

EBULLITION OF ORGANIC LIQUIDS OF HIGH MOLECULAR WEIGHT

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Many communications deal with the vapour tension of organic liquids of high molecular weights, e.g. with that of di-esters, petroleum products, and silicones, but the number of papers discussing the stability of these substances under various stresses is rather limited.

MURPHY et al. [1] and MURPHY and RAVNER [2] placed the substances under investigation into glass cells kept in a thermostat and allowed oxygen at atmospheric pressure to bubble through them at various temperatures. In the case of silicones, decomposition was ascertained by changes in the infrared spectra, or by changes of viscosity values. In the case of di-esters, after oxygen treatment over a pre-determined time, the overall uptake of oxygen was noted and the form, i.e. whether as peroxide, carboxyl, or carbon dioxide, the oxygen was fixed by the substance.

LATHAM, POWER and DENIS [3] operated oil-diffusion pumps with various substances and allowed, for a certain period, air at atmospheric pressure to enter the hot pump which was then isolated again from the atmosphere. The basis of comparison was the number of air-inflow cycles tolerated by the substance before it became unsuitable for the operation of the pump.

REICH [4] has demonstrated exactly the slight decomposition of substances of low boiling points in diffusion pumps at low pressures. His process was as follows. The pump orifice, vacuum gauge, and evacuated space were placed into a thermostat-jacket, and the final vacuum was measured at various temperatures between the 0° and 100 °C limits. With $\log p$ values plotted as a function of $1/T$, the former ran parallel with, but above, the vapour tension curves when the orifice temperatures were higher; at lower temperatures this progress in parallel changed, the final vacuum curve tended to turn towards higher pressure values.

The fact that final vacuum curves run above tension curves can be explained thereby that vacuum gauges, and ionization-manometers are calibrated to dry air, whereas oil vapours dissociate much more easily than do air molecules; with oil vapours the gauges indicate pressure values thirteen to

fourteen times greater than do gauges with dry air at pressures equal to those of oil vapours.

At lower temperatures the vacuum curve runs above the lengthened high temperature section, i.e. there is a deviation of the actual tension values from the values arrived at by the extrapolation of high temperature values according to the Clausius—Clapeyron equation. This deviation cannot be caused but by the decomposition products of the oils kept boiling in the pump.

Based upon REICH's experiments, BÄHLER and NÖLLER [5] constructed fractionation pumps for the several types of oil, in which no sign of the tension-difference due to decomposition products, as just mentioned, was observed at orifice temperatures around 20 °C. The principle of fractionation is as follows. The several nozzles of the diffusion pump are fed from separate vapour chambers, the substance loses the more volatile components and decomposition products of the operating fluid when boiled below the nozzles at lower positions, the uppermost nozzle that produces high vacuum receives only oil vapours free from volatile components and decomposition products.

In a former communication [6], the author has stated that the material of which pumps are made, or the catalytic action of that material, also the geometrical shape of the pump-walls, in part affect the decomposition of such substances, at low pressure ebullition. The vortices generated in the vapour phase enhance decomposition, these vortices being caused, in a decisive measure, by the shape of the vessel and of the vapour manifold of the pump. In this paper mention is made also of the findings that primary decomposition of high-molecular weight substances in diffusion pumps is due to slight oxidation, to double-bond formation through dehydrogenation, or to fixation of oxygen in a form that is liable to enter further reactions. In this phase, the basic substance, i.e. the high molecular weight organic liquid suffers but small degradation; the molecules that participated in some chemical reaction do not widely differ in their vapour tension values from that of the intact molecules. The decomposition products are small: either hydrogen or water is split off and carried away by the pump.

In a second phase of decomposition, fractions with groups capable of further reaction are condensed to giant molecules in the course of polymerization or condensation reactions, and tar-like products result.

In a third phase of decomposition these tar-like products are cracked. This cracking produces the molecules which, though bulky, are smaller than the parent molecules, and are not discharged by the pump any more, thus lower the tension and spoil the final vacuum.

The decompositions occurring during ebullition in oil diffusion pumps have been investigated also by REICH and NÖLLER [7] who used an Omegatron, i.e. a small, radio-frequency type mass spectrometer, for this purpose. This

instrument was suitable to register with it the mass spectra in spaces at very low pressures of 10^{-5} to 10^{-6} torr. Species found in the evacuated space, and registered alongside with oxygen and nitrogen left behind from the air, were hydrogen, water vapour, carbon dioxide, methane, and carbon compounds in the C_3 , C_4 or even higher mass number range.

As shown by this review, research is mostly concerned with the decomposition processes taking place in oil diffusion pumps. Experiments have not yet furnished exact and absolute values, the published data refer only to the apparatus used for their measurement.

The aim the author set himself was to develop a method, more exact than those known up to now, for the investigation of the stability of high molecular weight organic liquids, since in the course of the preparation of such at least one distillation process is inevitable. The utilization of such liquids involves, in most of the cases, their being kept at ebullition. It is of interest to note that in the quite extensive literature we have scanned no mention is made of a method which would serve the exact definition of the highest related pair of one tension and one temperature value at which a compound can be subjected to boiling without decomposition. This prompted us to attempt the elaboration of such a method. Since this should be a simple and comparatively rapid one, from among the indications of decomposition suitable at all, e.g. change of spectrum, or viscosity, etc., we selected the changes observable in the vapour tension curve.

Thus our method could be reduced in essence to vapour tension measurements in the course of ebullition. In a suitable apparatus, the boiling point of the liquids was measured at various pressures, according to Roloff's method, and the logarithm of vapour tension was plotted as a function of $\frac{1}{T}$.

Boiling was started at a given pressure, say 4 mm Hg, and proceeded as follows. Boiling point was noted at 4 mm Hg, then at 5 mm Hg. Then pressure was re-adjusted to 4 mm Hg, and boiling points noted at this pressure, at 5 mm Hg, and at 6 mm Hg. After re-adjusting the pressure to 4 mm Hg again, boiling points were noted at this pressure, at 5, 6 and 7 mm Hg, successively. Thus, after each increment of one mm Hg, pressure was re-adjusted to the original starting value and a new series of measurements was begun and carried to a pressure one mm Hg higher than the final value of the preceding series.

As long as the substance under investigation did not decompose to such a degree as notably to change the vapour tension, the vapour tension curves registered in the several series coincided. However, a pair made up of one tension and one temperature value was found for each of the substances tested after which pair the repetition of boiling, begun under the original pressure, did not cause boiling at the original temperature but at a lower one

and from this point on the vapour tension curve for the further pressure values ran above the preceding, original tension curve.

At such recurrent registrations of the vapour tension curve, a period of about 12 minutes was needed to reach the first boiling point, about half a minute was needed to adjust the pressure by a unit increment and 2 minutes to reach a boiling point at the new pressure value, finally another two and a half minutes for the steady indication of the thermometer. Return to the

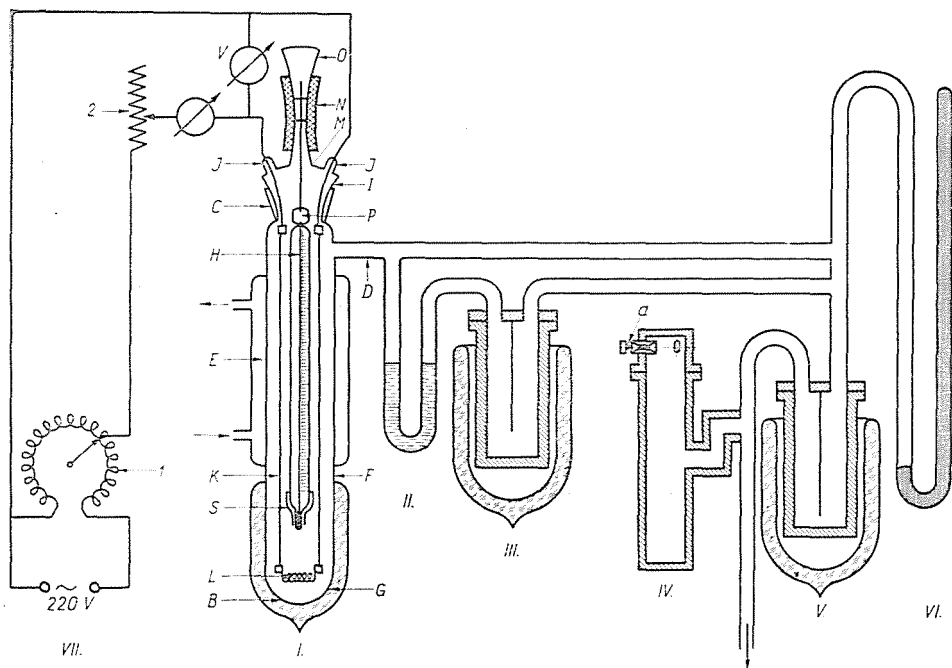


Fig. 1

original pressure required one to four minutes, and the higher the pressure from where to return the more slowly has this return to be effected.

This related pair of a temperature and a tension value has been designated the decomposition boiling point of the substance in question. The pressure under which a substance can be boiled without a notable change of its vapour tension is one mm Hg lower than the pressure value at the decomposition boiling point.

The most important part of our apparatus (Fig. 1) is the boiler (I) the present form of which being the result of successive modifications over years of HICKMAN's [8] tensiometer-hypsometer vessel.

The boiler-space itself is within a hard-glass cylinder with a hemispherical bottom (B), and a wide neck (C) carrying a conical ground glass joint. Below this conical joint a side-arm (D), with a conical end, leads to the vacuum

pump. Below this side arm a jacket (*E*) for the coolant (water) is sealed on, this jacket covers the boiler along two thirds of its length from the top. From the lower, not jacketed third part one section (*F*) of a few centimeters is left bare. The bottom of the boiler, for about one fourth of its length from the bottom upwards is set into a thermo-insulating evacuated jacket (*G*).

The length of the boiler tube is chosen to accommodate the available thermometer (*H*), the measuring range of which extends to 350 °C, so that the upper end of its scale lies within the straight section of the cooling jacket and that its mercury bulb, to protect it against splashes, be placed at least 3 cm above the level of the liquid under test, this liquid being not more than 50 cm³.

The upper end of the thermo-insulation jacket (*G*) sealed off at a pressure less than 10⁻³ mm Hg, and surrounding the bottom of the boiler, reaches 2. . . 3 cm above the upper part of the mercury bulb of the thermometer.

The 2. . . 3 cm bare section (*F*) of the boiler tube, between the cooling jacket and the evacuated jacket, is necessary for the preservation of the boiler tube wall, so that the wall of the boiler bottom heated to several hundred centigrades should not be in immediate contact with that part of the boiler wall which is kept at tap-water temperature.

The evacuated jacket reaches above the mercury bulb of the thermometer in order to permit the reading of the temperatures of the vapour just leaving the liquid, i.e. before the vapours begin to cool.

The entire length of the thermometer scale is within the straight section of the cooling jacket, viewing of the scale through a curved part of the jacket glass would make the reading of the temperature difficult and inaccurate.

Into the upper conical joint (*C*) a hollow ground-glass stopper (*I*) is fitted. This serves not only for closure of the boiler but also as the support of accessories. On the top of this stopper two thick molybdenum wires (*J*) are sealed in. These hold the heating element and provide electric contact. To these comparatively shorter lengths of molybdenum wires two equally thick rigid molybdenum wires (*K*) are fastened by screws, these wires reach down to 2 cm above the bottom of the boiler. Between these two wires (*K*) the immersion heater consisting of a thin tungsten wire coil (*L*) is suspended. Within the glass stopper and the boiler the molybdenum wires are electrically insulated by fire-clay beads strung up along the whole length of these wires. The cold resistance of the heating coil at 20 °C is 31 ohms.

At the centre of the top-plate of the stopper (*I*) a comparatively long, slightly tapered glass tube (*M*) is sealed, the thermometer is hung through this as follows. A length of rubber vacuum tubing (*N*) is slipped on to the tube (*M*) and the upper end of the rubber tube is closed with a conical metal stopper (*O*). From its narrow end a long screw-hole is bored upwards into this metal stopper. To the thermometer a metal cap (*P*) is cemented with Araldite, from the cap a long thin screw-rod (*R*) sticks out which fits the screw-hole in the

metal stopper (*O*). Thus, partly through a variation of the length of the rubber tubing (*N*), partly by the variation of the depth the screw-rod (*R*) is turned into the metal stopper (*O*), the position of the thermometer in the boiler tube can be adjusted as necessary.

To permit a rapid settling of the thermometer, a small aluminium funnel (*S*) is fastened to the mercury bulb. The stem of this funnel is punctured and slit so that the liquid condensing within the funnel should run over the mercury bulb and so back into the liquid.

As this description and the Figure show, this apparatus is a re-boiler with immersion heating, which functions also as a reflux condenser.

The electric heating unit (*VII*) is constructed as follows. The 220 V mains is connected to the two terminals of a toroidal coil (1). The sliding contact is connected to one of the poles of a slide rheostat (2) with a peak resistance of 50 ohms, and the sliding contact of this is connected to one of the poles of the heating coil.

The sample liquids of about 50 cm³ were made to boil with a current of about 20 V and 4...45 Amp, i.e. with an input of about 80...100 W.

Through side-arm (*D*) connexion to the vacuum system is established. In this system an U-tube manometer (*II*) filled with an oil of 0.9811 g/cm³ density is inserted, one of its arms opening directly on the suction line (*D*), the other arm leading to a freeze trap (*III*) filled with an acetone + dry ice mixture, this freeze-trap, in turn, being connected to the suction line. The U-tube manometer proved suitable to indicate the presence of volatile decomposition products which exist in the form of gases at tap-water temperature and in the pressure range employed but condense to liquids at -80 °C, if the partial pressure of such a component reaches the limit of sensitivity of the U-tube manometer which is one mm oil, i.e. 0.072 mm Hg. In the course of our investigations no indication by this manometer was ever noticed.

Apart from the U-tube manometer, this vacuum system includes a sealed-off full-length mercury manometer (*VI*) and another freeze-trap (*V*) before leading to the pumping system. This consists of a buffer-tank (*IV*) carrying on its top three needle valves (*a*) constructed here, for fine regulation, and this buffer tank is connected to a two stage rotation pump, type Tungsram Bp-200.

Pressure was maintained under dynamic conditions, meaning that during suction the selected pressure was assured by regulation through the needle valves. With any of the needle valves fully open a maximum pressure of about 16...18 mm Hg could be attained. Of course, with all the needle valves closed this pressure was appreciably lower than 1 mm Hg, since the final vacuum of the pump applied is 0.009 mm Hg.

Thus, utilizing the three valves, pressure could be regulated accurately and continuously from values less than 0.1 up to 50 mm Hg.

As mentioned, for the measurement of pressure within the system a sealed mercury manometer was used, this could be read to an accuracy of 0.5 mm Hg. Unfavourable experiences in the past have made us decide against the use of an oil manometer though, in principle, this is much more accurate but also rather unreliable in practice.

For the completeness of description it should be mentioned that the rubber gaskets were made of pararubber with low sulphur content, that all the joints were lubricated with Dow Corning high vacuum silicon grease. The scale of the thermometer was divided into centigrade units, 0.5 °C was the accuracy of the readings.

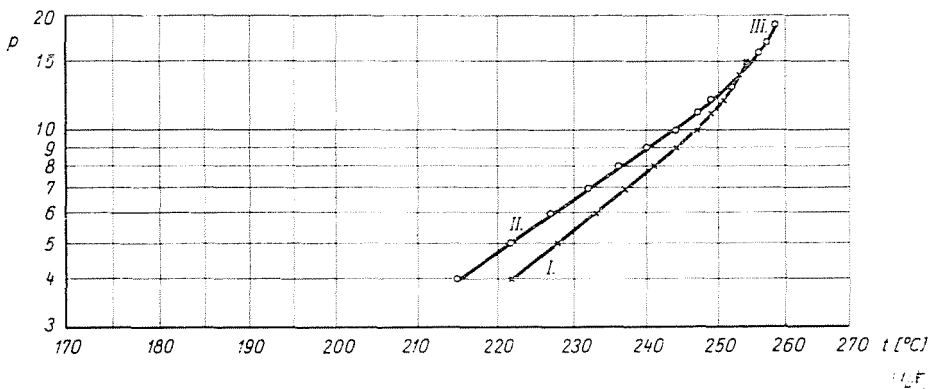


Fig. 2

Between the several series of experiments the apparatus was cleaned carefully: vessel, fire-clay beads, molybdenum wires, tungsten coil, thermometer and its small funnel, and screw-rod were washed first with xylene, then with industrial spirit, and last with ethanol; following this the glass parts were dried in an oven till perfectly odourless, the metal parts and fire-clay beads were heated to incandescence.

In the apparatus just described, the boiling decomposition point of several high-molecular organic liquids was determined according to the method mentioned.

In the several Figures, curve (I) is the vapour tension curve plotted on the basis of recurrent boiling of the non-decomposed substance, curves II and III are vapour tension curves plotted non-recurrently but continuously, for the decomposed substance.

Measurements were made with the following substances:

a) A preparation [10] obtained by a so-called mild distillation process between 170...175 °C. from steam turbine oil. In essence this is an Apiezon-type vacuum oil on naphthene basis prepared in our laboratory. It is a very

pure vacuum oil grade product. Its decomposition began at 13 mm Hg pressure and a boiling point of 252 °C (Fig. 2).

b) Di-2-ethylhexylphthalate. Received from the Research Institute of the Organic Chemical Industry, not vacuum oil grade, with a high (0.21 mg

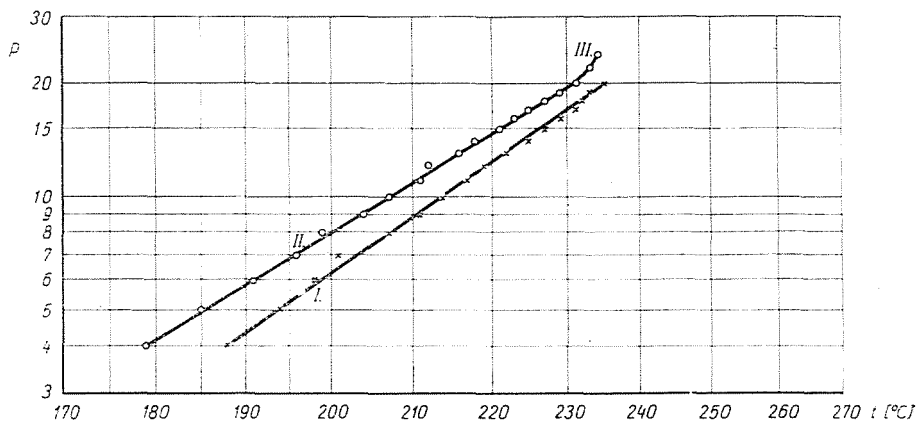


Fig. 3

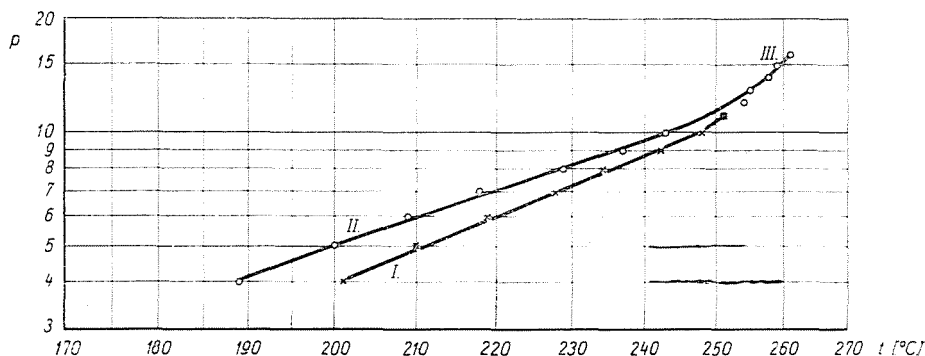


Fig. 4

KOH/g) acid number. Decomposition was noted at 235 °C and 20 mm Hg. Increasing the pressure and the temperature to 151 mm Hg and 312 °C, respectively, phthalic anhydride separates by sublimation and the boiling point falls quickly to 268 °C (Fig. 3).

c) Di-2-ethylhexylsebacate. Received from the Research Institute of the Organic Chemical Industry; not vacuum oil grade, with a high (0.1 mg KOH/g) acid number. Decomposition at a boiling point of 251 °C and under 11 mm Hg pressure. Increasing the pressure, the boiling point begins to oscillate between 250 and 262 °C at a pressure of 18 mm Hg, whereas at 16 mm Hg it stood at 268 °C (Fig. 4).

d) Dioxo-*iso*-octylphthalate (from an alcohol produced by oxo synthesis). Received from the Research Institute of the Organic Chemical Industry. Not vacuum oil grade, with a high acid number. Could not be tested in our apparatus since at ebullition under 4 mm Hg pressure its boiling point changed

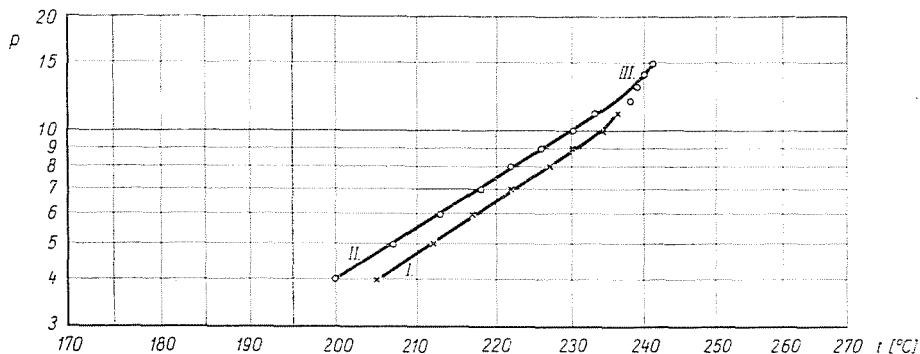


Fig. 5

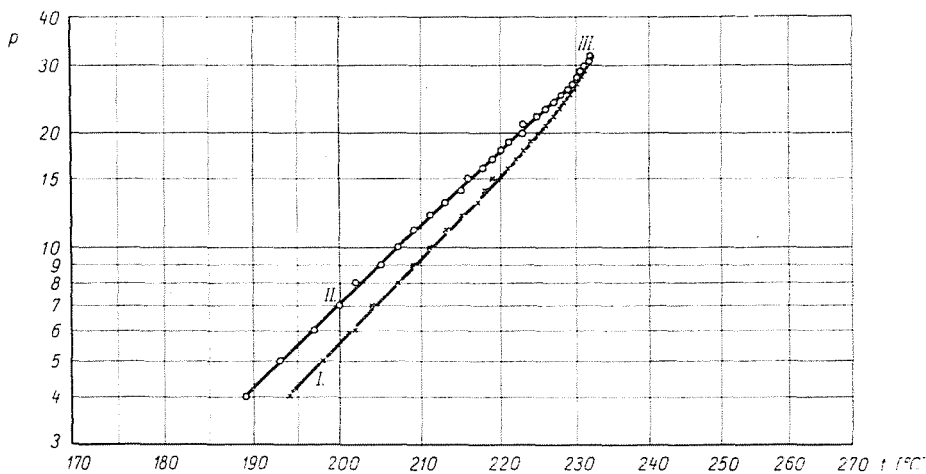


Fig. 6

constantly. The highest value that could be noted was a boiling point 262 °C at 5 mm Hg, this fell within a short time to 214...216 °C and this did not rise even after further increase of pressure, but oscillated within the temperatures mentioned. The liquid, originally as clear as water, turned green in the course of boiling.

e) Dioxo-*iso*-octylsebacate (from an alcohol produced by oxo synthesis). Received from the Research Institute of the Organic Chemical Industry. Not vacuum oil grade, with a high acid number. Its decomposition point is at 10

mm Hg pressure and 230 °C temperature. At a higher pressure, 14 mm Hg, its boiling point oscillates between 232 and 240 °C (Fig. 5).

f) Di-butylsebacate. Has been produced, around 1955, by the Albertfalva Chemical Co. This is a quite pure, vacuum oil grade product. Its decomposition occurs under a pressure of 29 mm Hg at a boiling point of 231 °C (Fig. 6).

g) Silicone oil, type D.C. 702, vacuum oil grade. It decomposes under a pressure of 52 mm Hg and at boiling point 266 °C (Fig. 7).

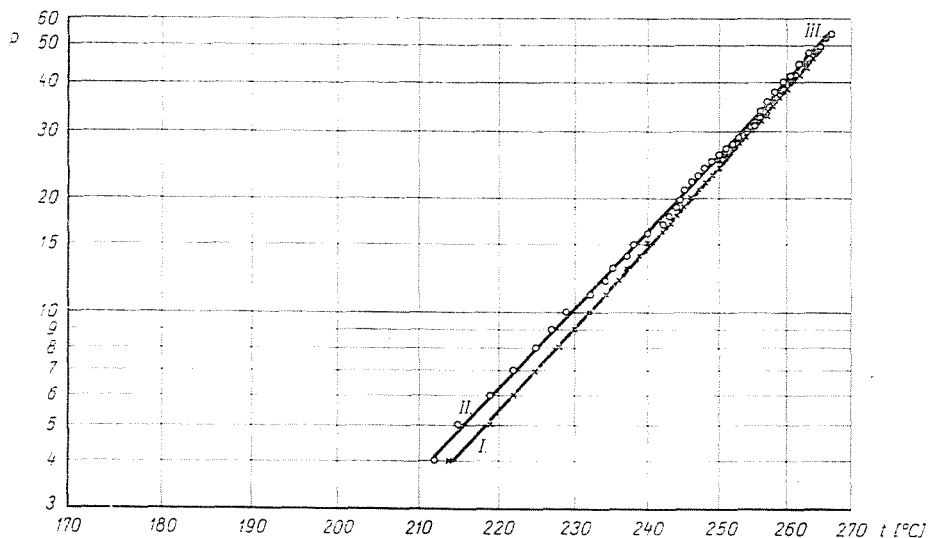


Fig 7

h) Silicone oil, type D.C. 703, vacuum oil grade. It decomposes under a pressure of 19 mm Hg at a boiling point 268 °C (Fig. 8).

The anomalous ebullition phenomena, e.g. the oscillation of a boiling point, observed with most of the di-esters above the decomposition boiling points suggest that essential chemical changes have taken place during the period the substances were kept boiling. The pressure and temperature values where the anomalies occur are much higher than the decomposition points of the several substances. This shows that the change in the vapour tension curve proposed for the indication of the beginning of decomposition is a sufficiently sensitive indication.

Vapour tension curves registered before, and after decomposition also give a qualitative indication of this decomposition. The two curves of the silicones scarcely deviate from each other, and meet at the decomposition point. In the case of other substances, the curves before, and those after decomposition are more divergent yet meet at the decomposition point thus showing that the process that started at the decomposition point did not

proceed during further boiling. Those products are to be considered the most sensitive, of which the new vapour tension curve representing further boiling does not join up with the last decomposition point of the previous curve, but lies above it, meaning that once these substances began to decompose this process continues during further boiling.

The decomposition points of not vacuum oil grade di-esters with high acid numbers, i.e. those that contain greater quantities of half esters are, at least with a good approximation, the same as those of the quite pure di-esters. For the vapour tension curves published on pure substances run very near to the vapour tension curves measured here of the substances under investigation

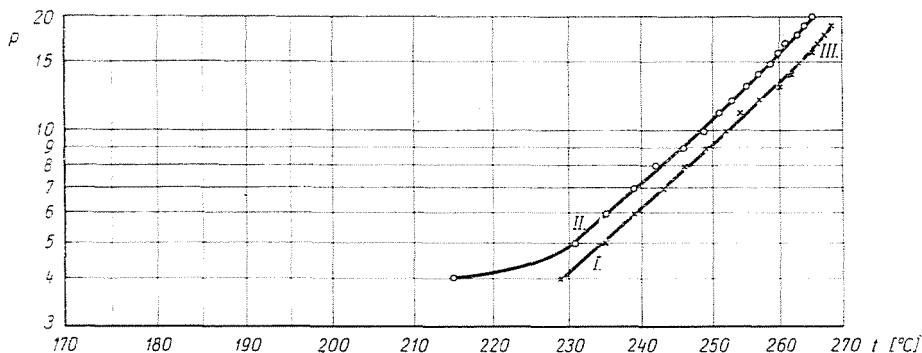


Fig. 8

Leaflets, and catalogues, on vacuum oils generally state their vapour tension at 20 °C. Of course, these are not experimentally verified data but values determined according to the equation of Clausius and Clapeyron from results of measurements carried out at higher temperatures. We thought it worth-while to calculate the vapour tension values pertaining to room temperature for the substances we investigated, both for their original and decomposed state.

	Vapour tension at 20 °C in mm Hg	
	original substance	decomposed substance
a) Processed steam turbine oil	$7.8 \cdot 10^{-6}$	$7.5 \cdot 10^{-5}$
b) Di-2-ethylhexylphthalate	$2.1 \cdot 10^{-4}$	$8.0 \cdot 10^{-4}$
c) Di-2-ethylhexylsebacate	$7.3 \cdot 10^{-3}$	$2.5 \cdot 10^{-2}$
d) Dioxo-iso-octylphthalate	could not be measured	
e) Dioxo-iso-octylsebacate	$1.5 \cdot 10^{-4}$	$3.0 \cdot 10^{-4}$
f) Di-butylsebacate	$7.4 \cdot 10^{-7}$	$3.0 \cdot 10^{-5}$
g) D.C.702 type silicone	$1.4 \cdot 10^{-7}$	$2.1 \cdot 10^{-7}$
h) D.C.703 type silicone	$1.3 \cdot 10^{-6}$	$3.4 \cdot 10^{-4}$

In dealing with a test method, the question arises whether its application can be extended, and whether it can be further developed.

Even in this series of investigations we came across a substance, the phthalate of oxo-alcohols, which can be subjected to molecular distillation but cannot be subjected to boiling even at the lowest boiling point. This suggests the question: what is the highest temperature and pressure at which the not boilable sensitive substances can be evaporated without their decomposition?

In view of the fact that methods for vapour tension measurements other than the ebulliometric ones are not only cumbersome and complicated but also most unreliable, it seems that for the substances mentioned only the method proposed by TREVOR [9] is suitable. The essence of this method is that the substance is evaporated from a large surface into vacuum and the vapour pressure is estimated by the revolutions of a very small air vane.

A further question awaiting investigation is how the decomposition boiling points of the substances are changed when pressure is maintained not by air but by an inert gas which excludes oxidation.

Neither would it lack interest to establish the points of decomposition of members of homologous series, and of inverse compounds, e.g. of dicarboxylic acid alcohols, or di-esters of α - ω glycol and monocarboxylic acids.

Finally, an extension of the method might serve for the investigation of the catalytic activity of metals, e.g. so that the metals in question were placed in the form of a wire-gauze into the vapour space.

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Summary

A method is presented whereby a pair of the highest related tension and temperature values can be found at which an organic compound can be kept boiling without decomposition, or without a decomposition that affects the vapour tension curve. The lowest pair of these values at which the vapour tension curve of the substance changes is called decomposition boiling point. The method consists in essence in the measurement of vapour tension values over successively increased sections of these values, the measurement being re-started at the end of each section. A description of the experimental apparatus is given, together with results concerning petroleum derivatives, di-esters, and high vacuum silicone oils.

References

1. MURPHY, C. M.—SAUNDERS, C. E.—SMITH, D. C.: Thermal and Stability of Polymethylsiloxanes. *Ind. Eng. Chem.* **42**, 2462 (1950)
2. MURPHY, C. M.—RAVNER, H.: Oxidation Characteristics of Some Diester-Fluids. *Ind. Eng. Chem.* **49**, 1607 (1952)
3. LATHAM, D.—POWER, B. D.—DENIS, B. T. M.: An Assessment of Some Working Fluids for Diffusion Pumps. *Vacuum*, **II**, 50 (1952)
4. REICH, G.: Der Enddruck von Öldiffusionspumpen unter besonderer Berücksichtigung des Dampfdruckes der Treibmittel. *Z. Angew. Phys.* **9**, 23 (1957)
5. BÄHLER, W.—NÖLLER, H. G.: Fraktionierung und Entgasung in Öldiffusionspumpen. *Z. Angew. Phys.* **9**, 612 (1957)
6. KÖRÖSY, L.: Über das Verhalten synthetischer Vakuümöle in Öldiffusionspumpen. *Periodica Polytechnica, Chemical Engineering* **5**, 41 (1961)
7. REICH, G.—NÖLLER, H.: Partialdruckanalysen des Enddruckes von Öldiffusionspumpen mit dem Omegatron. *Z. Angew. Phys.* 617 (1957)
8. HICKMANN, K. C. D.—HECKER, J. C.—EMBREE, E. D.: Direct Determination of Low Vapor Pressures. *Ind. Eng. Chem. Anal. Edition* **9**, 264 (1937)
9. TREVOY, D. J.—TORPEY, W. A.: A Vacuum Anemometer. *Rev. Sá. Instr.* 676 (1953)
10. ORTEL-AZAM.: Appareillage de Laboratoire pour la distillation des huiles pour pompes à diffusion. *Le Vide* **6**, 163 (1951)

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