III. CONSTITUTION OF LUBRICATING OIL

Apparatus for the Determination of Viscosity Temperatures Up to about 350 C

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Frames

2815-2815 2824-2825 2832-2835 2839-2846 2861-2863 2868-2869 2880-2884 2899-2900 2905-2312 2924-2953 2955-2962 2975-2980

Translation

111-7 2015

INTRODUCTION

In the general part of the last report concerning the constitution of lubricating oil (April Report III, 3), we suggested the development of the method of measurement for temperature-viscosity procedure as the point to be carried out first.

The following problems above all are to be solved by this investigation.

- 1. Which type of viscometer is most suitable for our purpose?
- 2. How can we obtain a constantly high temperature?
- (to 1.) For the viscosity determination of lubricating oil and such, of which only a limited amount is at our disposal and which determination has to be over the greatest possible temperature range, in our opinion the only ones to be considered are:
 - a. Apparatus with a capillary flow
 - b. Apparatus with a falling body.

In order to get an idea about the advantages and disadvantages of these two types of viscometers, one would have to determine to which order of magnitude the viscosities which are to be measured belong.

Thereafter the measurement for both types of viscometers is calculated and the errors to be expected with these viscometers estimated.

2814

SUMMARY OF THE EXPERIMENT

Erk and Eck have proved that the temperature-viscosity curve of oil can best be described by the von Vogel equation:

With this equation for viscosity flow, the constant was calculated between 20 and 100 C and after that extrapolated to about 350 C for Golden Shell, Heavy and two pure hydrocarbons. Differentiation of this equation gives the temperature coefficient of viscosity at this highest temperature. III-8

Although extrapolation over so great a temperature range is dangerous, it is to be assumed, however, that the determined value can be of use in the calculation of the calibration of the necessary apparatus.

	n	250 C 1 dn 1 dt	h	350 C 1 <u>dh</u> 7 dt
Golden Shell Heavy	1.5 c.p.	.010	.6 c.p.	.006
16 N Butylhentriacontane Cg5H72	.8	.006	.5	.004
Dihydrodiisoamylanthracene C24H32	.4	.012	.15	.007

For the measurement of a viscosity of about 0.1 centipoise a capillary flow with 0.2 mm diameter can be used. In case both the difference in heighth between the levels and the capillary length are about 10 cm, the flow time amounts to about 8 minutes (calculated according to Poiseuille Rule.)

The measurement in the apparatus with a felling body can be calculated according to the following formula (See Heinze 8) :

$$\int_{a}^{2} t(y_{v} - y_{0})g \frac{de^{3}}{\sqrt{3(d + 2b)^{2} + (2b)^{2}}}$$

where

$$t = t$$
 viscosity $t = t$ distance of fall $t = t$ distance of falling body $t = t$ density of falling body $t = t$ clearance

yo = density of oil

The clearance, needed for the measurement of low viscosity at high temperatures is 0.05 mm, when a magnetically reised falling body of

(1) Phys. Z. 37, 113, 1956

iron has a d = 1 mm, a felling distance of 20 cm, and the least falling time of 30 seconds.

The capillary is made for practical reasons of glass; on account of the smallness of the clearance, between 20 and 350 C the value of the fractional expression in the above formula changes about 10 per cent. A falling body with a greater diameter was selected, so that this deviation was still greater.

CONCLUSION

2815⁹

From the calculation it results that either a capillary flow type apparatus or a falling body apparatus remain technically feasible for the determination of the expected viscosity. In the latter case, however, on account of the small clearance rigid requirements are placed on the construction of the falling body and surrounding capillary, whereas moreover the coefficient of expansion must be as nearly the same as possible.

PLANS FOR WIDER INVESTIGATION

It is to be proved how a constantly high temperature is to be obtained for both types of viscosimeters.

III-17 2824

INTRODUCTION

From the calculation it results that for the expected low viscosities the capillary flow viscosimeter as well as the falling body viscosimeter are technically feasible. Experimentally it is to be proved, whether each of the two types can be easily handled at 350 C.

The manner in which the constantly high temperature is maintained best depends again on the type of viscosimeter. A viscosimeter with a falling body can be so simply designed that a metal block can be built in. Both types of viscosimeters can be placed in either a liquid or a vapor bath, since the former, however, must be renewed often in order to obtain a good visibility we have disregarded this solution and now only the use of the vapor bath will be taken under consideration.

SUMMARY OF THE INVESTIGATION

The viscosity of Spindle oil J2 was measured at various temperatures up to about 161 C, where the temperature by means of the vapors of a boiling liquid remained constent. A B.S.I. viscosimeter, that is a viscosimeter with capillary flow was used. With the same viscosimeter placed in an exactly regulated oil bath, the viscosity in the same temperature range was measured once more. The last measurement was made by means of a curve log // - log C = A/t ft. Moreover it was calculated which temperatures are to be placed in this equation in order to obtain that viscosity which was measured with the vapor bath. These temperatures displayed the following

variations of the temperature which prevailed according to the thermometer in the vapor bath: at 37 C + 0.3 C; at 65 C + 0.7 C; at 100 C + 0.6 C; at 116 C + 0.9 C; at 161 C - 1.8 C.

These variations were such that for the higher temperatures it was necessary to obtain another vapor bath, with a second glass wall surrounding the wall of the vapor space. The vapor of the inner space to be cooled flows between the two walls, thereby assuring that the viscosimeter was less strongly cooled down.

III-18

Such a vapor bath, for which however no viscosimeter with a suitable looped piece was made, was subjected to a first experiment.

2825

The two junctions of the thermocouples were brought into the vapor bath, that is from different heights and distance from the wall. The thermocouple in the vapor of benzophenone at 305 C showed temperature differences which varied according to the outer wall of the vapor bath even though it was provided with asbestos insulation. A small hole in the insulation made possible the handling of the viscosimeter.

CONCLUSION

A vapor bath gives - at least for oriented measurements - a satisfactory constant temperature.

PLAN FOR FURTHER EXPERIMENTS

A capillary flow viscosimeter and a falling body viscosimeter were made ready to be placed into the vapor bath. Difficulties such as oxidation, evaporation, etc. occur at highest temperatures.

111-22 2832

INTRODUCTION

In last month's report viscosity measurements were described which were carried out with a B.S.I. viscosimeter in a vapor bath up to a temperature of 161. C. These experiments lead to the conclusion that a vapor bath is very suitable at highest temperatures, supposing, that precautions have been taken to avoid heat losses; to that end a double wall around the vapor space has proved useful.

A question still open is which type viscosimeter has the advantage at higher temperatures. For the test a viscosimeter with capillary flow and a viscosimeter with a falling body exist. We will now report about the first measurement with a capillary flow viscosimeter at a temperature above 300 C.

SUMMARY OF THE INVESTIGATION

A B.S.I. viscosimeter was placed in a vapor bath in which the boiling liquid was benzonphenone (diphenylketone). In order to avoid the

oxidation of oil a suitable accessory apparatus makes it possible to evacuate the viscosimeter, then to fill dropwise with oil and thereafter introduce nitrogen above the oil. The oil level was stopped at the exact height by means of drawing off the excess oil with a fine capillary. As for the rest, the normal hendling of a B.S.I. viscosimeter was made difficult in our case because of the fact that no air was allowed in.

The first oil, that we filled in this way and heated to about the boiling point of benzophenone, RL3, a Venezuelean oil with E50 = about 25, proved to be volatile at 300 C. A part of it evaporated which condensed again on a colder place of the viscosimeter. The evaporation on the surface of the oil already suggests an error, which may be more inherent to the viscosimeter with capillary flow than the falling body viscosimeter. With pure materials this error is of slight significance, since with slight evaporation the viscosity remains constant, so that only the influence of the amount of liquid plays a part.

For the first measurement over 300 C it was considered expedient to eliminate the source of error caused by eveporation and a less volatile oil be used. Such an oil was Elk Bright Stock, A Pennsylvania oil with E50 = about 32.

At the temperature of boiling benzophenone, three series of measurements were made with this oil, for each series fresh oil was used.

Series I Temperature: 305 C III-23
Flowtime in seconds: 164.8; 164.8; 165.2; 166.2; 164.8; 2833
Series II Temperature: 304.5 C
Flowtime in seconds: 165.4; 165.8; 164.8; 166.2;
Series III Temperature: 305 C
Flowtime in seconds: 164.6; 165.2; 164.2; 164.6.

The differences between the various measurements of each series are less than 1 per cent. Also the mean value of the measurements agree well. From this good reproducibility, it may be concluded that the marks on the viscosimeter are sharp enough to be observed in spite of the blur caused by the flowing benzophenone along the partition, and the smallness of the window in the insulation. The agreement between series moreover shows that the adjustment of the level, which occurred in the absence of air was accurate enough.

CONCLUSIONS

The measurement of the flowtime of Elk Bright Stock at the temperature of boiling benzophenone was found to give good reproducibility.

PLANS FOR FURTHER INVESTIGATION

To determine the flowtime of Elk Bright Stock in vapor bath at other temperatures and in so far as possible also in a very reliable liquid bath.

The viscosimeter which has been in a flame in order to mount a looped piece shall be calibrated enew.

INTRODUCTION

III-29 2839

III-30

2840

The conclusion of last month's report was, that at the temperature of boiling benzophenone good reproducibility of flow time results with a B.S.I. viscosimeter. Now we shall establish that this is also the case at the temperature of boiling naphthalene, eniline, monochlorobenzene and benzene. The circumstance, that some measurements made in a precisely regulated oil bath agree closely with those mentioned above, increases confidence in the reliability, as does likewise the fact that the measurements lie on a smooth curve over the whole temperature range, which is extended by means of a measurement in a water bath at 30 C.

Since the measurements correlate satisfactorily and no further modifications were necessary. The calibration was accomplished.

SUMMARY OF THE EXPERIMENT

Elk Bright Stock was examined with a B.S.I. viskosimeter at the temperature of boiling naphthalene, emiline, monochlorobenzene and benzene.

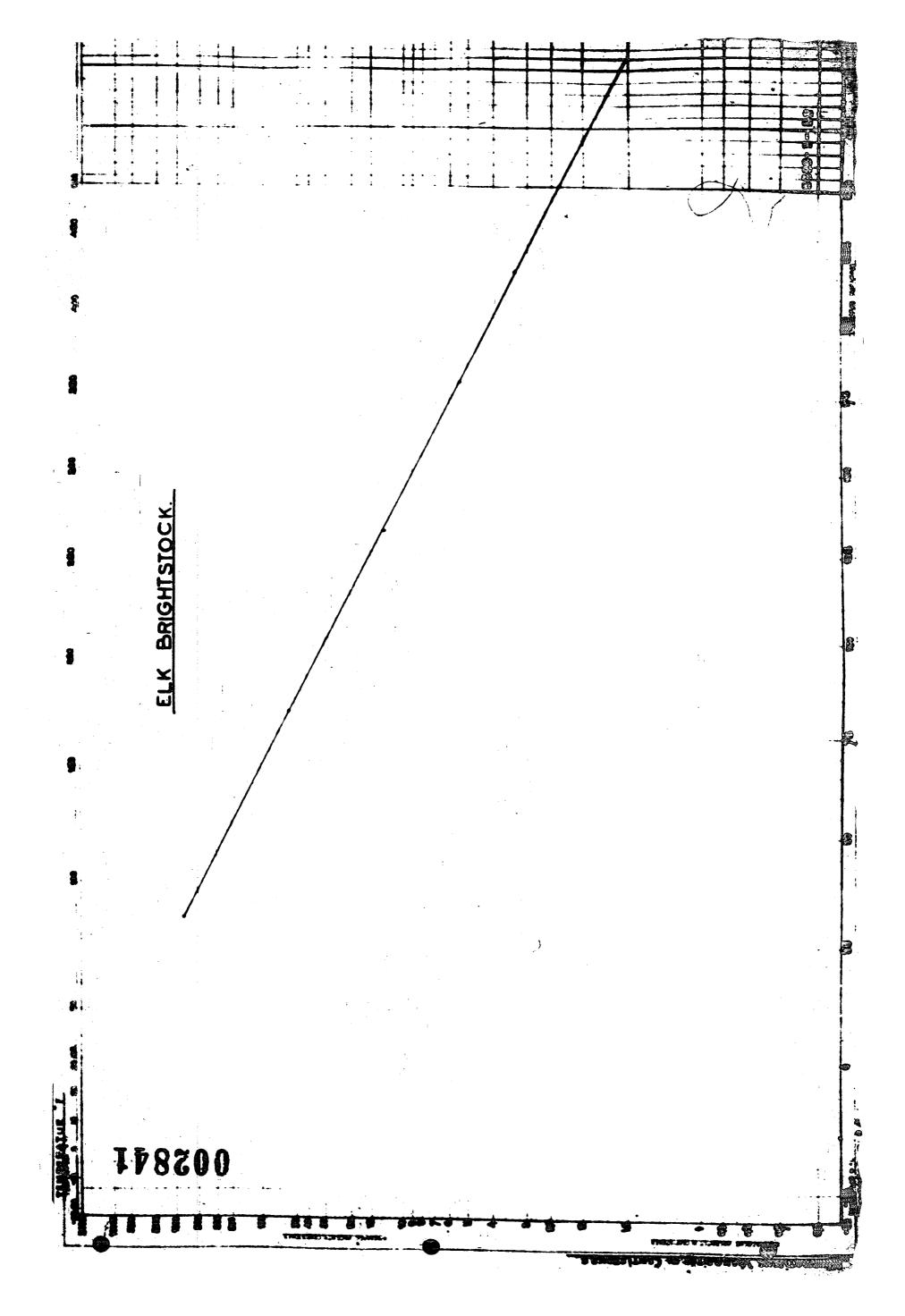
Boiling naphthalene: Temperature: 217.8 C.
Flowtime in seconds: 353.6; 359
Boiling eniline (anhydrous): Temperature: 179.2 or 179.7 C.
Flowtime in seconds: 587.0 or 583.8
Boiling monochlorobenzene: Temperature 131.6 C.
Flowtime in seconds: 1379; 1375
Boiling benzene: Temperature: 80.5 C.
Flowtime in seconds: 6111; 6095.

The above values increased to give a flow time of 8592.0 seconds when placed in the middle of a water bath at 30.0 C.

Besides the measurements in the vapor bath, the same measurements were carried out in an oil bath where the temperatures chosen were as close as possible to boiling smiline and boiling monochlorobenzene.

Oil bath: Temperature: 179.6 C.
Flowtime in seconds: 588.2; 584.4; 587.0
Oil bath: Temperature: 131.6 C.
Flowtime in seconds: 1385; 1380.

The measurements in the vapor bath and in the oil bath are in very good agreement. Since the measurements thruout the whole temperature range were carried out without appreciable difficulty, the viscosimeter can be considered useful to carry out the calibration.



This calibration was carried out at 15 C with two oils. Thereby it results, that in order to obtain the number of centistokes, the number of seconds is to be multiplied by the following factor:

10 0il: 0.009195; 0.009203; 0.009195 20 0il: 0.009215; 0.009203.

The multiplication factor is dependent on the temperature and varies proportionally with the linear expansion of glass. Since the viscosimeter is made from Pyrex glass this means an increase of only 1 per cent between 25 and 305 C. Over the whole temperature range therefore, we calculate with a constant multiplication factor of 0.00921.

For the viscosity of Elk Bright Stock we obtained the following results:

30.0 C	791 centistokes
80.5	56 . 2 **
131.6	12.7
179.5	5.89
217.8	5,30
305.0	1.52.

From the above illustration Number 5659-5-B2 it is evident that when the viscosity is plotted on ASTM paper with log(100Vg \$ 0.8) against log T, one obtains nearly a straight line. The measured viscosities at the highest temperatures are somewhat higher than would follow from the rectilinear extrapolation of the measurements at lower temperatures.

CONCLUSION

A viscosimeter with capillary flow was used for the measuring of viscosities at the higher temperatures. The highest temperature, at which viscosity can be measured is limited by the volatility of the oil.

PLANS FOR FURTHER INVESTIGATION

111~31 2842

Several representative oils were examined over a wider temperature range. The viscosity-curve on ASTM paper (viscosity log paper) again in these cases varies a little from the straight line; so the number of measurements can be limited.

In the meanwhile a falling body viscosimeter was delivered to the laboratory. With such a viscosimeter the evaporation of the oil was less troublesome.

INTRODUCTION

111-52 2845

As announced, the viscosity of a limited number of oils was measured

over a wide temperature range. We have obtained the following results with a synthetic Bright Stock.

SUMMARY OF THE INVESTIGATION

The viscosity of synthetic Bright Stock TMC 8225 was found to be:

37.8 C	706 centistokes
60.1	216
98.7	48.1
131.6	20.7
183.2	8.06
244.6	გ.83
306	, 2.23

At temperatures around 100 C and beyond, the vapor bath and the viscosimeter with the factor of 0.00921 were used; at temperatures below 100 C we used a liquid bath and a viscosimeter with the factor 1.58.

The viscosity-curve makes nearly a straight line on ASTM paper.

PLANS FOR FURTHER INVESTIGATION

Aromatic and naphthenic oils are to be investigated.

IN TRODUCTION

III-33 2844

The viscosity-curve was systemicatically determined on an aromatic and naphthenic oil. Evaporation was troublesome with naphthenic oil. With castor oil such was the case to a still greater degree. Oriented measurements were made with a falling body viscosimeter, a viscosimeter type which can prevent evaporation.

SUMMARY OF THE INVESTIGATION

The viscosity of a B.P. oil (IMC 6996) was determined at several temperatures below 100 C in the middle of a liquid bath, with a viscosimeter with a factor of 0.0634. The following values were found:

37.8 C (100 F)	182.5 centistokes
60.7 C	42.9
98.8 C (210 F)	9.69.

The viscosity was determined at several temperatures above 100 C in the middle of a vapor bath with a viscosimeter with a factor 0.00921. In order to control the agreement of both viscosimeters, measurements were made with the latter one at temperatures below 100 C as well. Of course it was found to have a very long flow time, for example, more than 5 hours 6 37.8 C.

37.8 C (100 F)	183.9 centistokes
98.9 (210 F)	9,72
152.0	4.38

184.5 C 1.96 centistokes 245.2 1.058 506.5 0.677

Plotted on ASTM paper, the viscosity-curve shows a clear deviction from a straight line. The viscosity at higher temperatures is higher than may be expected from the measurements carried out by means of extrapolation power temperature.

During the determinations of the viscosity of the Venezuelan oil BD₁ indications were found of the loss of volatile components. A brown deposit became evident on the somewhat colder parts of the side of the viscosimeter. The discoloration raises the question of whether oxidation also occurs with evaporation. On this basis the nitrogen, which was analyzed by passing it through a pyrogallol-KOH solution and over CaCl₂ and P₂O₅. The analysis showed that the oxygen content amounted to only 0.06-0.07 per cent.

III-34 2845

Since measurements at 280 C are in many cases unreliable owing to possible evaporation, it was decided to make a series of measurements up to about 240 C and after that to repeat some of the first measurements of the series. This repetition of measurements at a lower temperature necessitates that a little fresh oil be added in order to maintain the proper level.

For the viscosity of BD₁ the following values were found.

37.8 C (100 F) 98.9 C (210F)	46.6 centistokes 5.574 2.98	183.5 C 244.4 98.9 C (210	1.51 centistokes 0.891
131.7 C	£,00		5.619

Plotted on ASTM paper the viscosity curve of the Venezuelan oil BD1 also deviated from a straight line.

In the determination of the viscosity curve of castor oil over a large temperature range, the evaporation was even more annoying than in the case of ED1. The difficulties experienced on account of the vaporization of oils in the viscosimeter with effluent capillary has lead to the result that the development of the falling body viscosimeter, which we have discussed a few times already, will now be taken into consideration. There is at our disposal for the manufacture of a tube with uniformly round cross-section a KPC tube*, with a diameter of about 1 mm and a linear coefficient of expansion of 4.8 x 10-6. Calculations in the May report have already proved, that it is desirable that the falling body and tube have nearly the same coefficient of expansion. On this basis a falling body was rolled from a special metal celled "Fernico" which the N. V. Philips Gloeilampenfabrieken (Incondescent Lamp Works Company) in Eindhonen placed at our disposal and which has a

^{*} a precision capillary molten from metal bolts.

coefficient of expansion of 4.4×10^{-6} at 120 C and 5.0×10^{-6} at 270 C. Since the instructions showed that the metal is attached in the oil at higher temperatures, the surface of the falling body was nickel plated.

A series of measurements was made with the falling body, where the tube was suspended in a vapor bath. Formerly the addition of the deaerated oil was at the bottom of the tube. The rising oil carries the falling body with, it is fixed in its highest position by means of an electromagnet. After a few minutes in which the oil should be a constant temperature, the falling body is released. Orginally at a temperature fall times were obtained with variations of 1.3 per cent. In this case we obtained fall times with a variation of only 0.3 per cent by not cutting out suddenly the alternating current thourgh the electromagnet, but instead allowing a regular decline in current intensity and so demagnetizing the falling body.

III-35

likewise good results can not be attained when the temperature 28 rises to 245 C; at this temperature the reproducibility was good. Repetition of the measurement at 184 C gives an increased value of 8 per cent. The viscosimeter was dismounted. It turned out the nickel plating had peeled off the falling body. The experiments were continued with a gold plated falling body and a glass falling body.

CONCLUSION

Plotted on ASTM paper the viscosity curve of Balik Papen oil and Venezuelan oil BD₁ deviate clearly from a straight line. The viscosity at higher temperatures is higher than would be expected from the extrapolation of the measurements at lower temperatures. With the Venezuelan oil the measurements must be limited to temperatures below 245 C, since at higher temperatures the volatilization becomes troublesome. In the oriented measurements with the falling body viscosimeter good reproducibility of fall time was obtained

PLANS FOR FURTHER INVESTIGATION

The viscosity of several oils are to be examined over a wide temperature range. The investigation of materials which contain in addition to carbon and hydrogen many other atoms will begin simultaneously. For example, an ether with a long carbon chain will be considered. Such a material called dicetylether is already reported. A search through the literature concerning the viscosity of ether supports the experimental work.

The experiments on the development of a useful falling body viscosimeter will be continued.

INTRODUCTION

111-49 2861 viscosimeter are to be continued. In the last report the first results with a viscosimeter of this type were given. This viscosimeter consists of a precision capillary with about a 1 mm cross section in which is located a metal falling body, which can be raised to its highest position with an electromagnet. After the attainment of temperature equilibrium, the falling body is set free by means of swift and regular lowering of the current intensity in the electromagnet. The body passes in its fall two marks and can after that be brought up again by the introduction of fresh oil in the capillary. The surface of the falling body, which was made from a metal with low coefficient of expansion, was nickel plated.

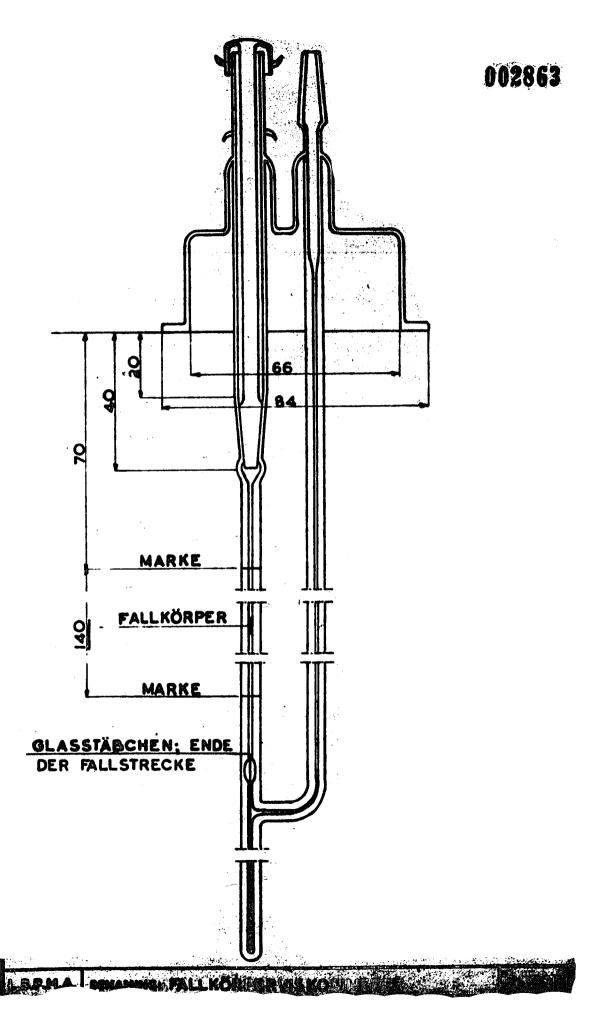
After a number of favorable measurements had been carried out, the nickel coating began to peel off. We experimented with gold plate to obtain better results. The falling body was newly polished, carefully cleaned of grease and hung in a gold bath. This bath contained 2 g. gold chloride, 1 g. potassium cyanide, 15 g. sodium sulfate and 60 g. of disodiumphosphate per liter of water. It gives a good gold plate of 0.001 mm thickness. The repeatibility proved to be very good on a series of measurements carried out with the gilded falling body. After a while however, the gold plate just as with the nickel plate began to peel off. Fortunately, better results were obtained almost simultaneously in another direction, so that further experiments will be given up until a durable falling body can be made from metal.

The better results were obtained with a falling body made from glass. The use of a falling body which cannot be raised by an electromagnet is made possible by a modification to the viscosimeter such that not much observing time is necessary for the standardization of temperature equilibrium. The glass falling body was originally cut from a solid glass rod, and the end plane ground. Such a falling body vibrated to some degree and the reproducibility of falling time was not as good as a falling body with a somewhat pointed head. However, when our expert falling body with a somewhat pointed head. However, when our expert mechanic made a falling body of the required form, this last difficulty was also removed. In what follows we did not carry out again the measurements with the gilded falling body, but limit ourselves to the description of the final form of the viscosimeter with a falling body made of glass.

SUMMARY OF THE INVESTIGATION

III-50 2862

The final form of the falling body viscosimeter was shown in the foregoing illustration 19094-A4. The most important parts are the falling body and its proper precision capillary. A short distance from the end a second capillary opens into the tube (surrounding the falling body) in which the oil is kept under a slight pressure of nitrogen. As long as the glass stopper at the end of the tube is raised, the oil flows in, thereby raising the falling body with it, as soon as the falling body is up, the stopper is allowed to drop. The falling body them level, begins



to fall. This however, presents no difficulty because the oil is already in the feed capillary which has reached the proper temperature. It may be necessary to wait a few minutes between double determinations when the fall time is short. The time, necessary for the terminal face of the falling body to pass the distance between the upper and lower mark, is noted as the fall time. The terminal face is platinized in order to assure good visibility. Good reproducibility was obtained with the fall times.

CONCLUSION

The experiments in the development of a useful falling body viscosimeter lead to the manufacture of a viscosimeter with a glass falling body. We now have at our disposal an apparatus which can effect good service when the measurements with the capillary flow viscosimeter is made difficult by means of the evaporation of oil.

PLANS FOR FURTHER INVESTIGATION

A few oils are to be measured with both the falling body viscosimeter and capillary flow viscosimeter.

III 54 2868

INTRODUCTION

In the last report was described a falling body viscosimeter, which finds use when the measurements with a capillary flow viscosimeter are troublesome because of evaporation of the oil. At this time a few oils are being investigated with both viscosimeters.

SUILIARY OF THE EXPERIMENT

Pann. Neutral and LCT Penn. Eright Stock were tested with a capillary flow type viscosimeter (constant 0.00921).

The Hagenbach correction

8 if x capillary length kinematic viscosity 100%

was applied with)) = 1.00 and at the maximum amounted to 0.9 per cent.

Penn. Neutr	al TMC 748	LCT Penn. Br	ight Stock TMC 364
152.7 C 184.7 C 246.1 C 284.5 C 306.7 C	3.124 centistokes 1.658 " .984 " .775 "	80.6 C 132.2 C 183.5 C 245.3 C 307.0 C	59.6 centistokes 13.29 % 5.32 % 2.606 % 1.542 %

Both oils were tested in the falling body viscosimeter, whereby the viscosity was found when the density difference between the falling body and the oil was multiplied by a calibration constant. The oil density is determined simultaneously with the viscosity by hanging near the viscosimeter in the vapor bath a 5 cc pycnometer with a long calibrated stem. For the calibration constant eight values were obtained by means of comparison of every two measurements at the same temperature with both viscosimeters. Since the falling body and surrounding tube have the same coefficient of expansion, the calibration constant will change only slightly with the temperature, that is, no more than corresponds to the linear expansion of glass.

On this basis a single calibration value was averaged from the many and from it the viscosity calculated below.

Pennsylvania Neutral TMC 743

2869

memp.	Density	Dynamic	Kinematic	Deviation
C		Viscosity c.p.	Viscosity c.s.	%
132.2 184.2 245.4 285.5	0.7865 0.7540 0.7154 0.6913	2.487 1,264 0.713 0.527	3.161 1.667 0.997 0.762	1 0.4 1 0.7 4 0.8 1 0.5

L.C.T. Pennsylvania Bright Stock TMC 564

			•	
Temp.	Density	Dysomic <u>Viscosity</u> c.p.	Kinematic Viscosity C.s.	<u>Deviation</u>
0 80.8 183.5 244.6 305.8	0.8537 0.7903 0.7533 0.7148	50.2 4.16 1.951 1.111	58.8 5.27 2.590 1.554	- 0.5 - 1.0 - 1.2 1.0,2

In the last column of the above table are indicated the deviations in viscosity which were found when the measurements with the falling body viscosimeter were compared at the same temperatures with the measurements with the other viscosimeter. Although the agreement between the viscosimeters is fair, it can be said that the measurements with the capillary flow type viscosimeter are not substantially influenced by evaporation.

CONCLUSION

Two oils were investigated with a capillary flow type viscosimeter

and also with a falling body type viscosimeter. The agreement of the measurements show that evaporation has no influence. There are still a few oils more volatile than the ones mentioned before to be tested comparatively in both viscosimeters. The testing of pure materials has already begun.

February 1943

111-64 2880

INTRODUCTION

The investigation of the viscosity of pure materials was taken in hand. The first measurements were carried out with n-hexadecane, after that p-dicetylbenzene was investigated. Both materials were placed at our disposal by Prof. Wibaut. The preparation of n-hexadecane was described in Requeil des Traveux Chimiquis des Pays-Bas 58, 329 (1939). The value reported therein for the density d 20/4=0.77387 lies between the value of Evans d 20/4 = 0.7752 and the one of Deensley d 20/4 = 0.77335. The sample of p-dicetylbenzene was tested as to purity by Mr. Ir. J. Verheus, for that a cooling curve was determined. It proved that the temperature decrease between the solidification limits amounted to only 0.2 C. If one rejects the possibility of a mixed crystal formation with an isomer, which has nearly the same freezing point, on account of the improbability, it can be concluded, that the preparation has a purity > 99 per cent. The freezing point is 53.0 C.

SUMMARY OF THE INVESTIGATION

First the density of n-hexadecane was determined with the help of a pycnometer of about 5 cc capacity with a long calibrated stem. Two fillings were used, in order that two series of measurements would be obtained.

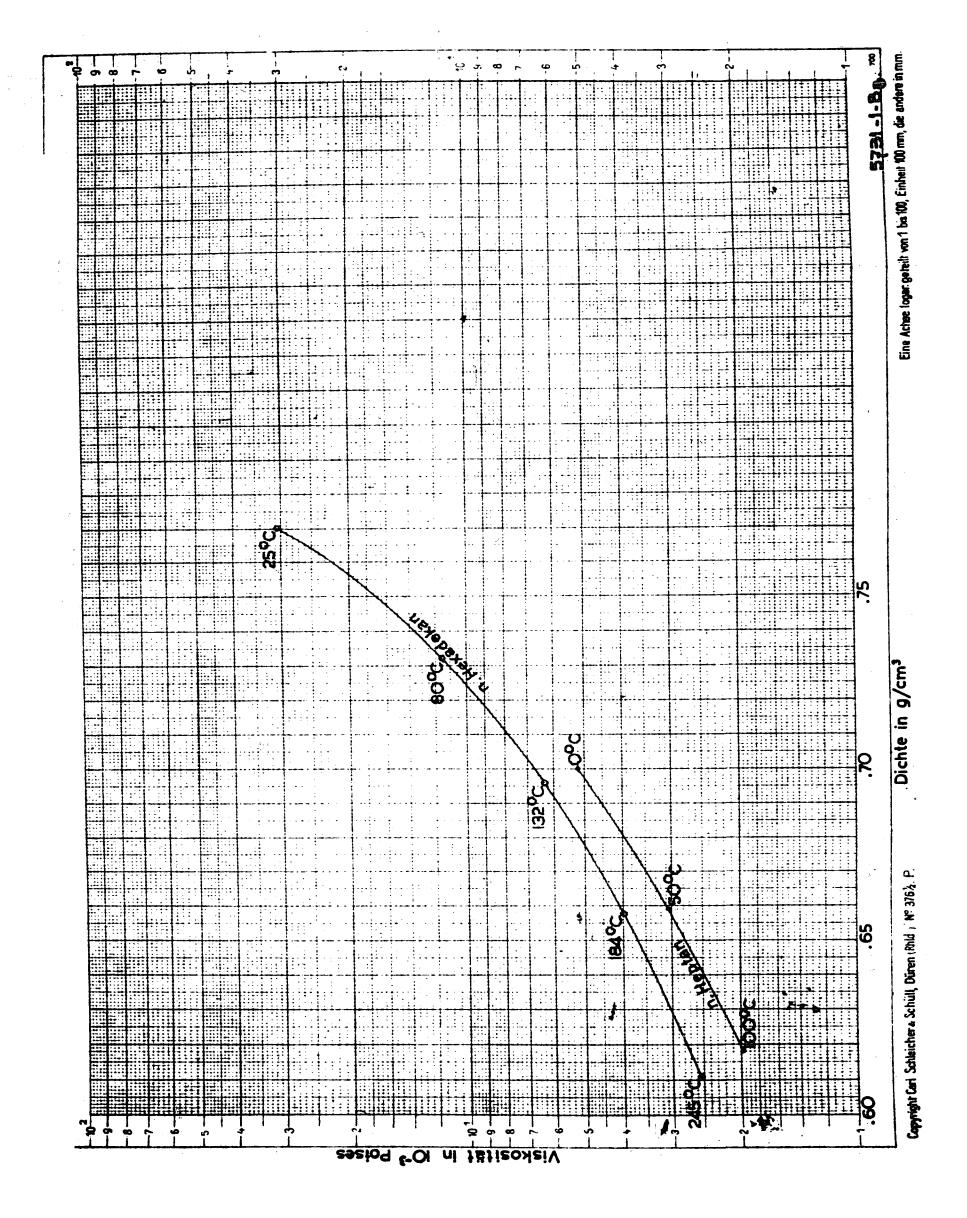
Density of n-Hexadecane

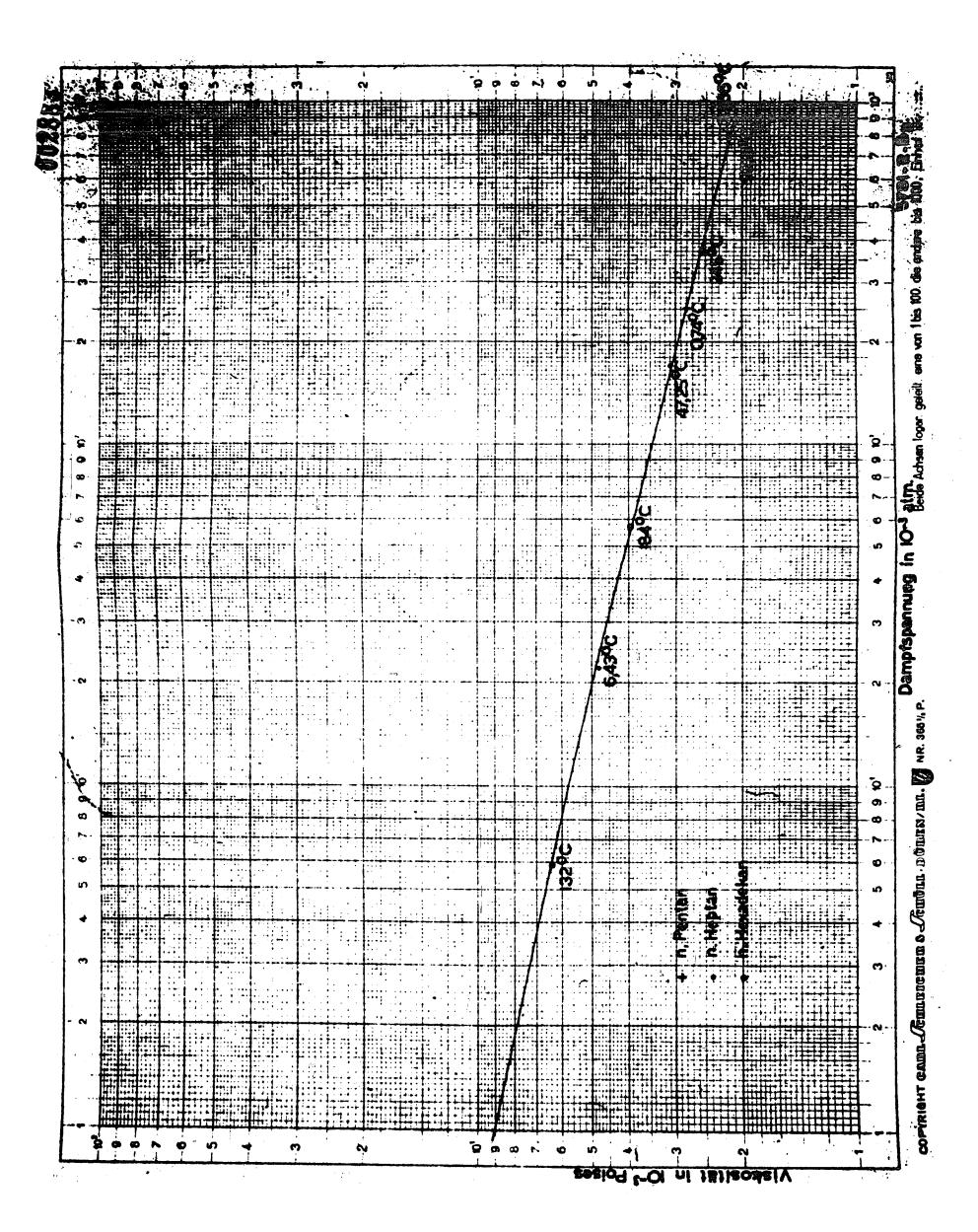
100 F 0.7621 g/cm ³	79.9 C	0.7326 g/cm ⁸
80.2 C 0.7321	131.5 C	0.6959
131.8 C 0.6965	183.5 C	0.6577
185.7 C 0.6577	244.2 C	0.613

For the determination of viscosity of n-hexadecane a capillary flow type viscosimeter with a narrow capillary was used, this was so that the Hagenbach correction amounted to no more than 0.1 per cent. By means of the calibration with water and oil it was established, that in order to obtain the kinematic viscosity in centistokes the flow time in seconds is multiplied by the factor 0.000291.

Viscosity of n-Hexadecane	111-65
(capillary flow)	2881
(Captaras) 110 m	

25.0 C	4.01 centistokes	5.09 centipoise
80.2	1,588	1,163
131.8	0.917	0.6 38
183.7	0.612	0.402
244.8	0.416	0.254





At approximately the same temperatures n-hexadecane was investigated with the falling body viscosimeter. A falling body whose calibration was established with water, was used, so that the fall time in seconds must be multiplied not only by the density difference between glass and liquid but also by the factor 0.00484, in order to obtain dynamic viscosity in centipoise. Calibration with an oil gave exactly the same value for the factor.

Viscosity of n-Hexadecane (Falling body)

25.0	C		3.07	centipoise
79.9	C		1,16	L
131.5	C		0.638	3
183.3	C	G .	0.399	•
244.2	-		0.25	2 .

One finds in literature a few values for the viscosity of n-hexadecane at temperatures lower than 100 C according to Evans , Ubbelahde and Aghte found in the year 1915, 1.136 centipoise for the viscosity at 80 C, while Evans himself found 1.172 centipoise. This new value lies between the two.

It is often recommended in literature to compare different viscosities of, for example, homologous materials with the same density. A similar point for discussion is also the comparison with materials of the same volatility.

While viscosities are almost always determined between 0 and 100 C such consideration remained Limited on adjacent homologs. This is now changed because of the measurements on n-hexadecane at higher temperatures. In the foregoing diagram the viscosity was plotted as a function of the censity and vapor pressure respectively.

On the viscosity density diagram (5731-1-B3), the viscosity of n-heptene is also plotted, here the values which Eavns had calculated for O, 50, and 100 C from the measurements of Thorpe and Rodgers were used. With similar densities, the viscosity of n-hexadecane and n-heptene differed widely.

On the viscosity-vapor pressure diagram (5731-2-B5) are plotted at the same time the viscosities of n-heptone and n-pentane, for which some measurements of Thorpe and Rodgers 11 were used. With similar vapor pressure the dynamic viscosity of such widely separated homologs as n-pentane, n-lootene and n-hexadecane varied only a little.

After hexadecene, p-dicetylbenzene was investigated. The 2684 density was determined with the above mentioned pycnometer of about 5 cc capacity with a long calibrated stem and the viscosity with the falling body viscosimeter. The density values in the table indicated as calculated were found with the formula $d^{\alpha} = 0.86407$ -6.173 x $10^{-4}t(-3.75 \times 10^{-8}t^2)$, which was calculated with the help of the method of small quadratics.

¹ J. Instr. Petre Techn. 1938, 24, 58 11 Phil. Trans. A. 1895, 186, 397.

Density of p-Dicetylbenzene

	Measured	Computed
67.3 C 78.5 100.6 132.2 185.8 306.3	0.8225 g/cm ³ 0.8152 0.8017 0.7820 0.7492 0.6715	0.8224 g/cm ³ 0.8155 0.8016 0.7818 0.7493 0.6715

Viscosity of p-Dicetylbenzene (Falling body)

Templ	Reported	Dynamic	Kinematic
	Density	Viscosity	Viscosity
80.6 C 152.2 184.0 245.3	0.8141 0.7818 0.7492 0.7104 0.6715	8.90 c.p. 3.50 1.848 1.062 0.676	10.93 c.s. 4.48 2.47 1.495 1.007

CONCLUSION

The viscosity of n-hexadecene was measured with both a capillary flow and falling body viscosimeter. The agreement of the measurements is satisfactory. No particular difficulty was experienced with the investigation of p-dicetylbenzene, melting point 55.0 \neq 0.1 C.

PLANS FOR FURTHER INVESTIGATION

The investigation of pure organic materials will be continued. The small samples of principally unbranched paraffins, whose investigation described by Dr. Hazes in Report 8975 are still remaining, will probably be investigated with the falling body viscosimeter. Between the viscosity-temperature curve to be gained in this way, the missing ones may be found by interpolation. The viscosity-vapor pressure diagram appears to be a valuable aid for this interpolation. The final group of viscosity-temperature curves of unbranched paraffins to be obtained were of great value in the valuation of the viscosity curves of organic meterials.

III-80 289**9**

INTRODUCTION

The viscosity of octadecylbenzene and 1,1-diphenylhexadecane were determined. The octadecylbenzene sample number 38/3988 was received from Prof. Wibaut on May 5, 1938. The multing point according to specifications was 22.4 G.

SUMMARY OF THE INVESTIGATION

The density of octadecylbenzene was determined with the help of an approx. 1 cc pycnometer with long calibrated stem, the viscosity was measured by a falling body type viscosimeter. The density values indicated in the table as calculated were found with the formula $d^* = 0.87217$ —6.606 x $10^{-4}t$ - 2.75 x $10^{-8}t^2$, which was calculated from the measurements with the help of the method of small quadratics.

Density of Octadecylbenzene

111-80 2899

	Measured	Computed
43.6 C	0.8433 g/cm ³	0.8453
81.0	0.8185	0.8185
132.4	0.7843	0.7842
184.0	0.7496	0.7497
245.6	0.7083	0.7085

Viscosity of Octadecylbenzene (Falling body)

Temp.	Reported	Dynamic	Kinematic
	Density	Viscosity	Viscosity
40.0 C	0.846	7.39 c.p.	8.74
81.0 C	0.819	3.00	3.66
132.4	0.784	1.440	1.837
184.0	0.750	0.851	1.135
245.6	0.708	0.552	0.737
285.8	0.682	0.404	0.592

Before the last measurement at 283.8 C, due to a small repair the constant of the viscosimeter was 0.00488 instead of 0.00484. Also Mikeskal has measured the viscosity of octadecylbenzene at other temperatures. In order to make possible a comparison between the first and second above mentioned measurements, the line log log (number of c.s. x 0.8) = 8.31899 - 3.33695 log T was drawn. By means of the second and third the line log log (number c.s. § 0.8) = 7.96633 - 3.19861 log T was drawn.

In this way one can interpolate between the individual measurements at the temperatures applied by Mikeska.

men os at one occapatation of	133.6 F	147.2 F	1 71 F 3,90	210 F 2,78
Mikeska (c.s.) New interpolated measurements	5.87 5.87	5,05 5,03	3,92	2.79

The density of 1-1 diphenylkexadecane was determined with a 1 cc pycnometer at the same time the viscosity was determined with a falling body type viscosimeter.

¹ Mikesks, Ind. Eng. Chem. 28, 70 (1936)

Density and Viscosity of 1-1 Diphenylhexadecone (Falling body)

Temp.	Density	Dyn. Viscosity	Kin. Viscosity
25.0 C	0.9070 g/cm ³ 0.8707 0.8364 0.8014 0.7607 0.7165	(34.9) cp	(38.5) cs
80.6		5.37	6.17
132.4		2.116	2.530
184.4		1.133	1.414
245.8		0.665	0.874
506.5		0.431	0.602

The measurement at 25 C was taken with a B.S.I viscosimeter with K = 0.0634. The new viscosity value lies about 5 per cent lower than the value of Londa and Cech 2 .

PLANS FOR FURTHER INVESTIGATION

The measurements on pentatriacontane are almost finished. We will begin with some other unbranched paraffins.

III-85 2905

INTRODUCTION

The viscosity of n-tetracosane (C₂₄H₅₀), n-pentatriacontane (C₃₅H₇₂) and n-tritetracontane (C₄₅H₈₈) was determined. The last two hydrocarbons were prepared in the laboratory of Prof. (Dr.) H. Bocker in Groninger. The n-tetracosane came from the laboratory of Prof. (Dr.) Wibaut.

Details about the preparation and further purification can be found in Report Number 8975 of Dr. W. M. Mazee. A sample of n-pentatria-contane whose preparation was described by Dr. Verberg in the March report (see III-75) was also investigated. Since this sample was large, it was possible to use both the falling body and capillary flow viscosimeter, and in this way the reliability of the first mentioned viscosimeter can be tested once more.

The measured results for the named unbranched paraffin hydrocarbons and the even earlier investigation of n hexadecane were treated in various ways.

SUMMARY OF THE INVESTIGATION

The densities of the normal paraffins were determined with the help of a pycnometer of 1 cc capacity, with a long calibrated stem; the viscosities were measured with the falling body viscosimeter.

2 S. Londa and J. Cech, Coll. Trav. Chim. Tchecoslovoque 6, 423 (1934)

Density and Viscosity (Falling hody) of n-Tetracosane CggH50

Temp.	Density	Dyn. Vis.	Kin. Vis.
56.2 C	0.7757 g/cm ³	4.61 c.p.	5.94 c.s.
80.2	0.7600	2.872	3.78
151.6	0.7264	1.365	1.878
184.0	0.6915	0.790	1.142
244.8	0.6501	0.482	0.741
506.0	0.6041	0.314	0.520

Density and Viscosity (Falling body) of n-Pentatriacontane C35H72

Temp.	Density	Dyn. Vis.	Kin. Vis.
80.5 C 110.4 131.9 184.0 245.0	0.7778 g/cm ³ 0.7592 0.7459 0.7131 0.6748 0.6343	6,68 c.p. 3,83 2,778 1,495 0,868 0,556	8.59 c.s. 5.04 3.72 2.096 1.286 0.877

Density and Viscosity (Falling body) of n-Tritetracontane C45H38

Temp.	<u>Density</u>	Dyn. Vis.	Kin Vis.
90.0	0.7808 g/cm ⁵ 0.7669 0.7543 0.7223 0.6850 0.6474	8.Gl c.p.	11.03 c.s.
112.4		5.66	7.38
132.1		4.15	5.50
184.2		2.125	2.942
245.5		1.195	1.745
308.2		0.750	1.158

A sample of n-pentatriacontane prepared by Dr. Verberg was investigated with a capillary flow viscosimeter (No. H21-40, Factor = 0.002685) as well as with the falling body viscosimeter.

Density and Viscosity of n-Pentatricontane C35H72

Temp.	Density	Dyn. Vis.	Kip. Vis.
80.4 C	0.7783	6.74 c.p.	8.66 c.s.
184.0	0.7133	1.494	2.094
245.6	0.6740	0.863	1.281
3<u>0</u>6.3	0.6539	0.553	0,872

111-86 2906

Falling Body Viscosimeter

Temp.	Dynamic Viscosity	Kinematic Viscosity
80.5 C	6.74 c.p.	8.66 c.s.
111.4	3.79	4.93
132.0	2.777	3.72
184.2	1.493	2.024
245.3	0.870	1.291
306.1	0.555	0.875

Difference in Viscosity Measurements after Conversion to the Same Temperature, Expressed in per cent of the Measurement.

	Prepared by Prof. Wibaut	Prepared Falling body	by Dr. Verberg Viscosimeter Hel. 40
Temp. 80.5 C 111.4 132.0 184.2 245.3 306.1	- 1.3 - 0.7 - 0.1 - 0.1 - 0.5 0	0 0 0 0 0	- 0.2 - 0.1 - 0.6 - 0.2

The agreement of the measurements with both viscosimeters is good, close as the agreement with the results of Prof. Backer with n-pentatriacontane.

The results for the normal paraffins obtained up to now are drawn graphically in various ways. III-87

2907

- The kinematic viscosity of n-nexadecane, n-tetracosane, n-pentatriacontane and n-tritetracontane are plotted on ASTM paper (See diagram 5758-i-B2). The measurements at the highest temperatures are no more off the line than the viscosity curve made at lower temperatures.
- The logs of the kinematic viscosity are plotted against the logs of the vapor pressure (See diagram 5758-2-B3). In an earlier report, the dynamic viscosity was used for this kind of plotting. However, all the data at our disposal shows that the agreement between various homologa is better when the kinematic viscosity is used. The number at the measuring point gives the number of C atoms in the concerned paraffin hydrocarbon. The data for n-pentane, n-heptane, and n-octane comes from Thorne and Rogers, and compiled with other data into a table by Evens1. The viscosity of methane at 90 C was borrowed from a publication by Bussler and Landermann11.

¹ J. Inst. Petr. Techn. 1933, 24, 38 11 J. Exp. Theor. Physics 1940, 10, 250 (Russian)

- 5. The logarithms of dynamic viscosity were plotted against the logarithms of the number of C atoms for several temperatures (See diagram 5758-3-B5). The points lie on a fairly good straight line. The measured results taken from Report No. 8975 of Dr. Mazee for n-C21H44 up to and including n-C45H88 lie on the straight line for 90 C.
- 4. The temperatures at which the dynamic viscosity reached 1, 2, 3, 4, and 5 were also plotted against the number of C atoms. (See Diagram 5758-4-B3). The relation was indicated again by a straight line, n-C45H88, however, deviated clearly.

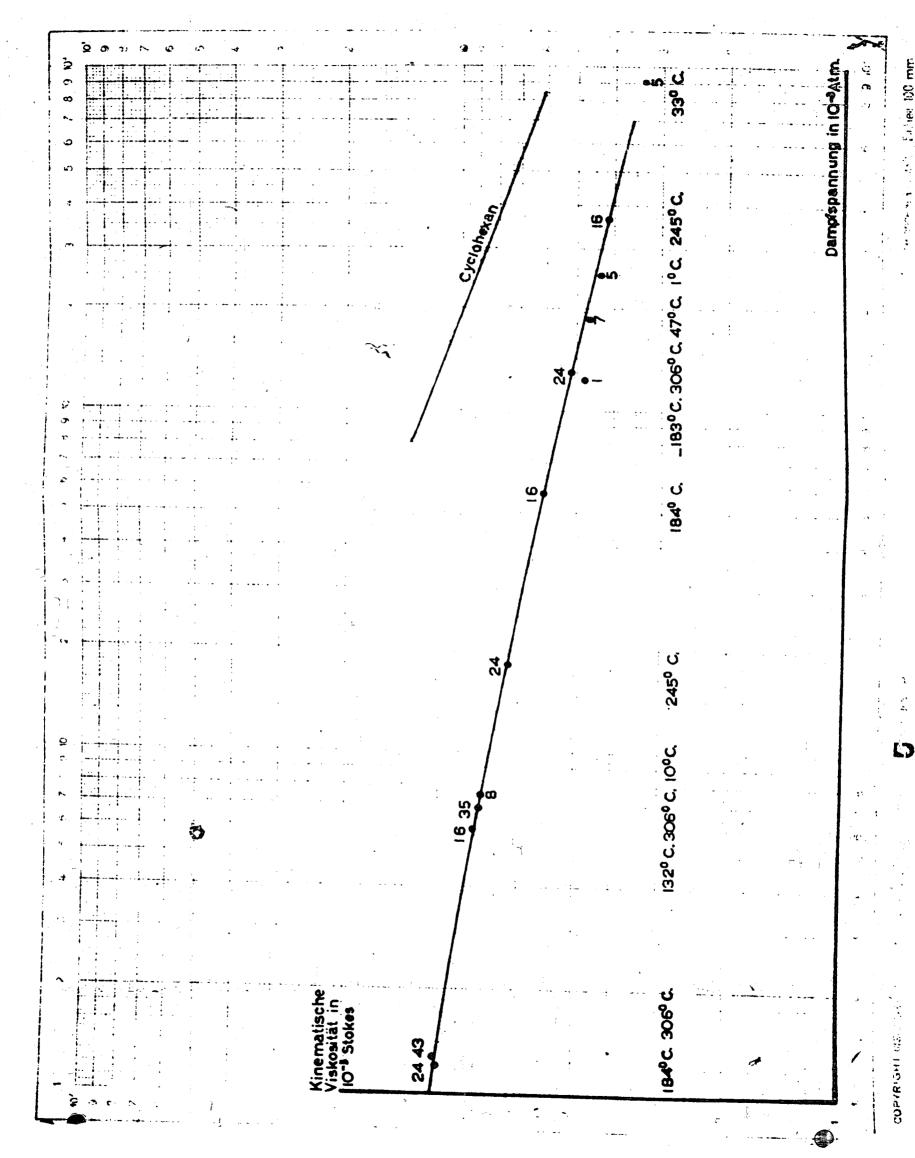
The regularity described under 3 and 4 lead us to the attempt to describe by a single formula the viscosity of various unbranched paraffins with melting points up to 500 C,

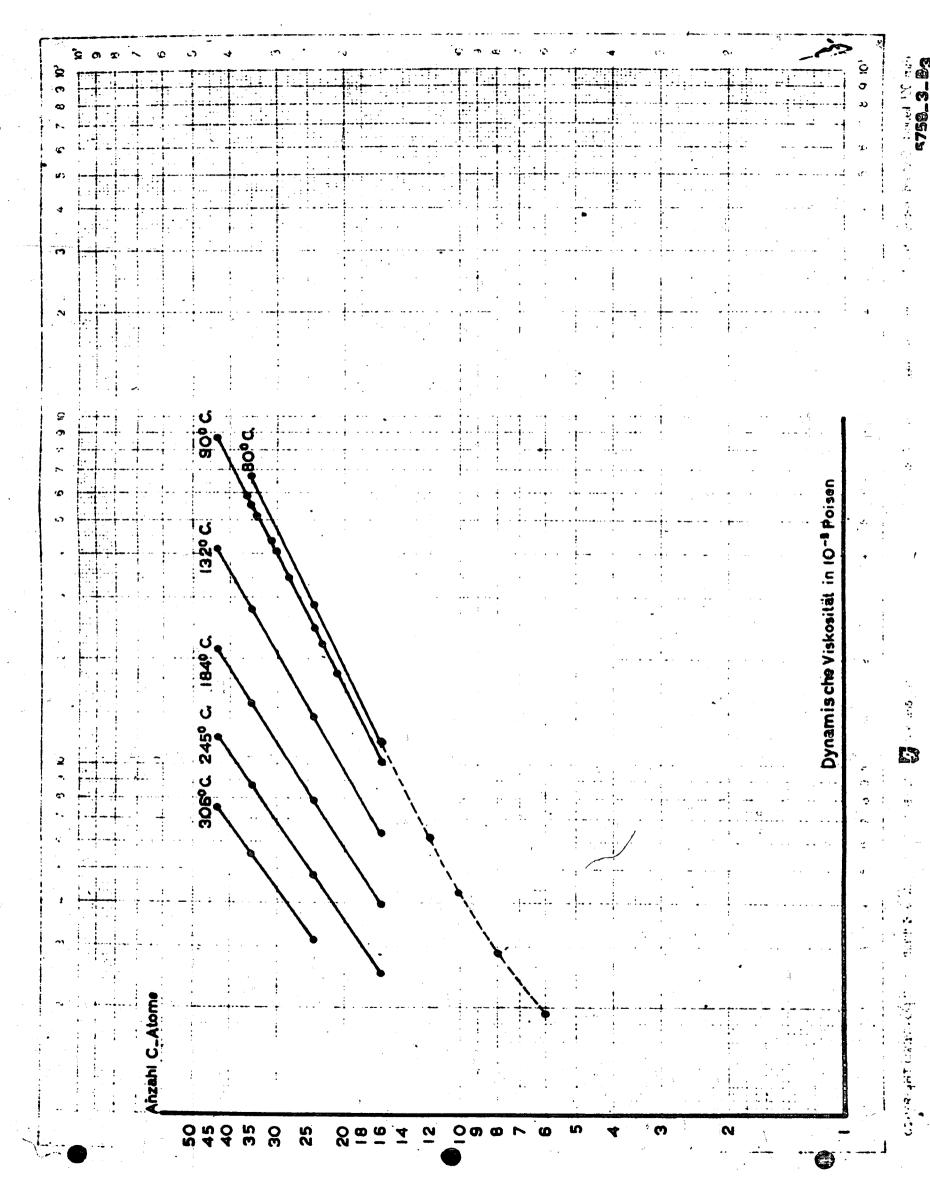
log M = AT log n + BT & C log n & D
in which the molecular weight M is used instead of the number of C atoms.
The coefficients A,B,C and D were determined by means of the application of the method of small quadratics to the difference of both parts of the equation; thus resulting from the Report 8975 of Dr. Mazee on the viscosity of n-C21H44 up to end including n-C45H88 at 70 C, 80 C and 90 C, and from the February up to end including n-C45H88 at 70 C, 80 C and 90 C, and from the February report (See III-65) on the viscosity of n-hexadecane at 25 up to 245 C, and report (See III-65) on the viscosity of n-tetracosane and n-pentatriacontane up to 306 C. The viscosity of n-tritetracosane at higher temperatures contane up to 306 C. The viscosity of n-tritetracosane at higher temperatures was still not known or sufficient at the time of the calculation, as III-88 was later proved, the regularity was not as good that described under 2908 was later proved, the regularity was not as good that described under 308 and 4. The method of the small quadratic gave the following values for the formula:

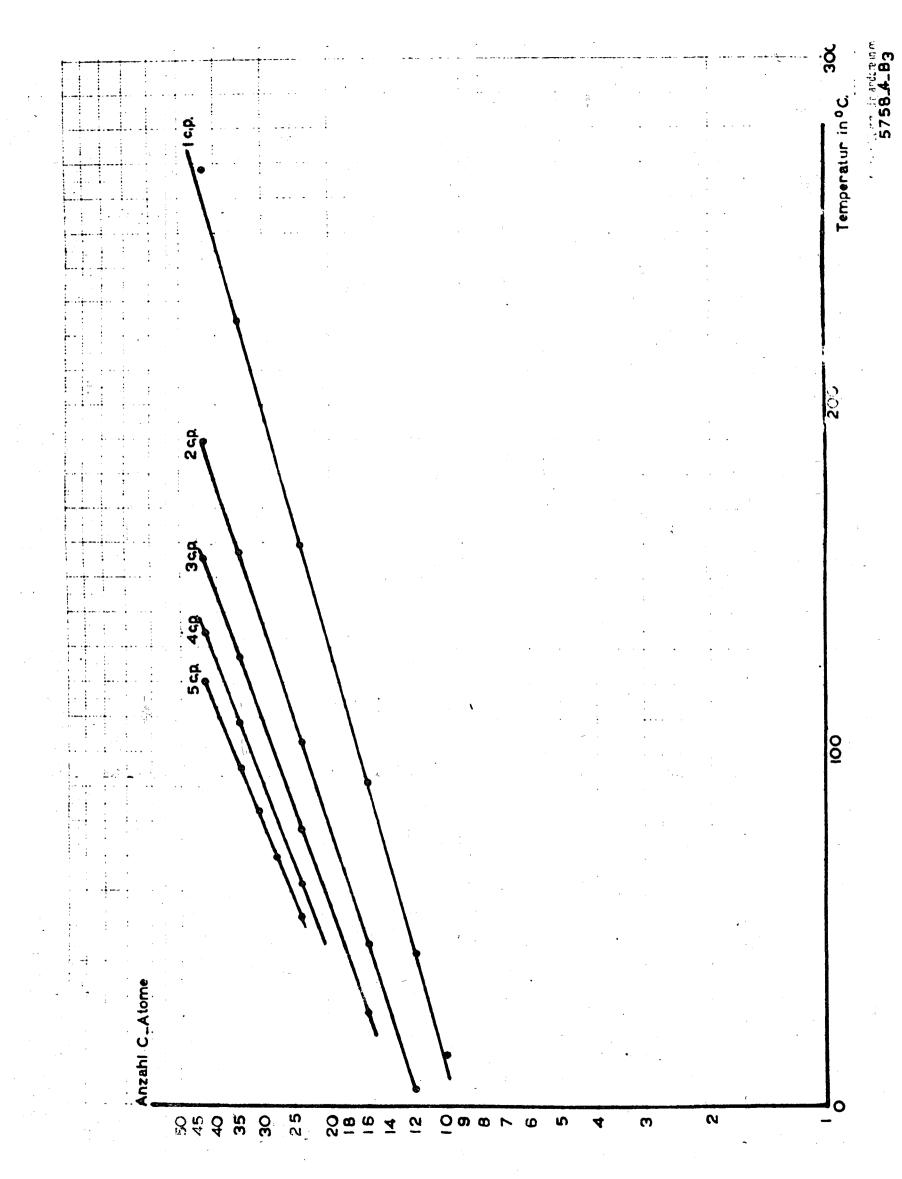
log M = 0.001410 T log 7 + 0.002530 T - 0.0605/(+ 1.4342, where T is in on and in centipoise.

The amounts that the molecular weights calculated by the formula vary from the true value are given in the table below.

Vary 110m the bide			Deviation Fo	rmula
Hydrocarbons	Molecular Wt.	at 70 C	at 80 C	at 90 C
Heneicosane Tricosane Tetracosane Octacosane Tricontane Hentricontane Tetratriacontane Pentatriacontane Hexatricontane Tritetracontane	296.3 524.4 338.4 394.5 422.5 436.5 478.6 492.6 506.8 604.7	/ 0.1 % / 0.0 / 0.2 / 0.5 / 1.6 / 2.1	- 0.4 \$ - 0.3 - 0.3 - 0.2 / 0.5 / 1.4 - 0.5 - 0.1 - 0.2	- 0.6 % - 0.9 - 0.6 - 0.5 / 0.1 / 0.4 - 1.5 - 0.7 - 1.0 - 1.0 ontinued)







(Continued)

Hydrocarbon	s Molecular	· Vt.			
Hexadecane	226.5	at 25 C	at 80 C	132 C 184 C	
		/ 2.1 %	10.4 %	f 0.9% f 0.7%	eldigelli
Tetracosane	358.4	at 56 C	80 C	132 C 184 C	
		1 1.4 %	- 0.2 %	-0.6% /0.3%	
Pentatriaconte	ne 492.6	at 80 C	110 C	132 C 184 C	245 C
•		- 0.8 %	- 1.9 %	- 1.7 % 0.0 %	f 2.6 \$

If for a single temperature the viscosities of branched paraffins or cyclic hydrocarbons are introduced, the formula gives a graph in which case the viscosity-temperature curve of these hydrocarbons cut the group of curves of normal paraffins. However, it should be borne in mind, that the formula varies considerably for normal paraffins with more than 35 carbon atoms.

CONCLUSION

The viscosities of n-paraffins at higher temperatures are lower than would be expected from a straight line extrapolation on ASTM paper at lower temperature measurements.

The kinematic viscosity from methans up to and including n-tritetracontane at the same vapor pressure are nearly the same.

The viscosity from hexadecane up to and including n-pentatriacontene can be expressed over a wide temperature range in a simple formula.

PLANS FOR FURTHER INVESTIGATION

To measure the viscosity of a few branched hydrocarbons.

May 1943

III--99 2924

INTRODUCTION

In last month's report were mentioned the viscosities up to about 300 C of a few aromatic hydrocarbons and a series of normal paraffins. The only viscosities of aromatic hydrocarbons determined were namely dissobutylnaphthalene, and in addition the branched paraffin hydrocarbons 3-ethylpentane, 10-nonylnonadecane and 7,12-dimethyl-9,10-di-n-hexylactadecane.

The disobutylnephthalene (Sample No. 40/4885) came from Prof.

Wibaut; Ir. Verheus determined d 20/4 = 0.9323 and n20/d = 1.5413 (Lerer 1) gives the following numbers: d 0/4 = 0.9424 and n 19/d = 1.5410.

The 3-ethylpentane, comes from Dr. Keulemans; has a boiling point of 93.5 C (Edgar 2) suggested for it 93.3 C.

Report No. 8975 contains more about the 10-nonylnonadecane of Prof. Backer and about the 7,12-dimethyl-9,10-di-n-hexyloctadecane of Prof. Wibaut.

In order to determine the influence of structure on viscosity, the viscosity of branched paraffins are compared with the normal paraffins. With regard to the structure of 3-ethylpentane (triethylmethane) and 10-nonylnonadecane (trinonylmethane) the comparison may be drawn from some other materials.

SUMMARY OF INVESTIGATION

The densities given below were determined with the help of a l co pycnometer with a long celibrated stem. The viscosities were measured with a falling body viscosimeter.

Density end Viscosity (Falling body) of Diisobutylnaphthalene C₁₈H₄₂

Temp.	<u>Density</u>	Dynamic Viscosity	Kinematic Viscosity
19.9 C 55.8 79.7 131.2 183.1 244.2 245.1 283.0 283.2	0.9324 g/cm ³ 0.9082 0.8915 0.8550 0.8171 0.7723	11.26 c.p. 4.71 1.527 0.767 0.437	12.40 c.s. 5.28 1.786 0.939 0.565

III-100

The measured viscosities are much higher than the values 2925 given by Lerer, for example 7 c.p. at 54.8 C.

Density and Viscosity (Falling body) of 3-Ethylpentane C7H16

Temp.	Density	Dynamic Viscosity	Kinematic Viscosity
20.0 C 37.8	0.6973 g/cm ³ 0.6823	0.380 c.p. 0.316	0.545 c.s. 0.464
			(Continued)

¹ M. M. Lerer, Ann. Off. Combust. liq. 8, 681 (1953)

² Edgar, J. Am. Chem. Soc. 51, 1483, 1544, (1929)

Density and Viscosity of 3 Ethylpentane (Continued)

Temp.	Density	Dynamic Viscosity	Kinematic Viscosity
50.0 65.0 80.0	 0.6711 0.6580 0.6441	0.280 c.p. 0.246 0.215	0.417 c.s. 0.373 0.334
art.uguspuguspugus)		

The density and dynamic viscosity at 20 C agree fairly well with the value of Edgar: d 20/4 = 0.6984 and N = 20 = 0.377.

Density and Viscosity (Falling body) of 10 Nonylnonadecane C28H53

Temp.	<u>Density</u>	Dynamic Viscosity	Kinematic Viscosity
20.0 C 80.2 131.9 184.1 245.2 283.3	0.8085 g/cm ³ 0.7691 0.7357 0.7008 0.6597 (0.634)	3.25 c.p. 1.431 0.799 0.481 0.366	4.23 c.s. 1.945 1.140 0.729 0.577

The viscosities agree well with those in Report No. 8975 for 0..90 C; for 80 C the report gives 3.26 c.p.

Density and Viscosity (Falling body) of 7,12-Dimethyl-9,10-di-n-Hexyloctadecane C32H66

Temp.	Density	Dynamic Viscosity	Kinematic Viscosity
20.0 C 50.0 80.6 132.5 184.4 246.0 284.3	0.8250 g/cm ³ (0.805) 0.7833 0.7491 0.7147 0.6733 0.6475	\$9.8 c.p. 11.55 4.87 1.839 0.943 0.533 0.391	48.4 c.s. 14.35 6.22 2.45 1.319 0.792 0.604

The viscosities agree well with those in Report No. 8975 for 40 C and 90 C; the value given therein for 80 C is 4.92 c.p.

The density was measured after a necessary repair and subsequent new calibration of the pycnometer.

The new results are treated in various ways.

III-101 2926

- 1. For valuation of viscosity-temperature curve of hydrocarbons with aromatic nucleus in graph 5773-1-B3 the log of the dynamic viscosities of diisobutylnaphthalene and the further investigated p dicetylbenzene, octadecylbenzene and l,l-diphenylhexadecane are plotted against temperature. For comparison one finds on the same graph the curve for the normal paraffins hexadecane, tetracosane, pentatriacontane and tritetracontane. For p-dicetylbenzene and octadecylbenzene with an aromatic nucleus and long paraffin chain, the influence of temperature on their viscosity is similar over the entire temperature range to the normal paraffins. A greater influence of temperature is noticeable with l,l-diphenylhexadecane with two aromatic nuclei and especially diisobutylnaphthalene with two condensed rings outside of the branched paraffin chain.
- 2. For valuation of viscosity-temperature curves of branched paraffins in graph 5773-2-B3, the logarithms of dynamic viscosity of 10-nonylnonadecane, and 7,12-dimethyl-9,10-di-n-hexyloctadecane are plotted against the temperature. As comparative material one finds on the same graph the curves of the normal paraffins hexadecane, tetracosane, pentatriacontane and tritetracontane. The influence of the temperature on the viscosity is noticeably greater for the branched paraffins than for the normal; least at the lower temperatures. At higher temperatures the difference is not great, over 200 C the curve of 10-nonylnonadecane nearly coincides with the curve of n-tetracosane.
- 5. The kinematic viscosities of diisobutylnaphthalene, 10-nonylnonadecane, and 7,12 dimethyl-9,10-di-n-hexyloctadecane are plotted on ASTM paper graph 5773-3-B3. In addition to the values in this report for 10-nonylnonadecane were used the viscosities at 0, 20, 40 and 60 C from Report No. 8975 by Dr. W. M. Mazee.

The viscosity varies slightly from a straight line with both branched paraffins, but only in the sense that at higher temperatures the experimental value is lower, which was also the case with normal paraffins. With disobutylnaphthalene, however, the viscosity varied markedly from the straight line. Here the viscosity at higher temperatures was higher than would be expected from the straight line extrapolation from the measurements at lower temperatures.

This was also established in the Oct.-Nov. 1942, Report (See III-33 ff) with Balik Papan oil and Venezuelan oil BD1 which contains many carbon atoms in ring structure, while from the Report of August 1942 (See III 29 ff) and Sept. 1942 (See III-52), it is seen that the viscosity curves of Elk Bright Stock and synthetic Bright Stock are nearly a straight line on ASIM paper.

4. For the branched paraffins 3,-ethylpentene, 10-nonylnonadecane 2927 and 7,12-dimethyl-9,10-di-n-hexyloctadecane the logarithms of kinematic viscosities were plotted against the logarithms of the vapor pressure.

The sample of 3-ethylpentane obtained from Dr. Keulmans added the following vapor pressure data: 0.66 atm. at 80 C; 0.40 atm. at 65 C;

0.22 atm. at 50°C. Extrapolation from a log p against 1/T diagram still gives 0.134 atm. at 37.8 C and 0.056 atm. at 20 C. The vapor pressure of both other branched paraffins was taken from Report No. 8975.

Graph 5773-4-B3 shows that the viscosities of the named branched paraffins are somewhat lower than the normal paraffins with the same vapor pressure. This is not the case with all branched paraffins, for example, not with 2,2,4-trimethylpentane whose viscosity was determined by Evans and which lies above this line for normal paraffins in the graph.

The 3-ethylpentane and the 10-nonylnonodecane, which have the same structure give points on the viscosity-vapor pressure graph, from which an almost striaght line could easily be drawn.

5. On graph 5775-5-B3 is the viscosity for a large number of hydrocarbons at 80 C plotted against the number of carbon atoms. For the normal paraffins there is a curve which was used for tabulating data for each one with less than 16 carbon atoms (from Evens 3). The isoparaffins and elefins on the table of figures (from Evens 4,5) are indicated by a line, the aromatics and naphthalenes by a point. Heavy (or thick) lines were drawn for 3-ethylpentane and 10 nonylnonodecane and likewise other substances which included oxygen or nitrogen, yet possess a structure with 3 long chains. For tricaprin, trilaurin, trimyristin, tripalmitin and tristearin, the data from Joglekav and Watson6 was used, for tri-n-butylamine and tri-n-anylamine, the data from Bingham and Spooner 7 was used.

From the graph it is evident that on the one hand the viscosities of the hydrocarbons differ from one another and on the other hand the points, which represent the molecules with three long chains lie very regular in relation to the line of the normal paraffins. Branch and ring formations have more influence on the viscosity than a single ester group or a nitrogen atom in a large molecule. The rest of which is made up of carbon and hydrogen. It is difficult to decide whether the influence of the temperature on viscosity is greater for the known triglyceride as well as the trinonylmethane than for the normal paraffins for the measurements of Joglekav and Watson only go up to 85 C, that is about up to the melting point of the like viscous normal paraffins. Moreover the temperature coefficient of the riscosity of triceprin varies so much from the other triglycerides that such an inaccurate statement should not be used.

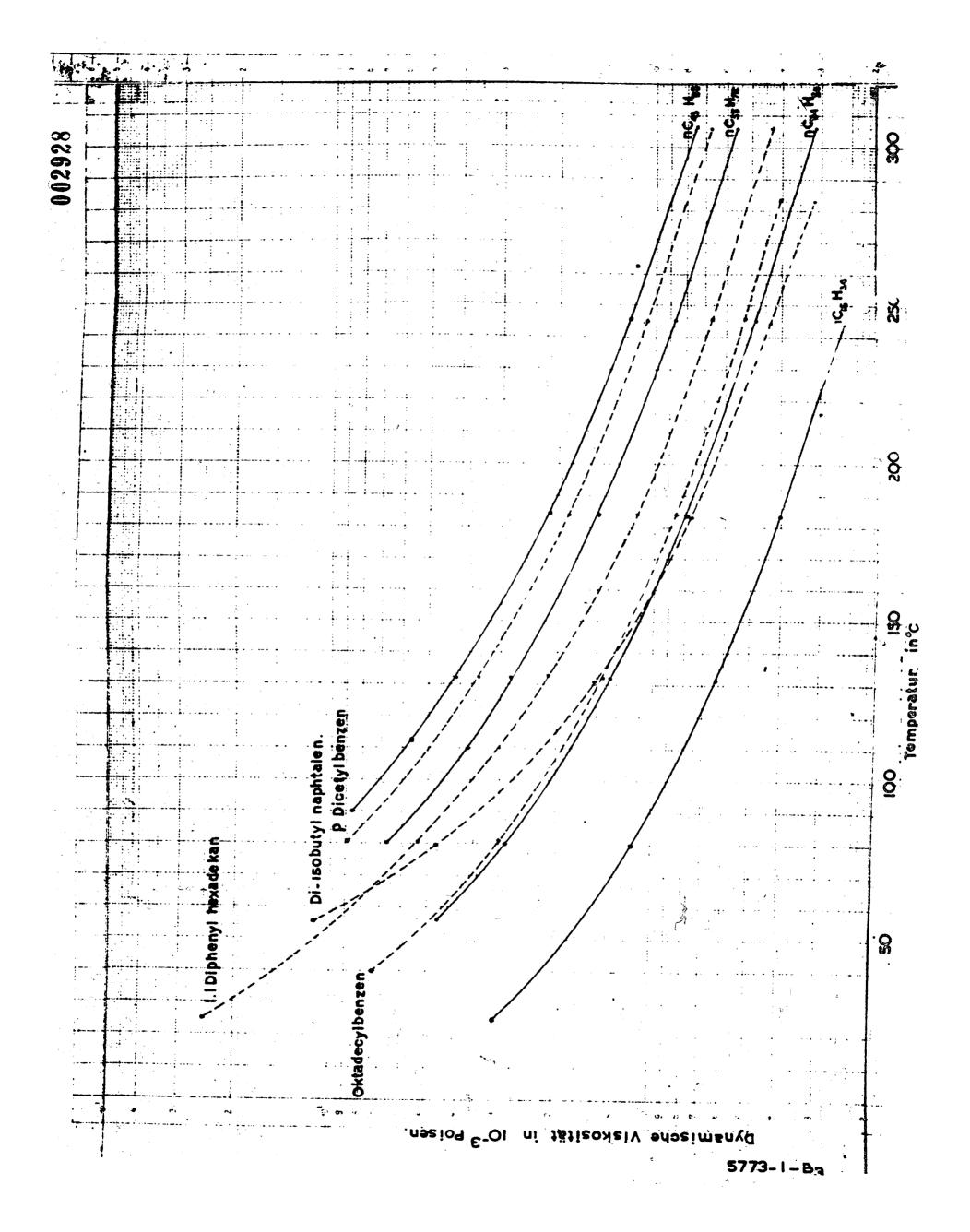
CONCLUSTONS

The branch hydrocarbons 10-nonylnonodecane and 7,12-dimethyl-9,10-dimethyl-10-

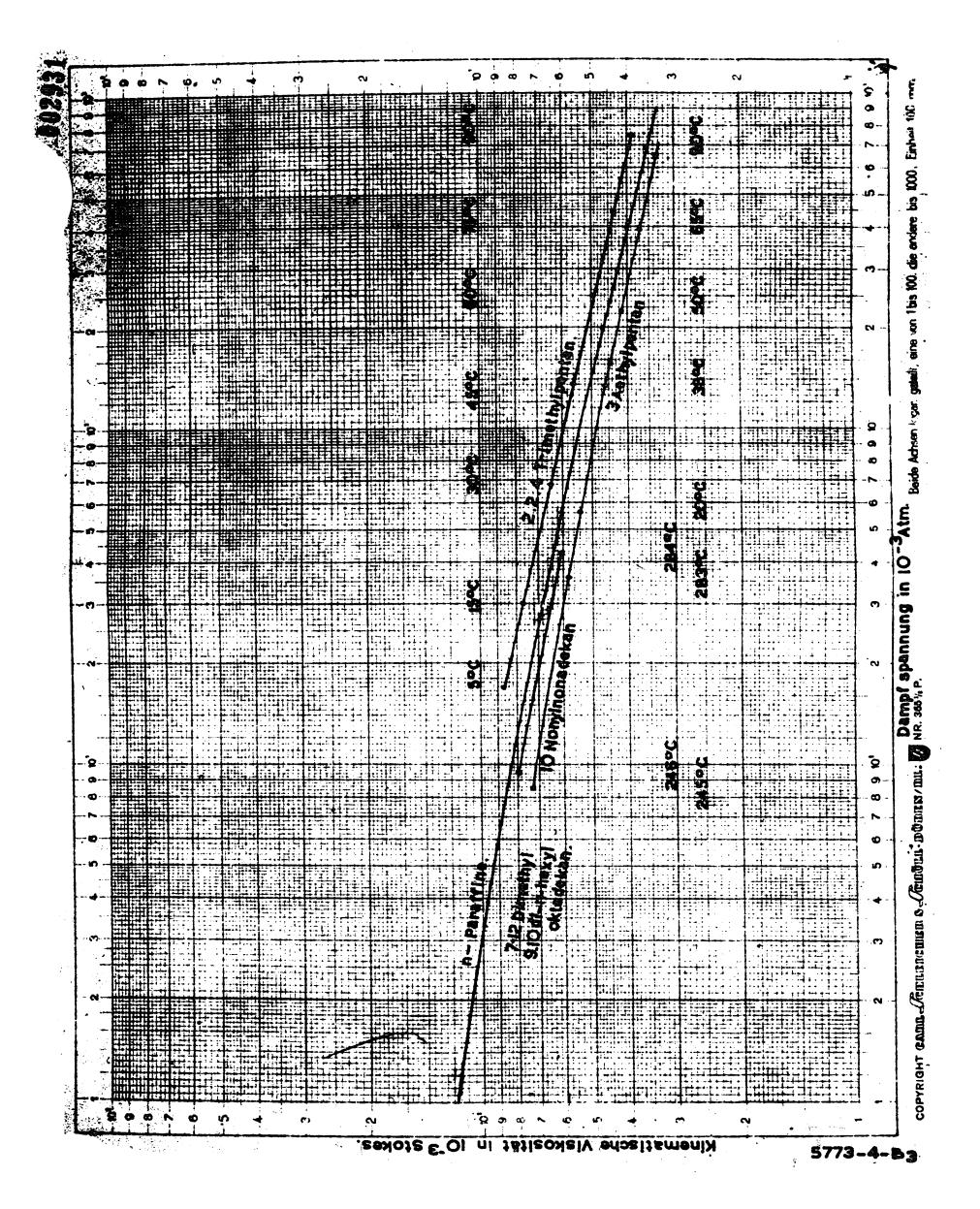
³ Evans, J. Inst. Petr. Techn. 24, 38 (1938)
4 " " " 24, 321 (1938)
5 " " " 24, 537 (1938)

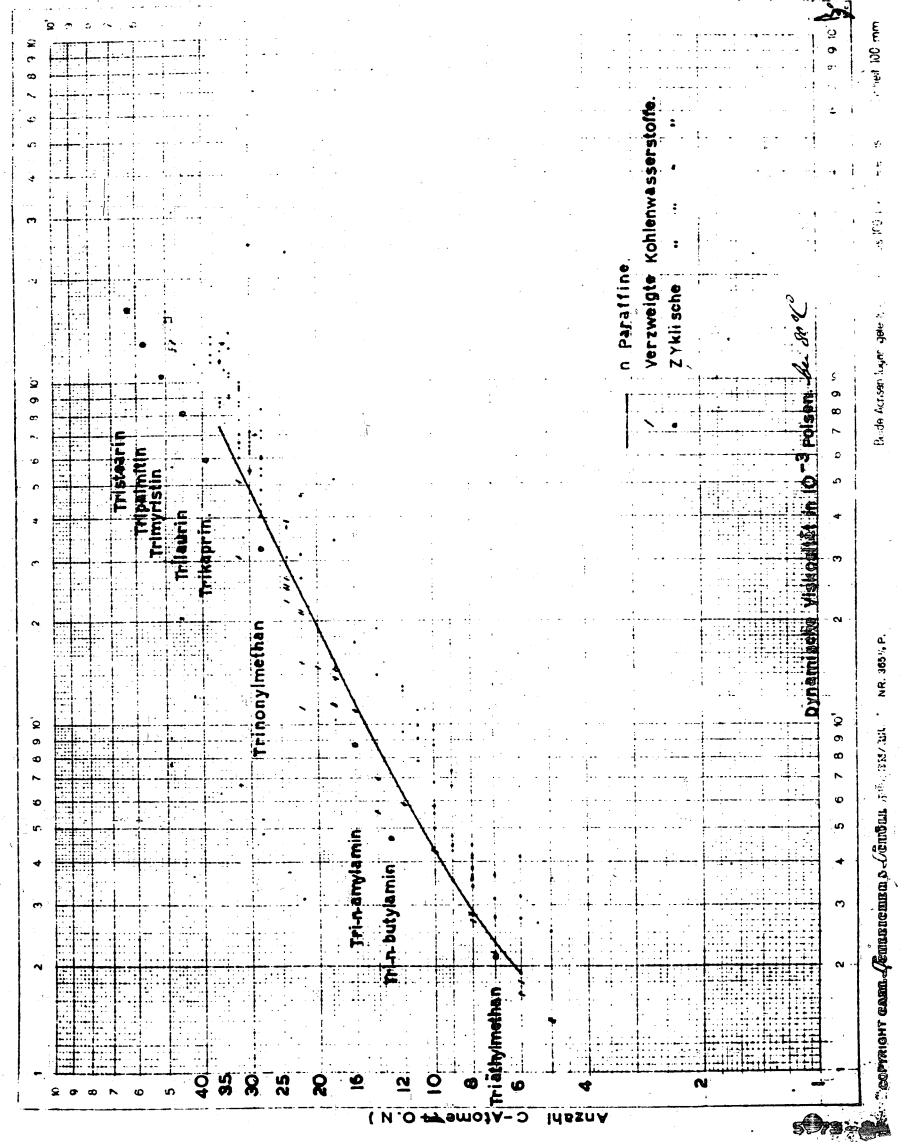
⁵ R. B. Joglekav and H. E. Watson, Journ. Soc. Chem. Ind. 47, 365T (1928)

⁷ E. C. Bingham and L. W. Spooner, J. Rheology 3, 221, (1932).



2930 CONTROL OF STREET AND ADDRESS. : į į • ; ; ;





is not a little higher. So the curve for 10-nonylnonodecane, which at room temperature lies over that of normal $C_{28}H_{58}$, converges at higher temperatures with the curve of n- $C_{28}H_{50}$.

The viscosity of disobutynaphthelene at the higher temperature is higher than expected from a straight line extrapolation of the measurements at lower temperatures on ASTM paper.

2933

From the investigation of 3-ethylpentane and 10-nonylnonodecane, it is probable that hydrocarbons of this structure with similar vapor pressures have similar kinematic viscosities.

PLANS FOR FURTHER INVESTIGATION

There are still a few branched paraffins on hand to be investigated. Meanwhile Dr. Verberg will test Trioctodecylmethane. The viscosity time of these hydrocarbons, if they can possibly be purchased, will be compared with that of the triglycerides.

III-127 29**5**5

INTRODUCTION

Hitherto only viscosity measurements of hydrocarbons at high temperatures have taken place. In this report that follows, first the information about the acid containing substances will be discussed, after that the further treatment of the hydrocarbon information. This further work included the installation of a new gaging thermometer and the small correction that follows, the conversion to round off temperatures and the ordering of a single diagram.

The acid containing substance, whose viscosity will be discussed, is dicetylether. This ether with a melting point of 52.5-53 C. came from the laboratory of Herrn Ir. verhaus. Its viscosity was compared with the viscosity of normal paraffins. In this pemparison only the lower values mentioned in the literature refer to ether.

SUMMARY OF THE EXPERIMENTS

For all the viscosity meansurements an Anschitz thermometer with standard calibrated graduations was used. It had been standardized so that the calibrations had changed very little in the measurements of the past few years. The density and viscosity of the examined substance, based on the new calibrations and corrected to pure grade celsuis, were compiled in a table.

The density was plotted against the temperature in a diagram (Abb. 5800-1-B4), This made a line which deviated only a little from the straight line.

	Tamp. in °C	Dichte in g/cm3	Dyn.Viek. in ap	Kin. Yisk.* in es	Fluidität in poiss-l	Spez. Vol. in em3/g
n-Hexadukan	25	(0,771)	3,07 3,09		***	
C H 16 34	37,8	0,7621		3,98	32,6	1,297
10 54,	80	0,7325	1,161 1,167	1 505	00	
•	132	0,6958	0,634 0,636	1,585 0,911	86,1	1,365
İ	184	0,6573	0,397 0,401	1 '	157,7	1,437
	245	0,610	0,251 0,253	0,604	252 398	1,521 1,639
n. Tetrakosan	56	0,7759	4,63	5.02		•
^C 24 ^H 56 .	80	0,7602	2,886	5,97	21,6	1,289
24 36 .	132	0,7260	1,355	3,80	34,7	1,315
	184	0,6914	0,789	1,866	73,8	1,377
	245	0,6495	0,479	1,141	126,7	1,446
	306	0,6037	0,313	0,757 0,518	209 319	1,540 1,656
n.Pentatria-	80	0,7781				·
kentan	111	· · · · · · · · · · · · · · · · · · ·	6,75 6,82 6,81	8,65	14,86	1,285
	132	0,7587	3,78 3,81	4,98	26,5	1,318
C ₃₅ H ₇₂	184	0,7457	2,765 2,769	5,71	36,2	1,341
	245	0,7130	1,493 1,494 1,493	2,09	67,0	1,403
,	306	0,6744	0,864 0,868 0,863	1,281	115,7	1,485
!		0,6337	0,553 0,554 0,552	0,673	180,8	1,578
. Tritutrakontan	1 1	0,7809	8,63	11,05	11,59	1,281
C H 88	111	0,7676	5,77	7,52	17,55	1,303
	132	0,7542	4,14	5,49	24,2	1,326
	184	0,7224	2,127	2,94	47,0	1,384
	245	0,6849	1,194	1,743	83,8	1,460
·	306	0,6472	0,748	1,156	133,7	1,545
3 Äthylpentan	20	0,6973	0,380	0,545	263	1,434
	37,8	0,6823	0,316	0,463	316	1,466
	50	0,6711	0,280	0,417	357	1,400
•	65	0,6581	C,246	0,374	407	1,520
	80	0,6442	0,215	0,334	465	1,552
10 Nonylnon-	20	0,8085				
dakan	80	0,7693	3,27	4,25	30,6	2:500
	132	, 0,7355	1,427	1,940	70,1	•
·	184	0,7008	0,799	1,140	125,2	1,360 1,427
, j	245	0,6594	0,480	0,728	208	
•	283	(0,634)	0,366	0,577	273	1,517 1,577
7.12 Dimothyl	20	0,8230	39,8	48,4	2,51	
9110 dian. Hoxyl-	50	(0,864)	11,50			1,215
k todukan	8 C	0,7837	4,94	14,36	8,65	1,244
	132	0,7492	1,841	6,30	20,2	1,276
•	184	0,7149	0,948	2,46	54,3	1,335
!	245	0,6735	0,535	1,326 0,794	105,5	1,399
!	203	0,846	6,394		166,9	1,485
j		-,	· · · · · · · · · · · · · · · · · · ·	0,608	254	1;549

	Yomp. Dichte in g/cm3		Dyn.Visk. in ap	Kin. Viek. in oS	Fluidität in poise-1	Spez.Vol. in om3/g	
2 Dimethy:	40	0,7829	8,45	10,79	11,83	1,277	
Dokosan	80	0,7567	3,28	4,33	30,5	1,322	
	132	0,9223	1,489	2,06	67,2	1,364	
	164	0,6884	0,837	1,216	119,5	1,453	
	245	0,6472	0,498	0,769	201	1,545	
	. 283	0,6192	0,379	0,612	264	1,615	
	80	0,6145	9,03	11,09	11,07	1,228	
	132	0,7818	3,50	4,48	28,6	1,279	
	164	6,7491	1,846	2,46	54,2	1,335	
	245	(0,710)	1,060	1,493	94,3	1,408	
	306	0,6714	. 0,675	1,005	148,1	1,489	
· tau kryút anzem	40	(0,645)	7,37	8,71	13,57	1,182	
	во	0,8193	3,06	3,73	32,7	1,221	
	132	0,7844	1,444	1,841	69,5	1,275	
_	184	0,7495	0,850	1,134	117,6	1,334	
	245	0,7085	6,522	0,737	191,6	1,412	
	203	(0,662)	0,405	0,594	247	1,466	
1 Di: '.nyl	, 25	0,9070	34,9	38,5	2,87	1,103	
≠adukin	ં ઇંડ	0,87.2	5,46	6,27	16,32	1,148	
	132	0,8365	2,121	2,54	47,1	1,195	
	184	6,3016	1,136	1,417	68,0	1,248	
	245	c, we	0,666	0,975	150,2	1,314	
) i †	106	0,7165 1	0,431	0,602	232	1,396	
	20	0,∋32 3	-		_	-	
ophtralen :	5	0,9081	11,21	12,34	8,92	1,101	
į	80	C,5914	4,68	5,25	21,4	1,122	
ļ	132	0,8543	1,501	1,757	66,6	1,171	
	194	0,8164	0,759	0,930	131,8	1,225	
	245	: 0,7720	0,432	0,560	231	1,295	
į	233	0,7405	0,315	0,425	317	1,35C	

The reciprocal of the dynamic viscosity, whose fluidity is plotted against the reciprocal of the density is then plotted against the specific volume. According to Batschinkil these would fall in a straight line. That, however, does not apply for hydrocarbons.

It was noticed in this reference that if at the same temperature, yet ascertain and at various pressures (von Wijk and Mitarbeitein 2) the kinematic fluidity was plotted against the specific volume. The hydrocarbons with low molecular weights would give a straight line and the hydrocarbons with high molecular weights would give a curve.

111-130 2958

Recently measurements have been carried out and results obtained for hydrocarbons, now first attention will be given to investigating the acid containing substances namely dicetylether.

The density was measured with the help of a pycnometer of about 1 cm3 with a long calibrated stem, the viscosity was measured with a falling body viscosimeter.

After repair of the steambath with a suitable ground piece; the viscosimeter was calibrated for each measurement the calibration constant was found to be a value of 0.00487, which agreed very well with the earlier found value of 0.00488.

Density and Viscosity for Dicetylether C32H660 (Falling body)

Densi ty	Dyanmic Viscosity	Kinematic Viscosity			
0.8067 0.7908 0.7576 0.7259 0.6842 0.6586	9.04 c.p. 5.26 2.282 1.265 0.748 0.571	11.21 c.s. 6.65 3.01 1.747 1.083 0.867			
After 0.8073 0.7912 0.7577 0.7240 0.6842	rounding off the temperatures The converted values 9.24 5.33 2.238 1.266 0.748 0.569	ture 11,45 6,74 3,02 1,749 1,093 0,864			
	0.8067 0.7908 0.7576 0.7239 0.6842 0.6586 After 0.8073 0.7912 0.7577	0.8067 9.04 c.p. 0.7908 5.26 0.7576 2.282 0.7239 1.265 0.6842 0.748 0.6586 0.571 After rounding off the tempera The converted values 0.8073 9.24 0.7912 5.33 0.7577 2.238 0.7240 1.266			

¹ A. Batschinki, Z, physik. chem. 1913, 84, 63 2 W. R. von Wijk, c.s. Physica 1940, 7, 45

The diagram (Abb 5380-3-B3) compares the viscosity time of dicetyether with the viscosity time of normal paraffins. For n-hexadecane the higher paraffins, the data from this report was used; for the lower paraffins, the viscosity values from Evans tables were employed. Also in the figure are the viscosity values for di-n-amyl ether and di-n-butyl ether (Bingham and Spooner2) and from Von Thorpe and Rodger (3,4), the viscosity values for di-n-propyl ether, di-ethyl ether and ethyl propyl ether are plotted.

四-131 2959

Timmermans and others (5,6) examined various ethers at 15 and 30 C found for di-n-amyl ether 1.183 and 0.992 c.p.; for di-n-butyl ether 0.741 and 0.602 c.p., for di-n-propyl ether 0.448 and 0.376 c.p.; for diethylether 0.279 and 0.247 c.p. The agreement with the first mentioned values is good, with the exception of the yield of the diethylethers. For ethylpropylether Hilditch and Dunstan (7) with 0,3393 c.p. at 25 C found a higher viscosity than Thorpe and Rodger.

From the Figure (Abb. 5800-3-B3) it is clearly proved that temperature slope of the viscosity for the ethers with branched chains is about the same as that for normal paraffins. (Meanwhile the lower ether viscosities are more than the paraffins with a carbon atom.) Di-n-butylether and di-n-amylether are somewhat less viscous and dicetylether has about the same viscosity as the paraffin with the same number of carbon atoms.

The ethers had lower melting points than the paraffins with same number of carbon atoms for example, di-n-amyl ether -69 C as compared with n decane -32 C and dicetylether about 53 C, again n C32H66 about 70 C.

CONCLUSION

The density of the earlier investigated hydrocarbons follows almost a straight line with the temperature. The fluidity of the same hydrocarbons was plotted against the specific volume, as recommended by Batshinskii, forming lines, which distinctly deviate from the straight line。

The temperature slope of the viscosity for the straight chain ethers is nearly the same as for the viscosity of the normal paraffins.

PLANS FOR FURTHER INVESTIGATION

The hydrocarbons concerned must be furnished finally by several synthesis. Dr. Verberg has investigated the existing progrem with good prospects of success, This synthesis of aliphatic hydrocarbons, with a number of carbon atoms (if possible, consecutive) without hydrogen on account of double or triple bonds, can be added.

^{1.} Evans, J.I.P.T. 24, 58 (1938)

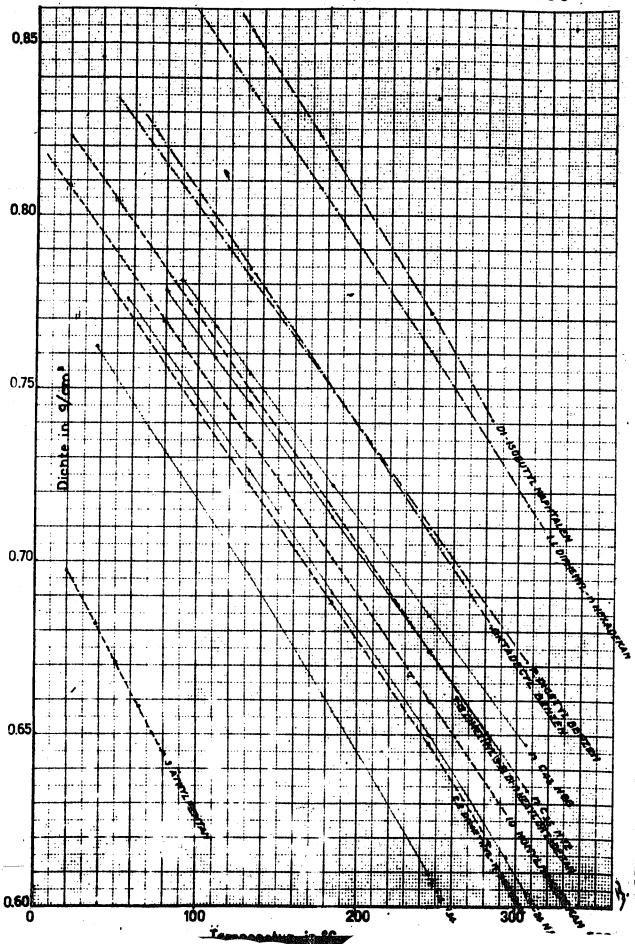
^{2.} Bingham and Spooner, Journ. Rhenology, 3, 221 (1932)

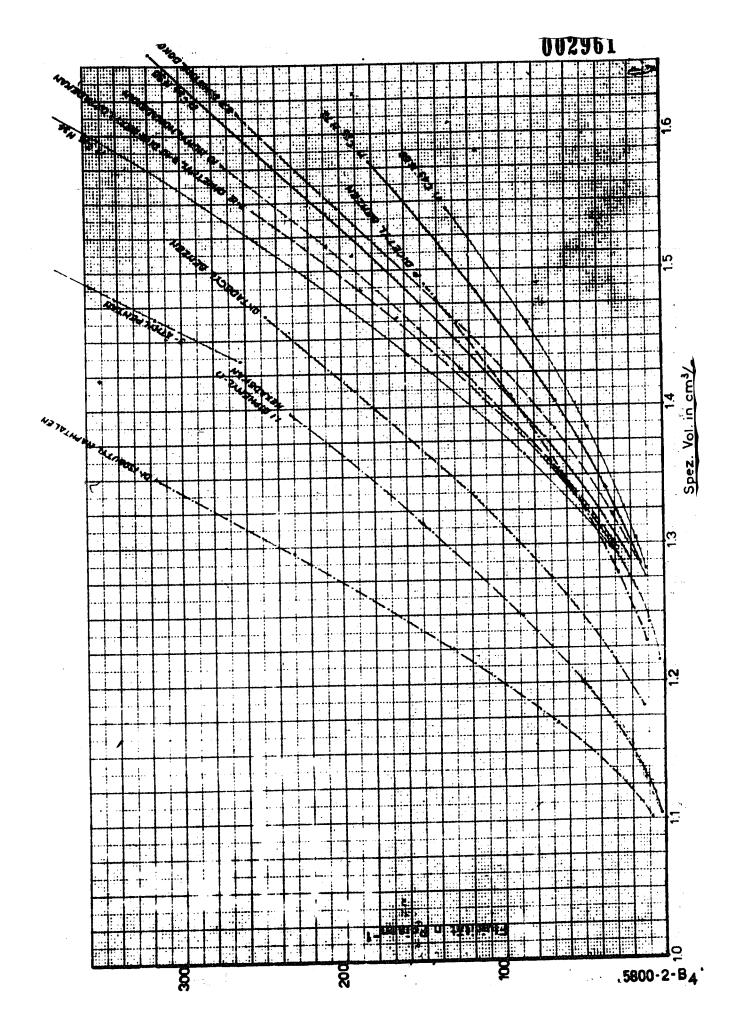
^{3.} Thorps and Rodger, Phil. Trans. 185 A, 397 (1894) 4. Thorpe and Rodger, Phil. Trans. 189 A, 71 (1897)

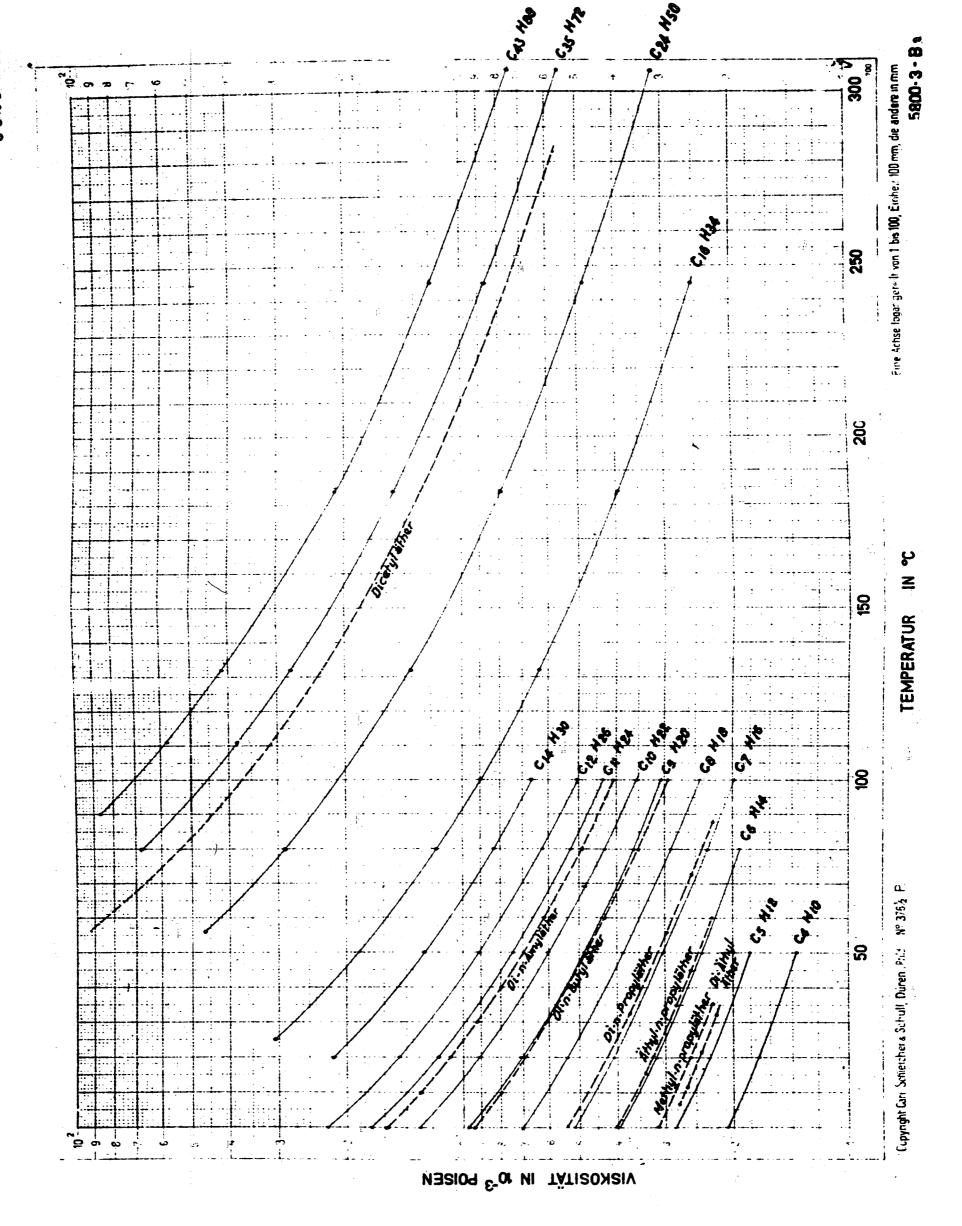
^{5.} J. Timmermans and F. Martin, Jour. chim. phys. 25, 411, (1928)

^{6.} J. Timmermans and Hennant Roland, Jour. chim phys. 27, 401 (1930) 7. Hilditch and Dunstan, 2t. Elek. Chem. 17, 929 (1911).









In the meentime the investigation of substances, which contain not only carbon and hydrogen but also acid, will be continued. Another determination of the vapor pressure curve for dicetyl ether will be worked on.

2975

INTRODUCTION

The preceding report included the accumulated information on viscosity measurements for hydrocarbons. This information has been greatly enlarged upon. The logarithm of the viscosity was plotted against the reciprocal of the value for the temperature. For the normal paraffins the deviation from the straight line is not very large. This led us to interpolate the viscosity of the paraffins (with help of a method of small quadratic) calculated from the linear relation between the logarithms of the viscosity and the reciprocal of the value of the absolute temperature.

SUMMARY OF THE EXPERIMENT

The viscosity of the twelve investigated hydrocarbons was plotted on hyperbole-logarithm paper. From drawing 5826-1-B4 it is evident that logarithms of the viscosity plotted against the reciprocal values of the temperatures give no straight lines in general. The viscosity time for hydrocarbons over a large temperature range cannot be described with the formula N = a / b/t. For the normal paraffins the deviation remains such that the formula, complete with a deviation curve, is useful for interpolation purposes.

Using the method of the small quadratic) the following viscosities were computed for n-hexadecene, n-tetrucosane, n pentatriacontane and n-tritetracontane.

$$n - C_{16}H_{34}$$
 $\log \eta = 2.0663 \text{ / } 758.26/T$
 $n - C_{24}H_{50}$ $\log \eta = .2.0316 \text{ / } 882.81/T$
 $n - C_{35}H_{72}$ $\log \eta = .1.9435$ $971.95/T$
 $n - C_{45}H_{88}$ $\log \eta = .1.9063$ $1026.46/T$

The differences between the computed values for $\log \eta$ and the experimental values are plotted against the temperature in drawing 5826-2-B4. With the help of the formula and the accompanying deviation curve were the values (of $\log \eta$ and also η) for rounding off temperatures computed.

The figures enclosed in parenthesis in the table are extrapolation from a straight line, whose numbers however were obtained by interpolation. In diagram 5826-3-B2 the logarithms of the viscosities of n-hexadecane, n-tetracosane, and n-pentatricontane and n-tritetracontane are plotted against the logarithms of their molecular weights. The measuring points for like emperatures are connected by a straight line. The handbook of Engler and Höfer states and Uhbelohde and Aghte agree that the viscosities

TABELLE.

	n, Tetrakosan n, F		n, Po	entatrickonten		n, Tritotrakontan		
eS log	og T) In co	in a	lcg T	Then o	7 7 18	log N	7) in op	n in os
5)		- 1	-do		†		 	†
0	i]	* *	- [i	ł	1	1
6	i	!!		i		ļ	1	1
7 0.7210	210 (5.25)	(6.74)		İ]			l
0 0,629(290 4.26	5.50		ł	i .	•	i	I
17 0.5418	418 3.48	4,54		i	ł	!	1	!
B7 0.460¢	606 2.89	3.80	0.8284	6.74	8,66	!	ł	1
03 0.3876	876 2,44		0.7417	5.52	7.15	0.9363	8.63	11,05
53 0.3199	199 2.09	2.80	0,6608	4,58	5,99	0.8504	7.09	9.15
27 0, 2566	569 1.806	2.44	0. 5853	3,85	5.07	0.7690	5.87	7,64
18 (0. 1980	980 1.578	2.15	0,5173	3.29	4.37	0.6973	4,98	6,54
27 0.1428	428 1.389	1,908	0.4541	2,65	3.61	0,6302	4,27	5,65
68 0.6912	912 1,234	1,711	0.3945	2,48	3.35	0.5668	3.69	4,92
2 0.0430	430 1.104	1.546	0.3391	2,18	2.97	0,5071	3.21	4,32
20 0.9974	974-1 0.994	1.406	0, 2870	1.936	2.66	0,4508	2.82	3.83
9 0.9542	542 0 .90 0	1.284	0,2384	1,752	2.40	0. 3975	2,50	3,42
0,9132	132 0.819	1, 180	0, 1924	1,558	2, 18	0,3471	2.22	3,06
9 0.8742	742 0,749	1,090	0,1485	1.408	1,986	G, 2998	1,994	2,78
0.8562	62 0.686	1.007	0, 1067	1.278	1.818	0.2552	1.600	2,53
0,7997	97 0.631	0.936	0.0665	1.165		0.2127	1,632	2,31
6 0.7644	44 0.581	0.871	0.0279	1.066	1,545	0,1723	1,487	2,12
9 0.7301	01 0.537	0,814	.9906-1	.979		0.1334	1.360	1.960
3 0.6967	67 0.497	0.761	0.9543	.900		0.0955	1.246	1,811
1) 0.6641	1 :		9196	.831		0.6591	1,146	1,680
0,6323	, ,		.8859	.769		0.0235	1,056	1.564
0.6014		· 1	1.8534	.714		0.9093-1		1.459
0.5715		- 1		i				1.362
1	1		•	· . •	1			1.275
:			- 1					1.200
•	0.57 C.54		0.5715 0.373 0.598 0 C.5418 C.346 0.564 0	0.5715 0.373 0.598 0.8216 C.5418 C.348 0.564 0.7907	0.5715 0.373 0.598 0.8216 .663 c.5418 c.346 0.564 0.7907 .618	0.5715 0.373 0.598 0.8216 .663 1.017 c.5418 c.346 0.564 0.7907 .618 0.958	0.5715 0.373 0.598 0.8216 .663 1.017 0.9559 C.5418 C.348 0.564 0.7907 .618 0.958 0.9235	0.5715 0.373 0.598 0.8216 .663 1.017 0.9559 0.905 C.5418 C.348 0.564 0.7907 .618 0.958 0.9235 0.638

Die in der Tabelle eingeklammerten Ziffern sind durch Extrapolation über einige Greden, die übrigen Ziffern lurch Interpolation erhalten. Im Diagramm 5826 - 3 - B 2 sind die Legarithmen der Viskositäten von n.Hexadokan, n.Tetrakosan, n.Péntatriakontan und n.Tritetrakontan gegen die Legarithmen der Molekulargewichte aufgetragen worden. Die Messpunkte bei gleicher Temperatur sind durch Geraden verbunden. Die im Handbuch von Engler und Höfer ') angegebenen und von Ubbelohde und Aghte herrührenden Viskositäten von n.Tetradekan und n.Oktadekan liegen nicht auf diesen Geraden, die viel rezenteren Messergebnisse von Evans !') für n.Dodekan aber wohl. Aus den Tabellen von Evans ist seiter ersichtlich, dass die niedrigen Paraffinkohlenwasserstoffe abweichen. Obwohl natürlich nicht fiststeht, dass die Viskositäten höherer Homologen wohl auf den Geraden liegen werden haben wir diese doch nach

^{&#}x27;) Engler-Höfer, Das Erdöl 191/, Vol. I, Soite 33.
'') E.B. Evans, J.I.P.T. 24 (1950), 38.

of n-tetradecane, n-octadecane do lie on a straight line and according to recent measurements of Evens 1 the same applies for n-dodecane. From the tables of Evens it is also evident that the lower paraffin hydrocarbons may. Although it has not been established that the viscosities of the higher homologs probably lie on a straight line, we have drawn these out for the higher molecular weights, because we could use that diagram for the purpose of valuating the viscosity time of other substances.

CONCLUSION

Through the most technical research we had found that for the normal paraffins of dodecane and tritetracontane there exists a linear association between viscosity and molecular weight.

PLANS FOR FURTHER INVESTIGATION

The viscosity time for various substances will be estimated with the help of drawing 5826 3-B2. The investigation of several esters, which has already started, will be finished.