeter[12], the liquid being tested is permitted to flow slowly by gravity from one bulb to another through a long capillary tube. The volume that flows through the capillary is fixed by the capacity of the upper bulb, which is completely filled and then allowed to empty itself, the time required for the emptying being measured. The definition of viscosity is such that, as has been pointed out in thecase of capillaries, the time of flow is proportional to the viscosity of the liquid. This is true in the case of the Ostwald viscosimeter.

Among the precautions necessary for a viscosimeter of this type are,[13]

(1) Keeping the capillary free from dust or air bubbles.

(2) Maintaining the temperature constant.

(3) Measuring the time with sufficient accuracy.

This instrument has certain decided advantages over the other viscosimeters, though it does have some faults. Among its advantages may be mentioned:

(1) Only 5 to 10 cc. of liquid are required.

(2) Several determinations can be made with the same sample with a minimum of handling.

(3) The experimental error in determining relative viscosities can be made very small.

(4) Laws of flow and absolute viscosities have been studied with capillary tubes, so that results can be accurately expressed in absolute units.

(5) The determinations can be made at any temperature with almost equal ease.

(6) The viscosimeter is much cheaper than most other types.

Among its disadvantages are the following:

(1) For practical purposes each viscosimeter must be calibrated with a standard liquid.

(2) Each viscosimeter is convenient for liquids of only a limited viscosity range.

(3) Results in the desired units are not read directly, but must be obtained by calculation or reference to a table or graph.

Being of glass, viscosimeters of this type can not be exactly duplicated, and the variations between different instruments are allowed for in a viscosimeter constant. This constant must be determined, as part of the calibration of each instrument.

Since use of corrections is always inconvenient and often uncertain, especial attention is given to the elimination of the necessity for corrections by improving the design of the apparatus and by suitable methods of calibrating and using it. Practically all errors can be eliminated by the methods discussed below, so that the application of corrections to the observed data is usually unnecessary

It may be mentioned that early investigators proved by experiment that it makes no difference whether the internal surface of the capillary is smooth or rough. In viscous flow, the layer of liquid actually touching the walls is stationary, while the velocity increases to a maximum at the center of the tube.

(1) Drainage Error

It is desirable to make the drainage both as nearly complete and as constant as possible. There are three general ways of making the drainage more nearly complete:

(1) By making the drainage surfaces more nerly vertical.

(2) By increasing the time of drainage.

(3) By increasing the volume of the bulb.

Bingham[14] gives the ideal shape of the upper bulb as that of two 60° cones placed base to base, which will eliminate the nearly horizontal surfaces at the top and bottom of a spherical bulb.

(2) Average Head

Since the liquid in the Ostwald viscosimeter flows under the force of gravity, the time of flow depends (1) on the head of the liquid, (2) on the density, and (3) on the force of gravity. None of these factors needs to be known if the pipette is calibrated with a standard liquid and used for determining kinematic viscosities in the same locality. These variables are all included in the calibration constant, $C = KV/t$.

(3) Kinetic Energy Correction

As the oil in the Ostwald type of viscosimeter flows from the upper bulb into the capillary, its velocity and kinetic energy increases, and this increase in kinetic energy must come from a loss of pressure or head. A number of investigators[15] have agreed that it is difficult to predict or determine it accurately. However, it it is possible to design the viscosimeter in such a way that correction is practically negligible, The kinetic energy correction becomes less as the length of the capillary is increased and as the velocity of the liquid flowing through it is decreased. It is also diminished if the ends of the capillary are expanded gradually (trumpet shaped ends) instead of abruptly.

From a practical standpoint, the necessity of a kinetic energy correction can also be avoided by calibrating the pipette with a standard liquid of approximately the same viscosity as that of the liquids whose viscosities are later to be determined, the correction then being included in the calibration constant, C.

The most satisfactory way[16] of determining whether a kinetic energy correction is necessary for a given viscosimeter is to measure the time of flow of the same liquid with different heads. If these are not constant a kinetic energy correction is necessary.

Kinetic energy corrections are primarily due to contraction and expansion losses at the entrance and exit of the capillary.[17] It is customary to include the kinetic energy correction in Poiseuille's equation as follows:

$$KV = \frac{w}{p} = \frac{\pi gHR^4t}{8LV} - \frac{mV}{8L\pi T}$$

w is the viscosity in poises.

m is the kinetic energy coefficient

The second term on the right hand side of this equation is the kinetic energy correction.

For most types of viscosimeters the correct value of m may only be found experimentally, since it is associated with the shape of the entrance and exit of the capillary. Values of $m = 0$ to $m = 1.12$ have been reported.

The kinetic energy correction needs special attention only when designing instruments for non-viscous liquids. In viscosimeters designed for more visvous liquids the capillary is large enough to make the correction negligible. Since the value of m is not known accurately, it is not safe to allow the kinetic energy correction to become appreciable and attempt to apply this correction to the results.

(4) End Correction

Associated with the kinetic energy correction is the so-called end correction. It has its origin in the choking effect that occurs at the entrance of the capillary. The end corrections can be made negligible or very small by having the liquid flow rather slowly through a capillary with trumpet shaped ends and no correction is necessary if the viscosimeter is calibrated with a liquid similar to that whose viscosity is to be measured.

(5) Surface Tension Correction

If a U-tube having arms of different diameters is partly filled with a liquid, the surface will be somewhat higher in the narrower arm than in the wide one. This effect is produced by the surface tension of the liquid. In the usual types of Ostwald viscosimeters, the equilibrium level of the liquid would be a little higher in the small bulb than in the large one. It is desirable to have the bulbs large enough and sufficiently near the same size that the surface tension correction is negligible. It becomes negligible if the viscosimeter is calibrated with a liquid of approximately the same surface tension as those whose viscosities are later to be measured.

(6) Constant Temperature Bath

The viscosity of many lubricating oils change by 1 or 2 per cent for each degree change of temperature in the vicinity of 100°F.[19] Usually the percentage change is less at higher temperatures and greater at lower temperatures. To have measurements accurate to within 0.1 per cent at 100°F, it is necessary to control the temperature to within approximately 0.05°F.

E. Modified Ostwald

In order to minimize any error in the head resulting from a slight tilt of the viscosimeter,[18] one bulb is placed directly over the other (see Fig. 4). This modified Ostwald viscosimeter is made to cover a large~~r~~ range of viscosities.

The oil is taken into the viscosimeter in the following manner: The instrument is held in an inverted vertical position with the end of the capillary arm[2] immersed in oil. Both bulbs on the capillary side of the viscosimeter are filled with oil by removing the air, and the oil brought into the working capillary up to the mark etched on it. After loading the viscosimeter in this way, it is placed in the constant temperature bath so that bulb A is below the surface of the bath liquid. During the heating stage the oil drains from the upper bulbs into the lower reservoir C. After the sample has attained bath temperature, the sample is drawn up to a point about 5 mm. above the mark between the bulbs A and B. Then the oil is released and the time for the meniscus to pass from the upper to the lower mark is measured.

The theoretical considerations affecting the design and accuracy of viscosimeters permit requirements to be meet as follows:

(1) Not more than a 5 cc. sample.

(2) Absolute accuracy within 0.5 per cent; duplicate determinations within 0.2 per cent.

(3) Measurements throughout the viscosity range of lubricating oils.

(4) Measurements at various temperatures.

If the total volume of the sample is to be 5cc. a conven-

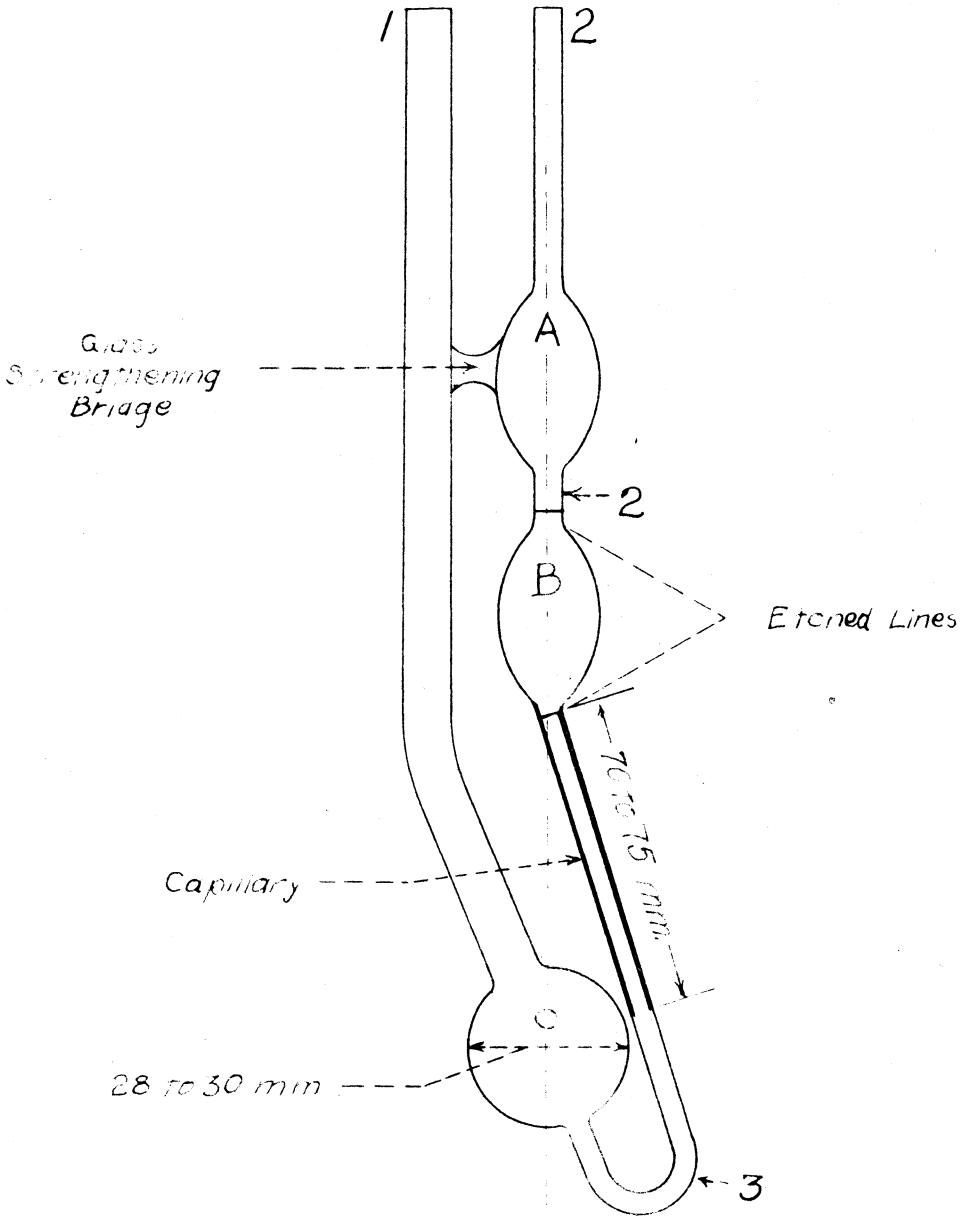


Fig. 4. Modified Ostwald Viscosimeter

ient capacity for the upper bulb is about 2.5 cc. To keep the drainage error as small as possible, the shape of the upper bulb should approach that of two 60° cones placed base to base.

The tube above the upper bulb must be large enough to prevent the collecting of liquids drops which will interfere with the free entrance of air. An inside diameter of approximately 0.18 cm has been found sufficient.

The ends of the capillary are made trumpet shaped since this construction decreases the kinetic energy, and end correction.

It is desired to have the time of efflux of 2.5 cc. to be between 150 and 2000 seconds. Too short a time of efflux will produce a slight error.

(1) General Specifications

Overall length, mm.---------240 to 260
Length of Capillary, mm.---- 70 to 75
Volume of bulbs A and B, each ml. 3 to 3.3
Distance from center of bulb B to center
of bulb C, mm.----85 to 95
Inside dia.
of bulb C, mm.--------28 to 30
of bulb 1, mm.-------- 8 to 12
of tube 2, mm.--------1.5 to 2.5
of tube 3, mm.-------- 3 to 5

The viscosimeter is illustrated in Fig. 4.

(2) Calibration

In order to calibrate the viscosimeter it is only necessary to fill it with the proper volume of a standard oil, and measure the time of efflux at the desired temperature according to the method previously discussed. The viscosimeter constant can then be obtained by dividing the known kinematic viscosity of the standard liquid by the time of efflux. That is, $C = K\bar{V}/t$

Another method of calibrating the Ostwald viscosimeter[20] is to use a quartz viscosimeter very similar to that of Washburn and Williams[20] which is calibrated by means of pure water at 20°C (68.0°F). Water can not be used directly for calibrating the modified Ostwald viscosimeter because its time of efflux would be too short. After calibrating the Washburn and Williams type viscosimeter with water as a standard it may be used to standardize other oils. These oils in turn maybe used to calibrate the modified Ostwald viscosimeter. It will then be calibrated against water as a standard through the use of an intermediate viscosimeter.

Advantages of Quartz Instruments

The advantages secured by using the quartz instrument are: (a) Its water constant at given temperature is not changed by cleaning with hot cleaning mixtures or by subjecting the viscosimeters to large temperatures variations. (b) The water constant at 25°C is 580 seconds and is repeatedly reproduced to about 0.03 second~~s~~ under a given set of conditions. It gives a precision of about 0.01%. The deviations from Poiseuille's law is very small. (c) An error of 1 cc. in the amount of liquid introduced does ~~not~~ not change the time of flow by as much as 0.05%. (d) A single instrument can be used for a large temperature range since its dimensions do not alter with temperature.

If it is desired to perform all calibrations at 100°F (37.78°C), the calibration constants at 60°F (15.56°C), 130°F (54.44°C) and 210°F (98.89°C) may be obtained as follows[22]:

Cal. const. at 210°F. = 0.996 x cal. const. at 100°F.
" " " 130°F. = 0.999 x " " " "
" " " 60°F. = 1.001 x " " " "

The viscosimeter constant will vary with the temperature[21] but the change is small and readily computed. This correction arises because of the change of specific volume with temperature. If the viscosimeter is loaded at 25°C. and then used at some higher temperature a correction should be applied. Knowing the viscosimeter constant at two different temperatures, and for other temperatures one can interpolate or extrapolate.

For intermediate temperatures the viscosimeter constant may be readily computed from the known constant at the same given temperature by the following equation:

$$C_{t_2} = C_{t_1}\left[1 - \frac{V_2 - V_1}{0.785Hd^2}\right]$$

C_{t_2} = viscosimeter constant at temperature t_2.
C_{t_1} = " " " " t_1.
V_2 = volume of liquid in viscosimeter at temp. t_2.
V_1 = " " " " " " " t_1.
H = driving head, approximately equal to the distance between centers of efflux bulb and lower reservoir.
d = working diameter of lower reservoir.

Various other modifications of the Ostwald instrument are advocated by some investigators[23]. Ubbelohde's suspended level-type of instrument differs from the type described here only in eliminating loading errors and reducing surface tension errors. In the design presented here such errors are of negligible magnitude, Zeitfuchs has recently described another modification of the Ostwald instrument which also reduces loading errors. Slight modifications of the Ubbelohde type have been described by O. Fitzsimmons and by E. H. Payne and C. C, Miller.

Thousands of viscosity determinations have been made at 100°F (37.8°C), 130°F (54.4°C), and 210°F (98.9°C) with the modified Ostwald viscosimeter. Some twenty research workers have used it successfully. It has been found that different operators using different apparatus are able to check viscosities within 0.2 per cent. Hence it may be ~~is~~ said that the modified Ostwald viscosimeter is equal in accuracy to any now available.

F. Stormer Viscosimeter

The Stormer Viscosimeter is used for determining viscosities by measuring the time required for a definite number of revolutions of a rotating cylinder immersed in the sample placed in the test cup, maintained at a desired temperature by means of a water or oil bath, and driven by a definite weight.[24]

The weight attached to a string falls vertically from the instrument (see **Fig.** 5). The string pays out over a vertical pulley and the weight falls and unwinds from about the shaft of a large toothed wheel which lies in a horizontal plane. The large wheel fits into a small gear on the shaft of the viscosimeter cylinder. When the large wheel is caused to revolve by the falling weight, this shaft is turned, and the cylinder attached to its lower end is revolved in the liquid contained in the cup below. A screw gear at the top of this shaft fits into the teeth of an indicator

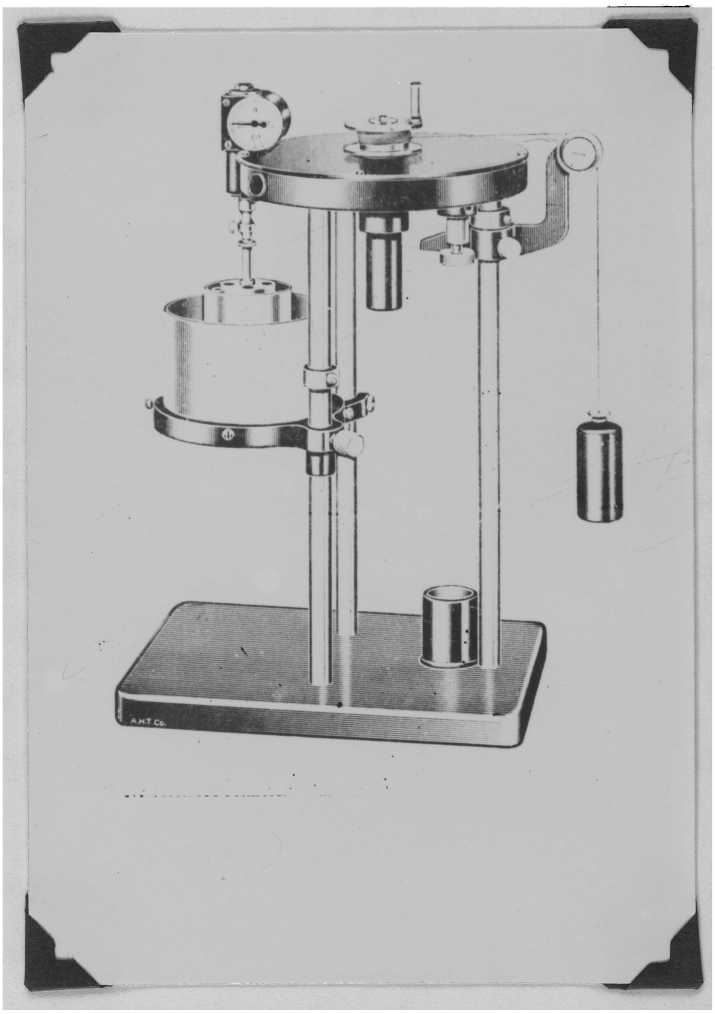


Fig. 5. Stormer Viscosimeter.

wheel and the whole instrument is so geared that a complete revolution of the indicator wheel represents 100 turns of the cylinder in the cup below. A small bath surrounds the container cup, and rough temperature control may be maintained.

The time is taken for 100 revolutions in water as unity. Then the relative viscosity of another fluid is obtained by dividing the time required for the cylinder to make one hundred ~~of~~ revolutions in the material under examination by the time required for the cylinder to make the same number of revolutions in distilled water, or other reference, using the identical procedure, at the same temperature, and with the same operating weight. The friction value of the machine must be taken into account for determining relative viscosities. The corrected time being the observed time minus the time for the cylinder to revolve 100 times in air. If a liquid is found too viscous for comparison with water, it is first necessary to determine the viscosity of an intermediate liquid, increase the weight and then use the intermediate liquid as a standard. After this it is possible to calculate the unknown viscosity in terms of water as unity.

For example, if a liquid of medium viscosity, say 6, is used as an intermediate to determine the viscosity of a very viscid liquid then the time for the unknown must be divided by the time for the known and this result multiplied by the viscosity of the fluid used (in this case 6) to obtain the viscosity with reference to water, which is the standard or unity.

Viscosities[25] can be determined and recorded in the absolute unit by means of a calibration table prepared by the user. Calibration is effected through the medium of castor oil or other standard solution, so that the number of seconds required for 100 revolutions of the spindle in the fluid is plotted against viscosity for a particular weight. The Stormer Viscosimeter is well adapted for such use as its readings are independent of the specific gravity of the fluid. This is not true of " flow through " viscosimeters for which the results are kinematic rather than absolute.

The application of the Stormer viscosimeter is limited to liquids whose viscosities are above 0.5 to 1.0 poise - i.e., to liquids from 50 to 100 times the viscosity of water.[26]

The[27] principal points of advantage which have been gained by the use of the Stormer Viscosimeter are:

Only a 50 cc. sample is required for the determination of the viscosity and the temperature of this small quantity may be easily controlled.

Only a few seconds are required to make a test and the temperature variations during the test are negligible.

The reading may be repeated an d checked with great ease, it being only necessary to wind the indicator back to zero in order to repeat the determinations.

The force exerted is constant throughout the experiment.

Different oils may be run successively without the loss of time, since a clean cup and a cleaning of the small cylinder puts the instrument in order for a new test.

However, with this viscosimeter there is not such a great variation in measurable viscosities as is found for some of the out flowing types of instruments.

Only the stop watch need be kept in mind by the operator, since the number of revolutions is automatically recorded and a convenient brake stops the revolutions of the wheel instantly at the desired point.

G. Redwood, Engler and Barbey Viscosimeter

The Redwood[28] No.1 and No. 2 instruments are the standard commercial viscosimeters in England and cover, respectively, the same range of viscosity determinations as the Saybolt Universal and Saybolt-Furol instruments.

Redwood standard seconds (R.S.S.) are the number of seconds required for 5o ml. of oil to flow through the Redwood No. 1 viscosimeter at a specified temperature.

Redwood Admira~~b~~ility seconds (R. A. S.) are the number of seconds required for 50 ml. of oil to flow through the orifice of the Redwood Admira~~b~~ility viscosimeter at a specified temperature. This is called the Redwood No. 2 instrument

The Engler viscosimeter is used in virtually all of Continental Europe andis the standard instrument in Germany. The Barbey is used to a limited extent in France, Spain and in a few other countties of Europe.

Engler seconds are the number of seconds required for 200 ml. of oil to flow through the orifice of the standard Engler viscosimeter at a specified temperature.

Engler degrees are the Engler seconds divided by the time in seconds required for 200 ml. of distilled water at 20°C to ~~run~~ flow through the orifice of the Engler instrument. This time is approximately 51 seconds and must be between 50 and 52 seconds.

Barbey fluidity is the milliliters of oil that flow through the orifice of the Barbey instrument in 10 minutes at a specified temperature.

VI. The Variation of Viscosity With Temperature

The viscosity of all liquids[29] and solutions decreases with rising temperature. Hagen first investigated the volume of water discharged through capillar~~y~~ies at different temperatures and found an increase with rising temperature. The first quanitative investigations were carried out by Poiseuille, who found that the viscosity n_t of water at the temperature t could be expressed in terms of the viscosity n_o at 0^o, and the temperature by the formula

$$n_t = \frac{n_o}{1+\alpha t+\beta t^2}$$

For small temperature intervals Meyer finds the quadratic term unnecessary, so that it becomes:

$$n_t = \frac{n_o}{1+\alpha t}$$

Vegetable[30] oils such as castor oil are generally considered to be ~~the~~ less effected by temperature than lubricating mineral oils, but blended mineral oils are now on the market with temperature- viscosity curves similar to that of castor oil.

Lubricating oils from different crudes vary in their temperature coefficient of viscosity and, in general, oils from paraffin base are less affected by temperature than those from naphthene base crude.

VII. The Variations of Viscosity with Pressure

Experiments[31] at higher pressures were first carried out almost simultaneously by Rontgen, and by Warburg and Sachs, who used capillary viscosimeters enclosed in glass piezometers. Rontgen observed a decrease in the viscosity of water with increasing pressure, which was also confirmed by Warburg and Sachs, who used pressures up to 150 kgms./cm^2. In addition to water they examined ~~the~~ liquid~~s~~ carbon dioxide, ether, and benzene. The viscosity of these increase with pressure.

Warburg and Sachs found that their results could be represented by a linear formula

$$n_p = n_o (1+\alpha p)$$

in which n_o and n_p are respectively the viscosity coefficients at atmospheric pressure and at pressure p, and α is a constant. If S is the reduction of volume produced by the pressure p,

$$n_p = n_o(1+\beta S)$$

and the constants $\underline{\alpha}$ and $\underline{\beta}$ are connected by the relation

$$\alpha = \beta z$$

z being the coefficient of compressibility. Warburg and Sachs give the following values of the constants:

	Ether	Benzene	Water
$\alpha \times 10^6$	730	930	-170
$z \times 10^6$	173	91	45
β	2.5	4.2	-3.8

It has been proved by experiment that all classes of oil exhibit an increase in viscosity when subjected to increased pressure. No definite laws can be laid down regarding this increase in viscosity due to pressure, but Hyde has shown that with extremely high pressures, of the order of 16,000 lbs./ in^2, the viscosity of mineral oils is about ten times greater than at atmosphereic pressure, whereas with vegetable oils such as rape and castor this increase reaches only four times.

While oils of mineral and vegetable origin retain their viscosity much more readily with rise in temperature than is usually the case with mineral oils, the influence of pressure seems to have an inverse effect as the viscosity of petroleum oils increases much more rapidly with rise in pressure.

VIII. EXPERIMENTAL ARRANGEMENT

A. Stormer.

A modification of the Stormer Viscasimeter was constructed in the Department of Physics (see Fig. 6). The dimensions are not the same as those found in the Commercial Stormer Viscasimeter. However, it was designed to operate on the same principle.

The Viscasimeter consists of a flat bottomed cylindrical cup having an internal diameter of two inches and a depth of 2 1/2 inches. As obstructions to prevent rotary flow of the liquid, two vertical vanes, or septa, 3/16 inch wide, were attached to the inner wall. These extended the entire length of the cup and are situated diametrically opposite each other.

Within this cup is a suspended stirrer or cylindrical rotor, the revolution of which is resisted by the viscosity of the liquid. This stirrer is a hollow monel metal cylinder 1 11/16 inches long and 1 11/32 inches in diameter, its lower end being entirely open and the upper end having four symmetrically placed perforations each 4/16 inch in diameter. The upper end of the rotor is a vertical rod or shaft which is concentric with the cylinder itself. It extends 2 1/4 inches above the rotating cylinder and is 4/16 inch in diameter.

The upper end of the rotor is attached by a collar and screw to the bottom of a vertical shaft which carries a pinion 1/2 inch in diameter with 16 teeth. This pinion is driven by a gear 5 inches in diameter with 160

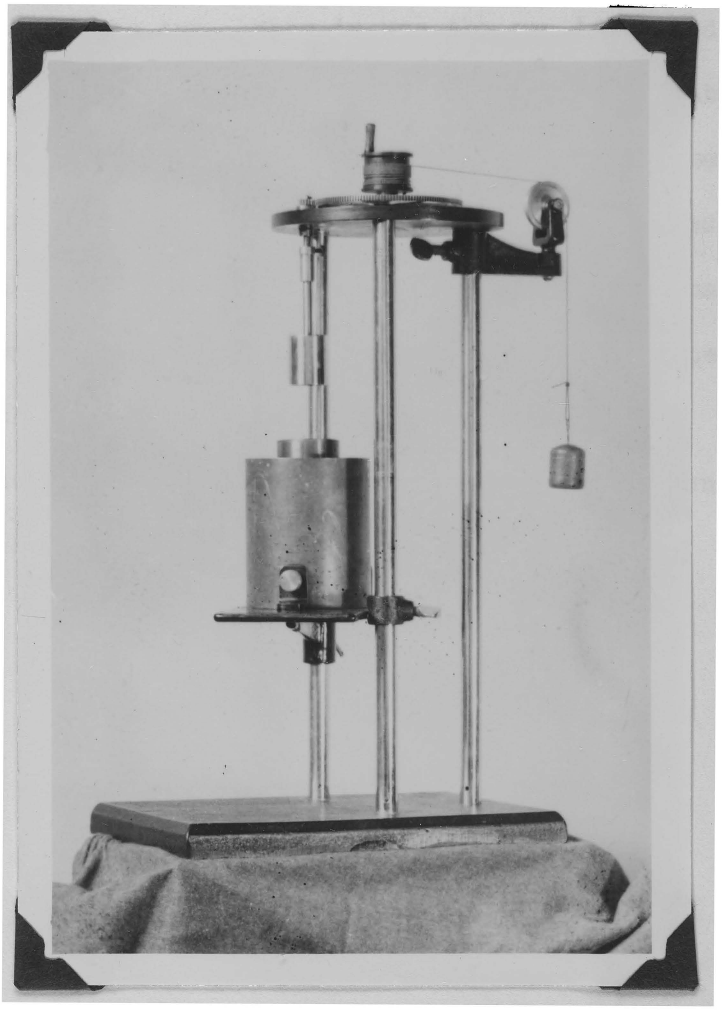


Fig. 6. Stormer Viscosimeter.

teeth. To this large wheel is attached a drum 1 3/4 inches in diameter and 1 1/4 inches in height, around which is wound a cord supporting the driving weight. A vertical pulley is used to apply the force exerted by the weight horizontally to the drum.

The stirrer is suspended so that its bottom is about 3/16 inch above the bottom of the cup. When in use the cup is filled to within about 4/16 inch of its top with liquid which thus stands about 4/16 inch above the top of the stirrer. The stirrer comes within about 1/8 inch of each of the side vanes mentioned above. To make a hundred revolutions of the stirrer the weight descends about 56 inches. The hundred revolutions is counted by observing ten revolutions of the large wheel, which has a 1:10 ratio with respect to the rotating cylinder.

Table II gives an exact account of all dimensions chosen in this viscosimeter.

Table II: Dimensions for the Stormer Type Viscasimeter.

Overall height	2 ft.
Size of base	9 x 13 1/2 in.
Length of supporting rods	20 in.
Diameter of large wheel, 160 teeth	5 in.
Diameter of small wheel, 16 teeth	1/2 in.
Diameter of supporting base for large wheel	8 in.
Thickness of supporting base	15/32 in.
Diameter of drum attached to large wheel	1 3/4 in.
Height of drum	1 1/4 in.
Inside diameter of test cup	2 in.
Height of test cup	2 1/2 in.
Width of septa or vanes Within test cup	3/16 in.
Inside diameter of bath	4 in.
Height of bath	5 in.
Inside diameter of cylindrical rotor	1 7/32 in.
Outside diameter of cylindrical rotor	1 11/32 in.
Height of cylindrical rotor	1 11/16 in.
Diameter of the four holes symmetrically Placed in top of the cylindrical rotor	.7/32 in.
Length of rotor shaft	2 1/4 in.
Diameter of rotor shaft	4/16 in.

B. Ostwald

The calibration of a Commercial Ostwald Viscasimeter was undertaken as a part of this study (see Fig. 7). Viscosities of a much lower range can be measured with the Ostwald than with the Stormer Viscasimeter. It was deemed advisable to calibrate the Ostwald instrument, so that it may be used to measure the range of viscosities not applicable to the Stormer Viscasimeter.

A Commercial Ostwald viscasimeter was obtained. The overall height of this instrument is 28 cm., the inside diameter of the large arm being 1 1/2 cm., and that of the small arm 4 mm. The diameter of the capillary is approximately 1 mm. A convenient size for the test sample is about 25 ml.

The calibration constants were determined with 25 ml. of a standard liquid. It is recommended that all measurements of viscosity be made with a test sample of 25 ml.

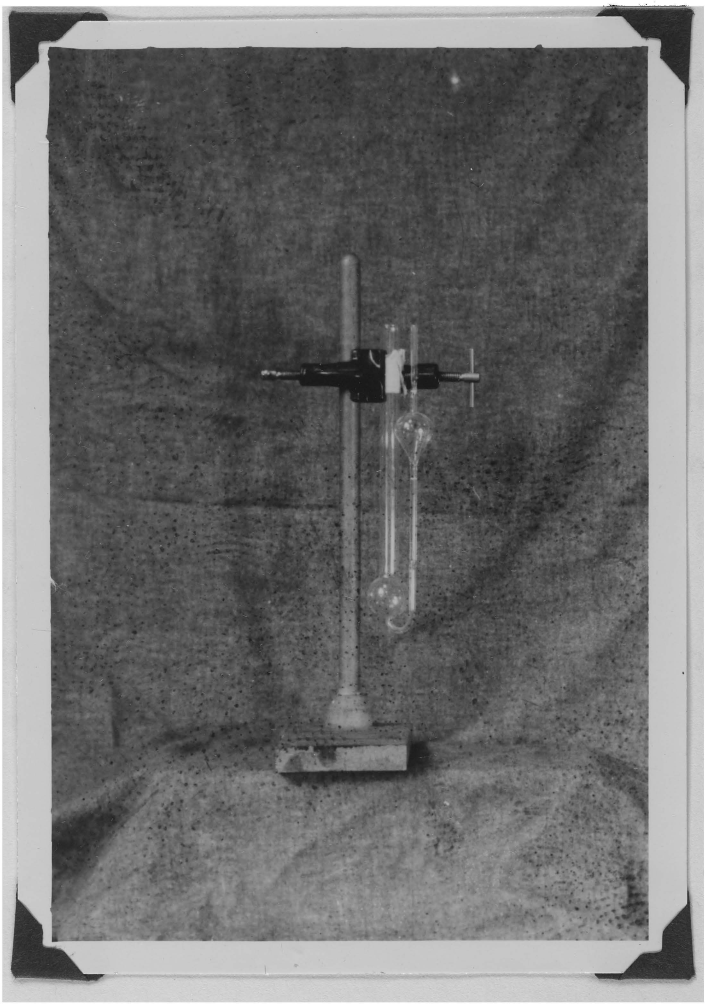


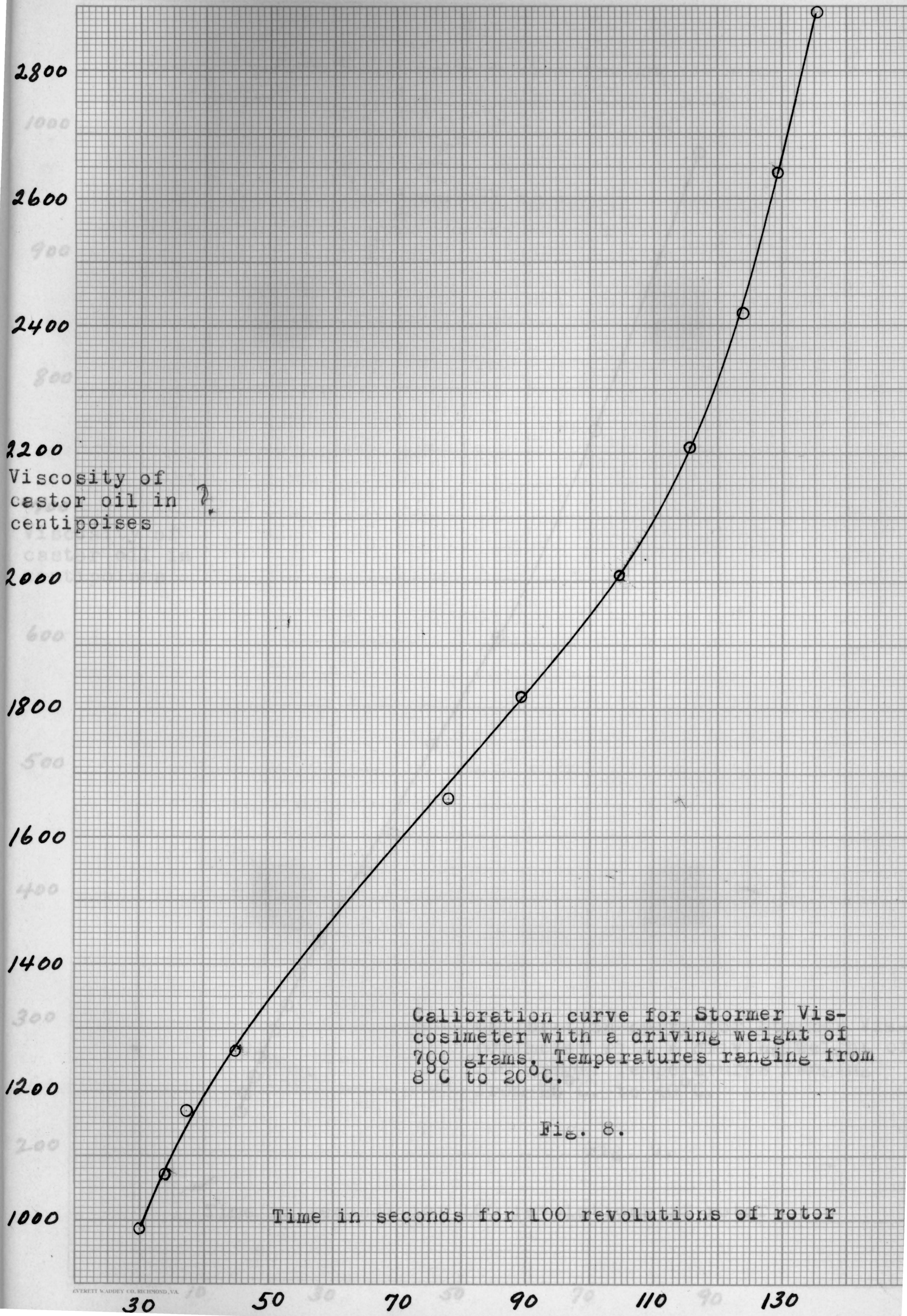
Fig. 7. Ostwald Viscosimeter.

IX. CALIBRATION AND RESULTS

A. Stormer.

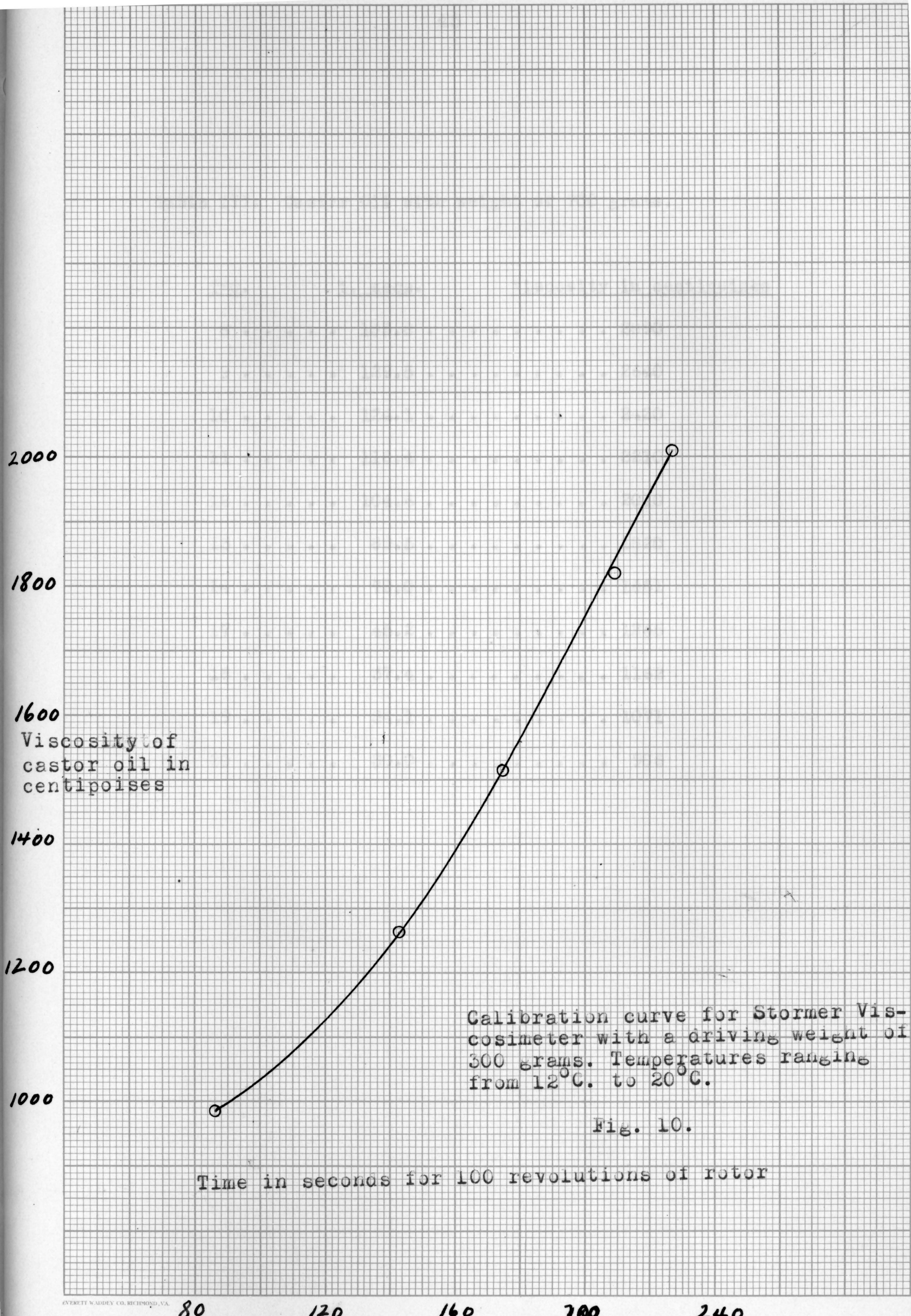
The Stormer instrument was calibrated through the medium of castor oil. A constant volume of 96 ml. was used for each test. Every precaution was taken to perform each test under exactly the same conditions, such as centering the stirrer within the test cup, submerging to the same depth each time and maintaining a constant temperature for each reading. The calibration curves were constructed by plotting the time in seconds for 100 revolutions of the stirrer against the viscosity in centipoises. The curves are given on the following pages (see Figs. 8, 9, and 10).

Several different determinations were made. Typical sets of data appear in Tables III and IV.



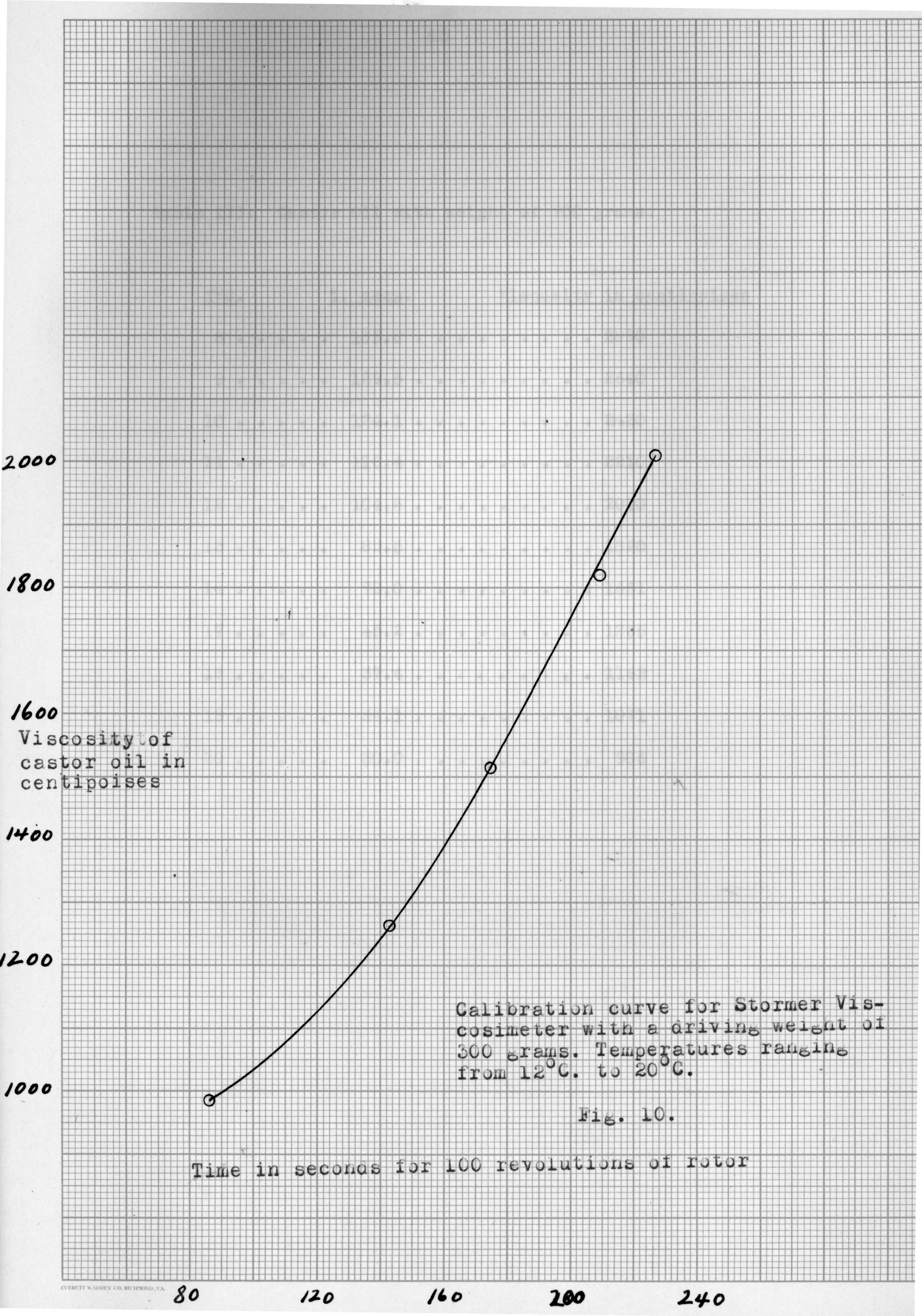
Calibration curve for Stormer Viscosimeter with a driving weight of 700 grams. Temperatures ranging from 8°C to 20°C.

Fig. 8.



Calibration curve for Stormer Viscosimeter with a driving weight of 300 grams. Temperatures ranging from 12°C. to 20°C.

Fig. 10.



Calibration curve for Stormer Viscosimeter with a driving weight of 300 grams. Temperatures ranging from 12°C. to 20°C.

Fig. 10.

Table III: Castor Oil with weight of 700 grams.

T°C.	t. secs.	Viscosity in centipoises
8	135.8	2890
9	129.5	2640
10	124.1	2420
11	116.4	2210
12	104.6	2010
13	89.5	1820
14	78.0	1661
17	45.2	1265
18	37.4	1162
19	34.1	1071
20	30.0	986

Table IV: Castor oil with weight of 300 grams.

$T^oC.$	t. secs.	Viscosity in centipoises
12	227.0	2010
13	209.4	1820
15	174.2	1514
17	143.0	1265
20	86.1	986
23	70.7	767
26	55.5	604
28	45.4	521
30	39.6	451
31	35.6	421
33	28.2	365
34	25.4	340
35	23.5	316
36	21.6	294
37	19.5	274
38	18.5	258
39	17.0	244
40	16.6	231

B. Ostwald.

In calibrating the Ostwald Viscasimeter 25 ml. each of distilled water and 100% absolute alchohol were used. The test liquid was introduced in the large arm. The sample was forced to about 1 cm. above the etched work on the working bulb. The time was taken for the meniscus to pass from the upper to the lower etched mark. Using the equation $KV = Ct$, the viscasimeter constants were determined at 20°C., 25°C., and 38°C.

The data and results are given in tables V and VI.

Table V: Determination of viscasimeter constant using 25 ml. of distilled water.

20°C. . . . . 96.4 sec.
20°C. . . . . 96.4 "
20°C. . . . . 96.4 "
20°C. . . . . 96.4 "
20°C. . . . . 96.4 "
viscasimeter constant= 0.01043

25°C. . . . . 87.0 sec.
25°C. . . . . 87.0 "
25°C. . . . . 87.1 "
25°C. . . . . 87.2 "
25°C. . . . . 87.1 "
viscasimeter constant = 0.01029

38°C. . . . . 71.0 sec.
38°C. . . . . 71.2 "
38°C. . . . . 71.3 "
38°C. . . . . 71.5 "
viscasimeter constant = 0.009630

Table VI: Determination of viscasimeter constant using 25 ml. of 100% absolute alcohol.

20°C.	154.3 sec.	25°C.	140.4 sec.
20°C.	154.2 "	25°C.	140.5 "
20°C.	154.1 "	25°C.	140.6 "
20°C.	154.0 "	25°C.	140.5 "
20°C.	154.0 "	25°C.	140.7 "
viscasimeter constant = 0.00986		viscasimeter constant = 0.00983	

38½°C.	112.2 sec.
38°C.	113.0 "
37¾°C.	113.5 "
37¾°C.	113.8 "

viscasimeter constant = 0.0098 $\not-$

X. DISCUSSION

Preliminary determinations were made on the Stormer Viscasimeter using distilled water as a standard liquid. It was found that the results were inconsistent, which supports the observation of other experimenters[26] that the Stormer instrument is proper for the study of viscosities ranging above ~~from~~ 0.5 to 1.0 poise, that is, several times the viscosity of water.

Calibration of the Stormer Viscasimeter was actually made through the medium of castor oil. Several determinations were made. Each set of data was very consistent.

It was found that the rotating cylinder must be centered exactly in the middle of the test cup, and the test cup must be held very stationary. If the test cup was allowed to become shifted from the center, the results were in error by as much as one second to over one minute depending upon the time for 100 revolutions of the stirrer. In the region around 5^{0}C. the error was sometimes as large as one minute. At very low velocities there seemed to be a slight drag in the instrument, due to air bubbles collecting within the rotor. The friction appeared to be uniform under all conditions.

In calibrating the Ostwald Viscasimeter it was found that air bubbles must not be allowed to be trapped in the liquid. When air bubbles were trapped errors as large as ten to thirty seconds occured.

For future work with the Stormer Viscasimeter, it is recommended that the test cup be made larger and a thermometer holder placed on the inside. Provisions for holding the test cup perfectly sationary would insure results with greater accuracy. Also that the side vanes should not extend to the top of the test cup. The present arrangement with the side vanes extending to the top causes the liquid to overflow during operation, thus changing the volume of the liquid under test.

XI. ACKNOWLEDGEMENT

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