of material received through the courtesy of Dr. H. S. Miner. I also tender my thanks to the Christiania Minekompani, of Christiania, Norway, for many mineral specimens for examination.

NEW HAMPSHIRE COLLEGE, DURHAM, N. H.,
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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CASE SCHOOL OF APPLIED SCIENCE. NO. 2.]

ON VISCOSITY AND LUBRICATION.

BY CHARLES F. MABERY AND J. HOWARD MATHEWS.

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Excepting the work done in this laboratory during the last fifteen years in determining the composition of American petroleum, so far as we know, no attempts have been made to ascertain the composition of lubricating oils with reference to the hydrocarbons or even the series of hydrocarbons of which they consist.

Neither the composition of the oils nor the source of the petroleum from which the various products were manufactured have been relied on as a means of distinguishing differences in quality or durability, except a general distinction between straight hydrocarbon oils and compounded oils. Until comparatively recently, the refiner had to rely for high viscosity on mixtures of animal or vegetable oils with oils separated from petroleum, and the latter were obtained from Pennsylvania, Ohio, or other similar natural oils ordinarily referred to as paraffin oils, since they contained the solid paraffin hydrocarbons, C_nH_{2n+2}. Naturally, the refiner became convinced of the superiority of his compounded oils over straight hydrocarbon oils, and this idea has been maintained so persistently, it still prevails very generally with consumers of lubricating oils.

But within the last ten years, other varieties of petroleum have been found to yield lubricating oils with superior viscosity and wearing qualities which makes it no longer necessary to rely on compounded oils either for use on bearings or in cylinders. This is of especial importance with reference to cylinder oils, for it is well understood that the conditions of high temperatures and highly heated steam in cylinders lead to saponification of the animal or vegetable oil used in compounding, with consequent corrosion of the cylinder. As is well known, castor oil is one of the very best lubricating oils, especially for durability, but its general use is precluded by its high cost. It is now possible to prepare straight hydrocarbon oils fully equal in viscosity and wearing qualities to castor or any other high viscosity vegetable oil.

Viscosity is generally accepted as a standard of value in classifying lubricating oils, but it is not certain that it is reliable as indicating the durability and wearing qualities of oils differing widely in composition. There is little doubt that a confirmation of viscosity by chemical data and frictional durability tests may be depended on to give accurate information for commercial use. The viscosity of lubricating oils has received much attention and several methods and forms of apparatus have been suggested for its determination, but for the most part of arbitrary construction and comparison, and differing so essentially that determinations made with different instruments are not easily and readily comparable. As thus determined, viscosity is but an arbitrary standard based on an assumption that the outflow of a liquid through an orifice, influenced as it is by several physical conditions, is a correct measure of surface viscosity between bearing surfaces. It is merely a relative comparison with an oil arbitrarily selected as a standard, or with water or by means of a metal apparatus arbitrarily constructed. But with the use of water, evidently, the conditions of temperature must be stated in the results, for the viscosity of water is quite different at different temperatures, and slight variations in temperature have likewise an important influence on the viscosity of oils.

It is, therefore, necessary to know the temperature coefficient of water, and it would be interesting to follow out a series of observations with an homologous series of hydrocarbons, although the possibility of such an investigation is almost precluded by the immense labor necessary in separating in an acceptably pure form the individual hydrocarbons. We have on hand, members of the different series C_nH_{2n+2}, C_nH_{2n}, C_nH_{2n-2}, C_nH_{2n-}, and we have made a series of observations on some of the individual hydrocarbons. Interesting results have also been obtained on the viscosity of mixtures, showing the influence of the hydrocarbons of the different series.

In attempting to arrive at a series of determinations which should avoid the errors in methods in which differences in specific gravity, and accurate observations of temperature are neglected, it was evidently inexpedient to use any of the commercial methods, especially since, as explained above, the data afforded by those methods are merely empirical, and with no definite relations to a common standard. The well-known method of Ostwald was selected, therefore, as best suited for these determinations, and the apparatus employed needs no detailed description. In this method a definite volume of liquid flows through a capillary tube under a definite head. In the calculation, the pressure under which the liquid flows through the capillary, is corrected for its density in the Ostwald formula:[1]

[1] Ostwald-Luther, Physico-Chemische Messungen., p. 20.

η = The viscosity of the liquid examined,
S = Density of the liquid examined;
t = Time of outflow of the liquid examined;
η_0 = The viscosity of the standard liquid;
S_0 = Density of the standard liquid;
t_0 = Time of outflow of standard liquid;

$$\eta = \eta_0 St/S_0t_0.$$

The values thus obtained, express the ratio of the viscosity of the liquid under examination to a standard liquid used for reference. Water is the standard liquid most commonly chosen, and the values of η are referred to as "Specific Viscosities," *i. e.*, the ratio of viscosity to that of water at that particular temperature. The advantage of using water consists in the ease with which it may be obtained sufficiently pure, and in the fact that the value in absolute units for the viscosity of water is the best known of any liquid, and specific viscosities may be converted easily into absolute units. The specific viscosities obtained at different temperatures are not comparable, since they express only the ratio at the particular temperature chosen and take no account of the change in volume of the apparatus, especially in the size of the capillary. To compare the results obtained at different temperatures, it is necessary to convert the values into absolute units, using the known values for the viscosity of water at the temperature used.

From interpolation and extrapolation of the result obtained by Thorpe and Rodger[1] we obtained the values $\eta = 0.01007$ at 20° C. and $\eta = 0.004625$ at 60° C., where η is the coefficient of viscosity in absolute units, *i. e.*, dynes per square centimeter. By multiplying the values obtained at 20° and 60° by these numbers, comparable results are obtained.

Constant temperature was maintained by placing the viscosimeter in a glass thermostat through which observations could be made, and which was supplied with water from a larger thermostat maintained at a constant temperature by means of an electric thermo-regulator. The water was pumped from the larger to the smaller thermostat by means of a small lift-pump operated by a hot air engine. The temperature in the glass thermostat was held at 20° (± 0.02); since the viscosity of the oils, like that of most liquids, changes about 2 per cent. per degree, this small fluctuation is negligible.

The measurements at 60°, were made in a glass thermostat of about 10 liters capacity in which the temperature was maintained by superheated steam injected at the bottom through a small orifice. The steam could be easily regulated and the temperature readily maintained at 60° (± 0.02). In observations on the paraffin hydrocarbons, it was found that viscosity increases with some regularity in the homologous series with decreasing percentages of hydrogen.

These hydrocarbons were obtained by long-continued fractional separations under systematic conditions, and their identity was shown by analysis and critical examination; but it is doubtful whether the homologues can be completely separated even by very prolonged distillation unless much larger amounts of material are used than is possible on a laboratory scale.

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[1] *Proc. Roy. Soc.*, 1894; *Z. physik. Chem.*, 14, 361.

TABLE 1 (20°).

Hydrocarbon.	B. P.	Sp. gr.	Specific viscosity.
C_7H_{16}	98–100°	0.724	0.51
C_8H_{18}	125°	0.735	0.60
$C_{10}H_{22}$[1]	172–173°	0.747	0.96
$C_{10}H_{22}$	174–175°	0.753	0.95
$C_{10}H_{22}$	163°	0.745	0.89
$C_{12}H_{26}$[1]	209–210°	0.762	1.25
$C_{12}H_{26}$	212–214°	0.769	1.49
$C_{15}H_{32}$	158–159° (50 mm.)	0.793	2.79
$C_{15}H_{32}$[1]	155–158° "	0.796	2.75
$C_{16}H_{34}$	174–175° "	0.799	3.35
$C_{18}H_{38}$	199–200° "	0.813	5.97

In Table 1, it will be observed that viscosity increases somewhat irregularly with every increment of CH_2, and that the change is greater with the increase in molecular weight. Since the proportion of hydrogen to carbon apparently influences materially the value of viscosity, it seemed desirable to compare the viscosity of hydrocarbons of different series. In Table 2, are given the values for hydrocarbons with the same boiling points, but members of different series.

TABLE 2 (60°).

Series.	B. P.	Sp. gr.	Specific viscosity.
C_nH_{2n+2}	294–296° (50 mm.)	0.781	10.88
C_nH_{2n-2}	294–296° "	0.841	21.23
C_nH_{2n+2}	274–276° "	0.775	8.51
C_nH_{2n}	274–276° "	0.835	15.63

The greater viscosity of the hydrocarbons poorer in hydrogen, is clearly shown. In comparing the viscosities of the two hydrocarbons boiling at 294°–296° it will be observed that the difference is greater than the difference between the viscosities of the two hydrocarbons boiling at 274°–276°. This demonstrates the influence of a decreasing percentage of hydrogen since in the first set, the change is from $2n+2$ to $2n-2$, whereas in the second set, the change is only from $2n+2$ to $2n$. Both viscosity and specific gravity increase with the decreasing hydrogen. Another possible influence must not be overlooked, however, namely, the internal structure of the different hydrocarbons. It is reasonable to assume that the straight or open-chain structure of the paraffin hydrocarbon C_nH_{2n+2} behaves differently under the stress of internal forces on which viscosity depends, from the ring or cylic structure, which must be accepted for the other series, until more is definitely known concerning their constitution. Certainly this is plainly shown in lubrication, where the paraffin hydrocarbons are of comparatively little value.

If, then, the lower series furnish lubricators with greater viscosity, the addition of a member of a higher series should give a mixture lower in

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[1] Of approximately this composition.

viscosity. Observations were therefore made on mixtures of pure hydrocarbons of the different series with reference to variations of viscosity, and the results of these measurements are given in Tables 3 and 4.

TABLE 3 (20°).

INFLUENCE OF A SOLID PARAFFIN HYDROCARBON.

Hydrocarbon.	B.P.	Sp. Gr.	Specific viscosity.
(a) Penn. distillate C_nH_{2n-2} filtered......	312-314° (50 mm.)	0.868	87.42
(b) Same cooled to −10° and filtered.....	312-314° "	0.868	88.16
(c) $b + 2.35$ per cent. solid paraffin C_nH_{2n+2} of same B. P......................	312-314° "	0.868	82.30
(d) Penn. distillate C_nH_{2n} cooled to −10° and filtered.......................	276-278° "	0.861	37.57
(e) $d + 2.5$ per cent. solid paraffin hydrocarbon C_nH_{2n+2} of same B. P..........	276-278° "	0.860	36.39

The amounts of solid paraffin hydrocarbons added in these experiments were all that the oils could hold in solution at that temperature. Although no appreciable changes appear in specific gravity, there were material changes in viscosity. Table 4 shows that the diminution in viscosity still holds at a higher temperature, but in a less marked degree even when a larger portion of the paraffin hydrocarbon is introduced.

TABLE 4 (60°).

INFLUENCE OF A SOLID PARAFFIN HYDROCARBON.

Hydrocarbon.	B. P.	Sp. Gr.	Specific viscosity.
(a) C_nH_{2n-2}......................	294-296° (50 mm.)	0.841	21.23
(b) C_nH_{2n+2}......................	294-296° "	0.781	10.88
(c) Pa. hydrocarbon C_nH_{2n}.........	274-276° "	0.838	15.63
(d) Pa. hydrocarbon C_nH_{2n+2}......	274-276° "	0.775	8.51
(e) c + 5 per cent. of d............	....	0.831	15.16

South American Oils.

Two well-fractioned distillates from South American petroleum of undetermined series, but doubtless poor in hydrogen, were examined at 20° with the following results:

TABLE 5.

	B. P.	Sp. gr.	Specific viscosity.
Distillate 1.............	155-160° (50 mm.)	0.884	8.14
Distillate 2.............	215-220° "	0.896	19.57

So far as viscosity is an indication of lubricating value, it is evident that these distillates are inferior to the Pennsylvania distillates of the same gravity. The heaviest Pennsylvania distillate examined, with lower gravity than the South American distillates, *viz.* 0.08687, had a viscosity of 88.16 as compared with the numbers 8.14 and 19.57 for the latter. But on the other hand if we consider the properties of distillates taken at the same temperatures, the South American distillates have a much greater gravity and viscosity. It is evident therefore that neither gravity nor boiling point can be depended on for lubricating value unless the source of the oil is known. The method of manufacture has also much to do with relation of specific gravity and lubricating value.

Valuation of Lubricating Oils.

The various standards which have been proposed for the valuation of lubricating oils, are based on their physical properties, especially on specific gravity and viscosity. Both specific gravity and viscosity are, however, unreliable, unless the source and composition of the oil are known, and unless viscosity is still further defined by frictional tests on bearings under definite conditions which demonstrate the wearing quality of the oil. As is well known, many lighter oils have a greater viscosity than other heavier oils. With these limitations, the property of viscosity has a direct relation to lubricating value.

An ideal lubricator is evidently one which holds two bearing surfaces at a sufficient distance from each other to prevent friction between them and at the same time has the least possible amount of internal friction so that the work necessary to overcome the friction of the oil particles upon each other may be reduced to a minimum. If the oil has too great an internal friction, considerable mechanical energy is expended in overcoming this friction and in conversion of mechanical energy into heat, which should be avoided as far as possible. The choice of a lubricator must, therefore, depend upon the weight to be supported and upon the speed desired. At a high speed, an oil of small internal friction should be chosen, but for slow heavy work, an oil of greater viscosity must be used to support the weight, and because of the slow speed, the greater internal friction of the oil is of less consequence. The viscosity of an oil then, with a knowledge of its composition and with the aid of frictional tests, gives a direct measure of its usefulness as a lubricator under any given conditions, since viscosity is merely another term for internal friction.

But viscosity measured at ordinary temperatures may lead to erroneous conclusions concerning true lubricating value for higher temperatures. This would be especially true for light loads and high speeds where the temperature is considerably higher than the surrounding temperature. The viscosity of all liquids decreases with rise of temperature, but not to the same extent for all liquids. In general, the decrease is about 2 per cent per degree centigrade, within ordinary ranges of temperature. The following table shows the dependence of viscosity on temperature for two Pennsylvania distillates.

TABLE 5.

Hydrocarbon.	B. P.	Viscosity in dynes per sq. cm. at 20°.	Viscosity in dynes per sq. cm. at 60°.	Change in viscosity per degrees C.
C_nH_{2n-2}	312–314° (50 mm.)	0.8803	0.1320	2.12%
C_nH_{2n}	276–278° (50 mm.)	0.3783	0.0723	2.02%

The first oil shows a greater variation per degree than the latter of the C_nH_{2n} series. The coefficient of the more mobile C_nH_{2n+2} distillate with the same boiling point at temperatures above its melting point, should be still smaller. Small differences in the temperature coefficient of viscosity should also be expected in the same series when members of different boiling points are compared. It may readily occur then that two oils have quite different viscosities at high temperatures while at lower temperatures the value should be the same.

The viscosity of a hydrocarbon oil may be changed, as is commonly done, by the addition of viscous vegetable oils such as castor. Such blended oils, made to meet specifications for a required viscosity, are in common use. For certain kinds of work, such oils are doubtless serviceable, but probably have less durability than mineral oils of equivalent viscosity. In cylinders where the oil comes in contact with superheated steam, the vegetable constituents must be saponified to a greater or lesser extent, with consequent danger of corrosive action by the free acid. There is in fact at present, less necessity for the use of compounded oils to obtain desirable viscosity and wearing qualities since the recent development of oil territory which yields heavy products.

Durability tests on compounded oils and pure distillates by a frictional machine in the Case mechanical laboratory have shown the superior frictional qualities of the mineral oils.

Allusion has been made to the fact that viscosity alone cannot always be relied on to give a correct estimate of the wearing qualities of a lubricating oil on a bearing. Much time has been devoted to the wearing qualities of oils in this laboratory, and some of the results were presented in a paper at the New York meeting of the American Chemical Society, December, 1906. The machine employed in these tests was constructed by Prof. C. H. Benjamin for the mechanical laboratory of Case School of Applied Science. It consists of a bearing in two sections so arranged that the upper section can be raised, and when in position can be weighted by means of strong springs on the axle to be lubricated. Attached to the upper section of the bearing is a lever arm extending outward over the platform of a scale, and the outer end rests on a support standing upright on the scale platform by which the scale registers by changes in weight the varying pressure caused by changes in friction. An oil cup is connected with the bearing in such a manner that a regular supply of the oil to be tested is permitted to flow over the journal. A thermometer is also inserted in the bearing close to the journal for the purpose of indicating the changes in temperature during a test. An examination of a lubricating oil by this method, consists in allowing the oil to run on the axle at the rate of six to eight drops per minute for two hours, noting the temperature and pressure on the balance every five minutes. At the end of this period the flow of oil is stopped and the journal allowed to run until the oil ceases to lubricate, which is immediately shown by greatly increased frictional pressure and a large rise in temperature. The crucial test of the oil is the time it can support the axle after the flow is stopped.

The number of revolutions was set at about 500 per minute, and an occasional reading of the speed was taken to be sure that the axle was revolving under fairly constant conditions. The pressure on the axle exerted by the spring set on the upper half of the bearing was equivalent to 1300 pounds. In practice, evidently every oil should be tested under an equivalent of the load and speed it is expected to carry. The results of several of the oils tested are given below. Every oil was run for two hours with continuous lubrication, and the time stated in the table is reckoned from the end of the hour when the flow was stopped, to the time when the oil refused to lubricate, which was indicated by sudden and large increase in temperature and frictional load. Such a durability test affords a fair comparison of the ability of the oil to support friction.

Having on hand a variety of hydrocarbons of the series C_nH_{2n+2}, C_nH_{2n}, C_nH_{2n-2} and C_nH_{2n-4} which have accumulated during the years one of us has been occupied in ascertaining the composition of American petroleum, an opportunity was afforded to ascertain by frictional tests whether hydrocarbons of a different series exhibit differences in wearing capacity corresponding to variations in viscosity. For the purpose of comparing the frictional qualities of these hydrocarbons with the requirements of lubricators in actual use, several vegetable oils were included, *viz.*, castor, sperm, and rape oils, which are the best lubricators of their class, and often used in compounding with petroleum oils as an aid to the viscosity of the latter. Some results of the best compounded oils are also included for comparison. The following elements were used in the calculation of results:

Constant of lever arm (determined by independent observations)	13.656 lbs.
Radius of lever arm	31.625 inches.
Radius of journal	1.61 "
Load	1,300 pounds.

$$\text{Formula: Coefficient of friction} = \frac{\text{Scale reading} - 13.625\ \frac{31.625}{1.61}}{1300}.$$

The real tests of lubricating capacity depend on temperature, measure of friction, and the time the oil continues to lubricate after it ceases to flow on the journal. The latter observations are given in the column headed "Test of durability." It is interesting to observe that the life

TABLE 6.

Oil treated.	B. P.	Specific gravity.	Specific viscosity 20°.	Test of durability. Minutes.	Temperature.			Coef. of friction.		
					Start.	2 hrs.	Break.	Start.	2 hrs.	Break.
Hydrocarbon C_nH_{2n}	274–276° (50 mm.)	0.861	37.57	120	76°	107°	124°	0.02	0.01	0.015
Hydrocarbon C_nH_{2n-2}	312–314° (50 mm.)	0.868	88.16	150	80°	130°	185°	0.01	0.02	0.02
Hydrocarbon C_nH_{2n-x}	228–230° (30 mm.)	0.923	94.3	210	75°	113°	164°	0.03	0.01	0.01
			Viscosity.							
Castor		0.97	104(210°)	150	70°	165°	225°	0.04	0.025	0.03
Sperm		0.94	192(90°)	140	70°	120°	160°	0.02	0.01	0.01
Rape		0.91	108(150°)	120	80°	160°	230°	0.03	0.02	0.05
Cylinder oil (compounded)		0.92	123(212°)	75	80°	180°	210°	0.05	0.03	0.06
Cylinder oil (compounded)		0.89	135(210°)	200	80°	185°	225°	0.07	0.03	0.06

of the individual hydrocarbons increases with the decrease in hydrogen, and in a similar ratio to the increase in specific viscosity. Doubtless the most valuable quality of an oil is its ability to reduce friction to the smallest value; of the hydrocarbons compared in this test, the one with least hydrogen, of the series C_nH_{2n-4} seems to show the best efficiency, as it also shows the greatest durability. Of the vegetable oils compared, the castor shows the longest life, but the sperm shows the least coefficient of friction, as it does also the lowest temperatures. The hydrocarbon C_nH_{2n-4} stands ahead of the vegetable oils in durability, and the equal of the sperm in temperatures and coefficient of friction. In the above table, temperatures are selected at the beginning of the test, at the end of two hours, and when the oil ceases to lubricate. The coefficient of friction is also calculated at these points. This method appears to be capable of giving valuable information concerning the nature of lubricating oils. Like all tests of such oils, the results are relative referring to some common standards. Evidently in practice, these standards must be based on the work required of the oil, taking into account certain data, such as speed of the journal and the load carried. The coefficient of friction as used above represents the fraction of one pound for each pound of load on the journal which is sustained by the oil in use.

With reference to the comparative value of the various series of hydrocarbons in petroleum from which lubricating oils are prepared, it must be understood that the series C_nH_{2n+2} has a low lubricating value; this was shown above in tests of specific viscosity. Lubricating oils prepared from Pennsylvania petroleum consist for the larger part of the series C_nH_{2n} and series C_nH_{2n-2}. Those from the heavier oils consist largely of the series C_nH_{2n-2} and the series C_nH_{2n-4}.

As to the structural constitution of the series of hydrocarbons in lubricating oils, at present nothing whatever is known. The series C_nH_{2n+2} is doubtless represented by the straight chain or its isomers, all with the open chain. The series poorer in hydrogen, no doubt have the cyclic ring structure of the form of condensed benzene rings in part, or condensed methylene rings, single larger rings than are at present recognized, or smaller rings with condensed side chains.

CLEVELAND. OHIO.

THE COLORED SALTS OF SCHIFF'S BASES.

II. THE HYDROCHLORIDES OF BASES FORMED BY CONDENSING *p*-AMINODIPHENYLAMINE WITH AROMATIC ALDEHYDES.

BY F. J. MOORE AND R. G. WOODBRIDGE, JR.

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In a paper recently published by one of us, in collaboration with Mr. R. D. Gale,[1] attention was called to the fact that bases of the general formula

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[1] THIS JOURNAL, **30,** 394 (1908).