late in the constrictions. When the pressure gradient was kept constant the permeability seemed to approach a steady value which was lower for lower gradients. A sharp increase in gradient always produced a sudden rise in permeability. Typical results of this type are shown in Fig. 3 where the permeability of a twice mudded core is plotted against flow for a section of its flow history.

It seems natural to think of the particles as forming bridges in the pore constrictions. These, then, might be expected to give way under a sufficient pressure difference and thus "open up" the core. With flow at a constant pressure gradient the permeability would be expected to approach a steady value when bridges had formed in most of the smaller constrictions.

The permeability to water was reduced by a single mudding to 50 or 60 percent of the original value but when the filter pack was kept from forming by removing it at intervals or by circulating the mud rapidly across the core face the
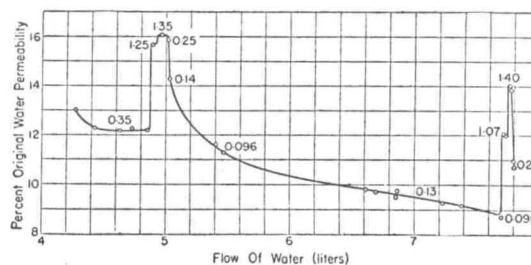

Fig. 3. Percent original water permeability of a twice mudded core *versus* flow. The pressure gradient across the core is indicated in atmospheres per cm by the figures. From 5 to 7.7 liters the decrease in gradient was gradual except for an increase to 0.18 atmospheres per cm at 5.5 liters.

reductions were much more than this. In one case the permeability was reduced to 4 percent of its original value in three successive muddings.

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The Effects of Pressure and Temperature on the Viscosity of Lubricating Oils

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The viscosities of three lubricating oils have been investigated at 100°, 130°, 210.2°F at pressures ranging from atmospheric to 4000 atmospheres (57,000 lb./in.²). While the oils were from fields widely separated geographically, their initial viscosities were matched at 0.4 poise at 130°F. At a pressure of 26,000 lb./in.² at 130°, however, the viscosities were strikingly different; the viscosity of the Pennsylvania oil increased 25-fold, and the Oklahoma oil 35-fold, but for the California sample the increase of viscosity was greater than 100-fold. The effect of pressure on the temperature coefficient of viscosity and the effect of temperature on the pressure coefficient of viscosity are discussed.

THE effect of pressure on the viscosity of fluid lubricants has been studied previously by several investigators. Experiments by Hersey[1] showed that the viscosity of oils increased considerably with moderate increase of pressure: further investigations by Hyde[2] at the National Physical Laboratory in England, Hersey and Shore,[3] and Kleinschmidt[4] in this country, increased our knowledge of the pressure effect of viscosity of oils of various kinds at several temperatures.

The increase of viscosity with pressure is a complicated phenomenon for even the so-called

[1] M. D. Hersey, J. Wash. Acad. Sci. 6, 525 (1916).
[2] J. H. Hyde, Proc. Roy. Soc. A97, 240 (1920).

[3] M. D. Hersey and H. Shore, Mech. Eng. 50, 221 (1928).
[4] R. V. Kleinschmidt, Trans. A. S. M. E. APM–50–4 (1928). Mech. Eng. 50, 682 (1928).

simple liquids of high degree of purity, for it has been shown that viscosity is in general a strong function of molecular structure in liquids.[5, 6] Consequently, it would be expected that the viscosity of lubricating oils under high pressures would be so intricately related to composition that analyses of data taken on bulk oils would be unsatisfactory. Previous investigations[3, 4] have shown, however, that the pressure coefficient of viscosity of mineral oils is greater than that of fixed oils, but there is no existing information on the relation of the pressure coefficient to the basic composition of a hydrocarbon oil which has been refined by various methods. It would appear desirable, if further tests are to be made on refined oils, that more about the chemistry of the oils should be known, especially their chemical and physical properties as related to the basic crudes and methods of refining. The purpose of the present investigation is to make a start in this direction, to study the effect of pressure and temperature on three hydrocarbon oils that have been refined previously in a known manner and tested extensively as regards their physical and chemical properties.

The three oils used in this investigation were provided by Professor H. A. Everett of the department of mechanical engineering who had previously studied[7] many properties of them in conjunction with Dr. M. R. Fenske of the Petroleum Refining Laboratory of this school. The oils were from Pennsylvania, Oklahoma, and California crudes, blended with bright stock and neutrals to have the same viscosity of approximately 0.4 poise at 130°F.

In order to study the effects of pressure and temperature, the rolling-ball viscometer of Hersey and Shore[3] was adopted as the most suitable type for these experiments. The rest of the pressure apparatus was of design similar to that developed by Professor P. W. Bridgman of Harvard,[8] and used by the author in previous investigations.[6, 9, 10] Professor Bridgman kindly loaned diagrams and cooperated with the author

in the building of the high pressure equipment of the physics department, and Mr. G. V. Luerssen of the Carpenter Steel Company contributed steel for the construction of apparatus. This investigation was made possible by the interest and cooperation of the Pennsylvania Grade Crude Oil Association which generously contributed funds. The experimental observations were made by the writer in the high pressure laboratory of the department of physics.

EXPERIMENTAL DETAILS

The rolling-ball viscometer and the auxiliary pressure apparatus are shown in Fig. 1. The viscometer was rotated through a known, small angle (10°) from its horizontal position by tilting the apparatus about an axis which was supported by an iron frame work. A handle attached to the upper part of the viscometer frame allowed the viscometer to be tilted by hand in either direction. In the viscometer, of dimensions used by Hersey and Shore,[3] a $\frac{1}{4}''$ ball bearing rolled down the bottom wall of an axial hole, 10 inches in length and 27/64 inches in diameter, when the viscometer was inclined to the horizontal. In order to measure the viscosity of a liquid in this apparatus, it is necessary to know the time required for the ball to traverse the length of the inclined path. To measure the roll time insulated electrical contacts with external connections were fitted into two steel plugs which were screwed into both ends of the viscometer to make it pressure tight. Both the plugs and washers were of conventional design used in high pressure investigations. It will be noted that when the ball reaches either end of its path, the relay circuit is completed through the viscometer and oil film to the ball which touches the insulated contact. The time of roll can be recorded by any of several means; in these measurements a calibrated stopwatch operated by hand was found convenient for the purpose. The arrival of the ball at one of the contacts was signalled by a simple vacuum tube relay device.

The viscometer with its supporting frame was surrounded by a thermostated water bath which two stirrers kept in constant circulation. The

[5] P. W. Bridgman, Proc. Am. Acad. 61, 57 (1926).
[6] R. B. Dow, Physics 6, 71 (1935).
[7] H. A. Everett and F. C. Stewart, Penn. State College Bull. Eng. Exp. Station 44 (1935).
[8] P. W. Bridgman, *Physics of High Pressure* (Macmillan, 1931), Chap. II.
[9] R. B. Dow, J. Wash. Acad. Sci. 24, 516 (1934).

[10] R. B. Dow and M. R. Fenske, Ind. Eng. Chem. 27, 165 (1935).

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thermostat circuit operated a vacuum tube relay to control a gas valve which supplied one or two Meker burners that heated the bath. A thermometer, calibrated against one certified by the National Bureau of Standards, reading to 1/10 degree was used in this investigation for temperature measurement. The recorded temperatures are accurate to within $\pm 0.02°C$.

Pressure was generated by a hand pump which can be safely operated to 20,000 lb./in.^{2} without undue effort. The pump connected directly to an intensifier which permitted about a fourfold increase of pressure. Before this pressure could be used in the viscometer, however, means had to be provided for separating the transmitting liquid from the test liquid, and for measuring the pressure, the gauge on the pump being inaccurate for precise measurements. A cylindrical steel chamber connected between the intensifier and viscometer served both purposes; a flexible copper sylphon provided mechanical separation of the liquids, and a coil of manganin wire mounted on a suitable plug allowed the pressure to be measured by observing the change of its electrical resistance with pressure by means of a Carey-Foster bridge. It is known that the change of electrical resistance of manganin with pressure is linear.[11] The gauge was made of No. 40 B & S double silk covered manganin wire obtained from Driver Harris Company. The resistance was about 120 ohms at atmospheric pressure. Dr. L. H. Adams of the Geophysical Laboratory provided the important service of calibrating the manganin coil against the standard in his laboratory. The calibration obtained by Dr. Adams was 2.335×10^{-6} cm^2/kg. Finally, a connecting pipe from the cylindrical chamber led to a connection at the top center of the viscometer, thus completing the system under pressure.

METHOD OF COMPUTATION AND DATA

The absolute viscosities of the three oils are desired at the three chosen temperatures of 100°, 130°, and 210.2°F at various pressures within the experimental range. Since lubricating oils freeze at fairly low pressures at moderate temperatures, the pressure range was more restricted in the present case than is usual for most liquids.

[11] P. W. Bridgman, *Physics of High Pressure* (Macmillan, 1931) p. 73.

Consequently, the highest pressures used in this study are of the order of 55,000 lb./in.^{2}; in every case the highest pressure recorded is considerably
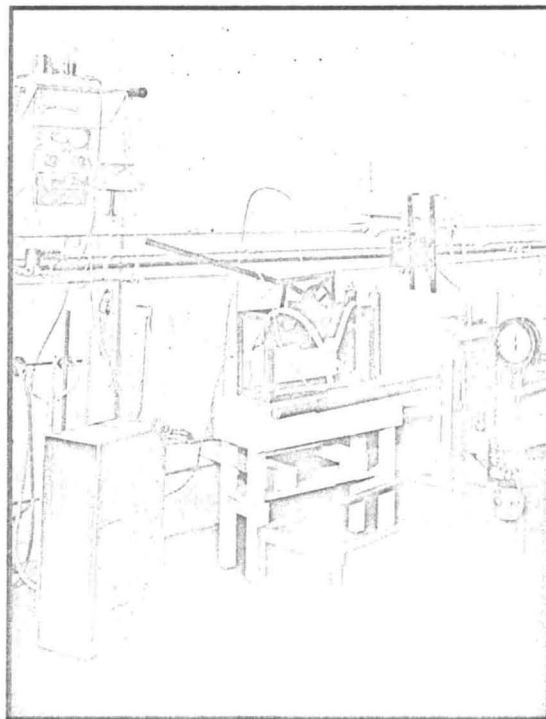

FIG. 1. Rolling-ball viscometer and auxiliary pressure apparatus.

below that where solidification begins. The beginning of solidification is noticed when the viscosity becomes abnormally great; when it is complete, the ball ceases to roll. The recorded data for a viscosity determination were then: the roll time in seconds, the thermometer reading in degrees Fahrenheit, and the pressure read on the Carey-Foster bridge in terms of length of slide wire. The roll time was taken as the average of roll times in both directions of tilt, and readings were recorded both for increasing and decreasing steps of pressure. When the roll time was less than 10 seconds, twenty or thirty observations were taken but as it increased, the number of observations was accordingly decreased. The corresponding pressures were obtained by multiplying the equivalent lengths of slide wire by the pressure coefficient of manganin, and converting the result to pounds per square inch.

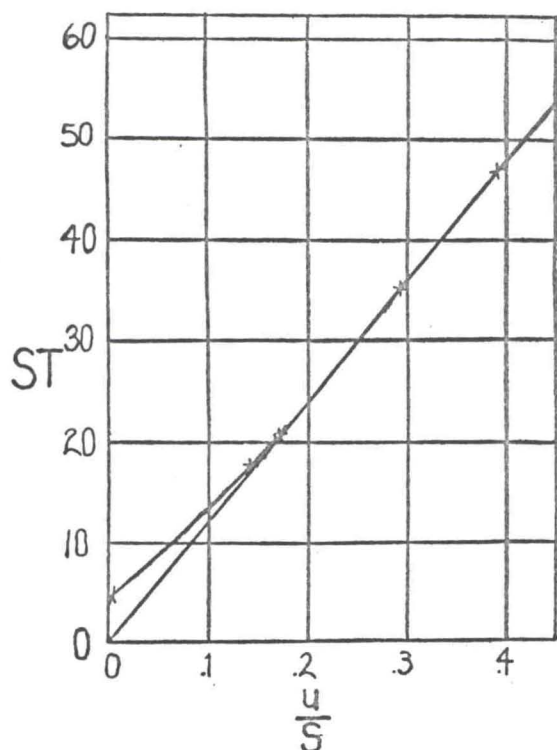The theory of the rolling-ball viscometer has been developed from a dimensional standpoint by

FIG. 2. Calibration curve of viscometer for 10° angle of tilt.

Hersey[1,3] and his method was followed in computing the absolute viscosities in poises. Since the roll times as measured are only relative, the viscometer must be calibrated by observing the roll times with liquids of known viscosity. This involves plotting a function ST against the function U/S. T is the roll time, U the kinematic viscosity, and S is a function of density equal to $(\rho_0/\rho-1)^{\frac{1}{2}}$ when ρ_0 is the density of the steel of the ball and ρ is the density of the oils in grams per cubic centimeter. Fig. 2 shows the calibration curve for the viscometer, when the angle of tilt is about 10°.

Writing the relation $\quad ST=f(U/S) \quad$ (1)

the Eq. (1) becomes $\quad ST=118(U/S) \quad$ (2)

for long roll times. Solving (2) for the viscosity $(\mu=\rho U)$

$$\mu = ((7.36-\rho)/118)T \quad (3)$$

on setting $T_1=118/(7.36-\rho)$ where T_1 represents the roll time in seconds for a viscosity of one poise

$$\mu = T/T_1. \quad (4)$$

Thus the computation of viscosity is done in one of two ways: if the roll time is short (region where the calibration curve departs from linearity) U of Eq. (1) is solved for by referring directly to the curve; if the roll time is long (region where ST varies linearly with U/S), Eq. (3) can be used directly to give μ. The values of ρ were obtained by interpolating the pressure-volume-temperature data of Dow;[9] since the change of volume of oils with pressure is not a strong function of compositon, it is sufficiently accurate to use the P-V-T data of Pennsylvania oil interpolated for 100°, 130°, and 210.2°F.

There are, however, various corrections to be made in applying the formulae. These have been discussed by Hersey. In the present case they reduce to two, namely the change in length of path due to pressure, and the initial acceleration of the ball. The first correction involves the change of length of the viscometer, change of diameter of the ball, and the change of position of the electrical contacts. The first two are negligible in these experiments but the effect of change of position of the contacts is appreciable. The correction was made by observing the change of length of the external stem of one of the end plugs of the viscometer for a certain pressure change. It was observed that at a pressure of 13,500 lb./in.² the stem was displaced 0.025

TABLE I. Data for calibration of viscometer; the functions ST and U/S.

LIQUID		ST	U/S
Kerosene		4.69	0.0055
Merusol		20.8	.173
Oil, S.A.E.	10	17.5	.143
" "	20	34.6	.293
" "	30	46.8	.390
" "	40	62.5	.467

inch, which amounts to a correction of 0.05 inch for both contacts. This negative correction was assumed to be linear with pressure. The second correction, that for the initial acceleration, was computed from Hersey's formula

$$\Delta T/T_0 = 0.21\{1-(1-8/KT_0^2)^{\frac{1}{2}}\}.$$

T_0 is the roll time and K is a constant equal to 8.3. This correction is also negative, amounting to 16.8 percent when the roll time is 1 sec. but vanishing if the roll time exceeds 10 seconds.

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U/S
0.0055
.173
.143
.293
.390
.467

Table I contains the data used to obtain the calibration curve of Fig. 2. Kerosene, a light mineral oil, and a series of four graded oils of viscosity S.A.E. No. 10, No. 20, No. 30, and No. 40, respectively, were used as calibrating liquids. The values of the kinematic viscosities of these liquids were directly determined at 100°F by Mr. C. E. Fink of our Petroleum Refining Laboratory. The author is indebted to him for carefully checking the viscosities in the standard viscometers of that laboratory. The density of the ball and the densities of the calibrating oils were determined in a conventional manner by weighing in specific gravity bottles.

Table II summarizes the data that were derived by computation. They were obtained graphically by plotting on a large scale the computed values of μ against pressure, drawing smooth curves through the plotted points, and then reading from the curves the values of μ corresponding to every one or two thousand units of pressure. The principal sources of error in these data are in the determination of the pressures and the roll times. The average inaccuracy of the former amounts to about 1 percent, while the latter, expressed in the unit of coefficient of viscosity, may be as high as 3 percent when the roll time is as low as 2 or 3 seconds. Another way of estimating the erratic error in the determinations is to consider the deviations of the computed values of μ from the curves that were

TABLE II. *Viscosity-pressure data.*

PRESSURE (lb./in.²)	VISCOSITY IN CENTIPOISES		
	Penn.	Okla.	Cal.
100°F			
14.2	83	94	114
1000	91	119	146
2000	106	145	183
3000	123	175	225
4000	145	209	278
5000	169	247	346
6000	198	293	433
7000	232	344	533
8000	268	405	655
9000	310	475	811
10 × 10³	357	557	995
12	485	775	1540
14	654	1060	2200
16	850	1430	
18	1100	1940	
20	1420		
22	1830		

TABLE II (*Continued*).

PRESSURE (lb./in.²)	VISCOSITY IN CENTIPOISES		
	Penn.	Okla.	Cal.
130°F			
14.2	41	43	42
1000	51	54	57
2000	60	66	68
3000	64	75	80
4000	73	85	99
5000	82	95	124
6000	91	102	154
7000	100	118	190
8000	111	131	232
9000	124	149	281
10 × 10³	143	170	340
12	191	231	490
14	249	318	692
16	315	428	960
18	408	564	1320
20	524	740	1830
22	663	940	2510
24	830	1170	3400
26	1030	1500	4540
28	1260	2030	
30	1560	2840	
32	1960		
34	2460		
210.2°F			
14.2	7	10	13
1000	9	12	15
2000	10	14	17
3000	13	16	19
4000	15	18	21
5000	17	20	24
6000	19	22	25
7000	20	24	27
8000	22	27	30
9000	24	30	33
10 × 10³	26	33	37
12	31	40	45
14	36	50	55
16	44	59	70
18	52	71	90
20	62	85	116
22	73	104	153
24	87	128	202
26	103	154	260
28	123	185	327
30	145	219	408
32	171	262	510
34	202	314	655
36	242	375	846
38	287	454	1080
40	337	549	1400
42	393	654	1790
44	457	770	2270
46	535	890	2890
48	627	1010	
50	732	1150	
52	846	1290	
54	973	1430	

drawn to smooth or average the results. In no case did the computed value of μ deviate by more than 1 percent from the value read from the curve which was drawn through the same pressure ordinate. In compiling the data of Table I, only three figures have been considered as significant.

DISCUSSED RESULTS

The data of Table II show significant differences for the viscosity of the three oils under pressure. Perhaps one of the most striking is the viscosities of the oils at 130°F at a pressure of 26,000 lb./in.²; at atmospheric pressure the oils have a matched viscosity of 0.4 poise but at the higher pressure the change amounts to a 25-fold increase for the Pennsylvania sample, a 35-fold increase for the Oklahoma sample, and an increase greater than 100-fold for the California oil. Further inspection of Table II shows that, likewise, the data at 100° and 210.2°F indicate that the effect of pressure is the greatest on the viscosity of the California oil and the least for the Pennsylvania oil. Assuming that the California oil is of more complicated composition from the standpoint of viscosity, due to the probable greater number of ring compounds or cyclo-paraffins (C_nH_{2n}), it is not surprising that the effect of pressure is greatest for this sample. It has been previously mentioned that the viscosity of liquids under pressure is a strong function of composition and one must admit that the viscosity effects in these oils are exceedingly complicated due to the corresponding complication of chemical makeup or structure.

The second order effects are: that of pressure on the average temperature coefficient of viscosity, and that of temperature on the average pressure coefficient of viscosity. Considering the effect of pressure on the *temperature* coefficient of viscosity computed between 100° and 210.2°F,

it has been found that for the Pennsylvania oil an increase of 20,000 lb./in.² increases the coefficient by 5 percent, for the Oklahoma sample an increase of 18,000 lb./in.² increases the coefficient by 7.8 percent, and in the case of the remaining oil, the increase amounts to 10 percent for a pressure difference of only 14,000 lb./in.². Now the effect of temperature on the *pressure* coefficient of viscosity, averaged over 10,000 lb./in.², is more noticeable although the changes occur in the same order; an increase of 110.2°F decreases the pressure coefficient by 18 percent for the Pennsylvania oil, 53 percent for the Oklahoma oil, and 76 percent for the California oil. Qualitatively, these oils show the same abnormality as pure liquids at high pressures in the relative change of viscosity with temperature,[5] most temperature effects being less at high pressures due to the constraining action of the high pressure on the normal thermal agitation in the liquid. These considerations show clearly that the influences of temperature and pressure on the first order effects of viscosity are correspondingly greater for the California oil than for the Pennsylvania oil.

In conclusion, it may be said that the changes of viscosity of these oils are remotely connected with the volume changes that occur in the pressure range of these experiments. For a pressure of 28,400 lb./in.² at 210°F the change of volume of these oils is about 10 percent, as contrasted to a change of viscosity which may be as high as 80-fold. It has been shown[12] with the available data on volume and viscosity that Batschinski's relation, which states that viscosity is a function of volume alone, is not valid for fluid lubricants at high pressures. The data of this paper likewise show the invalidity of the relation when viscosity is found as a function of volume.

[12] R. B. Dow, Physics 6, 270 (1935).