Vol. 32. No. 267. March 1946.

SOME PROBLEMS ENCOUNTERED DURING WELL SHOOTING OPERATIONS IN THE NOTTINGHAMSHIRE OILFIELDS.

By J. F. Waters, B.Sc.*

A great deal has been published on both the theory and practice of oil-well shooting for increased production, and the scope of the present paper is confined to some of the problems which have confronted the D'Arcy Exploration Company Ltd. in well-shooting operations in England.

The principal producing sandstones, the Rough Rock, lying at the top of the Millstone Grit, is 50–80 ft in thickness, and lies at an average depth of 2,000 ft below the surface. It varies in grade from a fine sandstone to a grit; its porosity varies from 0 to 25 per cent and its average permeability is 10 millidarcies, though there are streaks with a permeability up to 300–400 millidarcies. This was the sand normally shot, but, in addition, other sands were also shot in a number of wells.

Until mid-1943 the explosive charge was placed near the bottom of the Rough Rock, in order (*a*) to keep it as far as possible from the casing-shoe, and (*b*) to form a fissure system extending upwards and outwards from the shot, thus allowing gravity to assist drainage. Latterly it was placed opposite what were believed to be the more permeable sections, provided these were not too near to the casing-shoe.

In the early years of the war the technique employed consisted, briefly, in cleaning out with oil circulation both before and after the shot. The tamping consisted of a column of gravel, amounting to some 60–80 linear ft per 100 lb of explosive. The oil level was bailed down as low as practicable before the shot, in order to reduce the back pressure on the formation, and thus allow the immediate rush of oil into the hole following the shot, to help to bring the debris of the resultant fissures into the well, whence it could be cleaned out.

The explosive used has been exclusively blasting gelatine, which is lowered into the hole in thin, galvanized-iron containers, and dumped by means of a detaching hook.

To assist propagation, tetryl boosting pellets have been used, these being placed in the nose and tail of each container.

The methods of firing the charge have undergone some changes. The first shot was fired from surface by means of an electric cable lowered down the hole on a sand-line. Owing, however, in the next attempted shoot, to the electric cable becoming broken during the process of feeding in the gravel tamping, this method was abandoned in favour of the time-bomb.

The time-bomb used in the earlier shots consisted essentially of a cylindrical wooden mechanism case, about 7 in long and 2½ in in diameter, a small tinned canister to contain a priming cartridge, and a cast-iron, pressure-tight bomb-case in which the assembled bomb was lowered into the

---

* Anglo-Iranian Oil Company, Limited.

well. The firing mechanism, which was duplicated as a precaution against failure, consisted of an ordinary pocket-watch inserted in the top compartment of the mechanism case, and a No. 8 electric torch battery, housed in a suitable recess in the side of the case. The minute hand of the watch was removed and the glass replaced by celluloid through which a small contact pin was inserted and cemented. Two electric detonators in parallel were connected to a pair of leads from the base of the mechanism case, and the device was wired up in such a way that the circuit, consisting of the watch, the battery, and the detonators, was completed by the hour hand coming up against the contact pin at the expiry of the required delay.

It was found by experience that, in testing the bomb circuits by bringing the watch-hand against the pin, the watch-hand was liable to become damaged, with the possibility either of failure to fire or of premature firing when the bomb was in actual use. The rigid pin was, therefore, replaced by a small swept spring, which served as an electrical contact, whilst allowing the hand to brush over it without risk of damage.

The assembly of the bomb was completed by burying the detonators in the top of a priming cartridge inserted in the canister, which was then fitted over the lower end of the mechanism case. The bomb was then placed in the pressure-tight case ready for lowering into the well.

In 1943 it was decided to carry out some experimental shooting on wells which had been on steady production for some time. For this purpose wells of good productive capacity were selected. The time-bomb used was a clockwork type for percussion detonators. The clockwork mechanism releases a set of hammers which are forced down, and fire caps to which the detonators are attached. Apart from this change, however, the technique adopted was identical with that previously employed.

Using a light drilling outfit, the pump capacity was such that with oil in circulation cleaning out of the gravel was much slower than with the heavy outfits used in drilling the well. As a result of production, the condition of the hole was often such that it caved badly, especially on bailing down. Even where it was found possible eventually to clear the hole to shooting depth, there was always the danger of cavings falling in during the running in of the containers, thus isolating part of the charge, or between running the top container and placing the time-bomb. An attempt to overcome this difficulty was finally made by circulating down an asbestos-cement drillable liner. The liner, which was strong enough to hold back the cavings, but which would be shattered by the explosion, and therefore easy to clean out, was made up of 10- and 13-ft lengths, according to diameter. The liner was lowered on flush-jointed drill-pipe, lengths being added at surface as the drill-pipe was lowered down the hole. The method of making up the liner and placing it in position in the hole as shown in Fig. 1. The liner rested on a shoulder on the upper face of a brass setting base. Rotation of this base during backing-off was prevented by a specially designed cruciform anchor. The setting base was drilled out and provided with a ½-in pitch left-handed square thread, into which was screwed the setting tool. The latter is illustrated as an inset. The square thread was a slack fit, spinning-off being prevented by a bow spring, fitted into the setting tool, bearing against the thread of the setting base. Over-tightening was prevented by a stop stud, as shown. The setting tool was screwed on to the bottom end of the drill-pipe. The lengths of liner were joined by means of two diametrically opposite strips of iron about 4 in long, bent to form clips, set flush with the outside of the liner, and screwed into it on either side of the joint. The asbestos-cement could be readily drilled and tapped for this purpose. Rigidity of the column was assisted by a number of ¼-in brass alignment pins spaced round the section of each length of liner. At the top of the liner a clamp was bolted to the drill-pipe for the purpose of centralizing

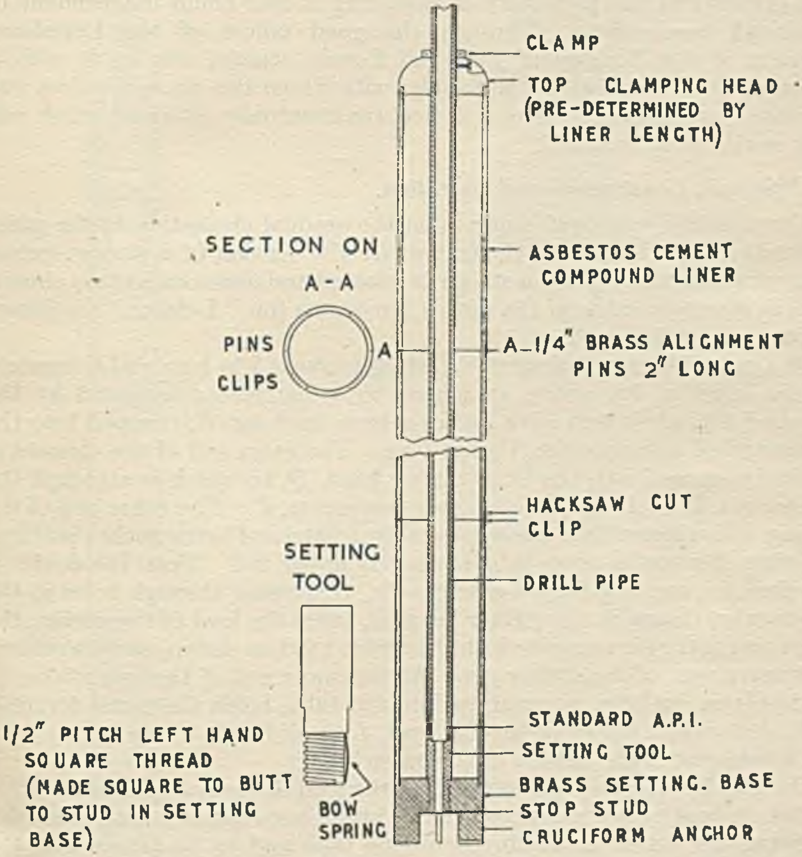


Fig. 1.

ASBESTOS-CEMENT LINER—SHOWING METHOD OF MAKING UP, AND LOWERING INTO POSITION IN THE HOLE.

it and of helping to maintain rigidity during lowering. After circulating to bottom, the drill-pipe and setting tool were backed off, leaving the setting base in position. The top clamp came up attached to the drill-pipe.

Although the asbestos-cement liner proved successful in the shooting of a few wells showing an abnormal tendency to caving, the difficulty of aligning it in the hole, resulting in trouble in the running of the containers, led to its abandonment.

As too much time was spent after each shot in cleaning out the gravel tamping, the use of gravel was abandoned in favour of crushed gypsum, of which supplies were, fortunately, available locally. This modification resulted in a marked improvement in the time of cleaning out.

The L-Delay.

The shortage of watches and other suitable types of clockwork mechanism resulting from war-time restrictions became acute. Attention was therefore directed to the possibility of designing a time-bomb independent of clockwork mechanisms. Through the good offices of the Petroleum Division of the Ministry of Fuel and Power, contact was made with a department of the Ministry of Supply, with whom the whole problem was discussed, and through whom a device was eventually obtained which will now be described in detail.

(i) *Principle, Construction and Operation.*

The principle employed depends on the gradual elongation to the point of fracture of a lead-alloy element under the tension of a strong spring. When fracture takes place, a striker is released and closes an electric circuit. Details of construction of the device, known as the " L-delay," are shown in part section in Fig. 2.

One end of the metal element, *A*, which is about $\frac{3}{4}$ in long and accurately turned down at its centre, as shown, to a diameter determined by the required timing, is held by a pin in a brass bushing, *B*, crimped into the lower end of a metal tube, *C*, 4 in long. The other end of the element is similarly secured into the brass striker head, *D*, to which is attached the striker pin, *E*, and one end of the tension spring, *F*. The other end of the spring, which is stretched during assembly, is attached to the anchor bushing, *G*, crimped into the outer tube *C* near its upper end. Until the device is required for use, a J-shaped starting-pin, *H*, passing through holes in the outer tube, *C*, and in the striker head, *D*, takes the load of the spring, the short arm of the pin engaging with the striker head, as shown, and preventing any movement of the striker pin. At the upper end of the outer tube, *C*, an insulator bushing, *K*, crimped into the tube, holds the metal terminal bolt, *J*, to which a rubber-covered lead, *L*, is soldered. An earthing lead, *M*, is soldered to the outside of the outer tube.

On withdrawing the starting-pin, *H*, the load of the spring is transferred to the element, which starts to extend slowly, but regularly until it breaks, allowing the striker to be forced up the tube and to be driven into the terminal bolt thus providing a metallic path through the " delay " between the two leads *M* and *L*.

(ii) *Safety Features.*

Safety in handling is amply provided for. In the course of manufacture, routine testing of a most scrutinizing nature is carried out. This is designed to maintain a check on the homogeneity of the element alloy, and to test the firing time and general reliability of the finished article, on the principle of extensive random selection. In addition the design incorporates the following safety features :—

(*a*) A small tab attached to the starting-pin indicates clearly the timing of the delay.

(*b*) Inadvertent withdrawal of the starting-pin is prevented by a small spring-clip.

(*c*) Should there be any fault either in the element itself or in the assembly of the device, it is impossible to pull out the starting-pin, for on withdrawing it a fraction of an inch, the short arm becomes disengaged from the striker-head and the long arm becomes trapped by the striker head starting to move under the tension of the spring, a small head at the end of the long arm preventing its withdrawal through the hole in the outer tube.

Fig. 2.

DETAILS OF "DELAY" (DIAGRAMMATIC).

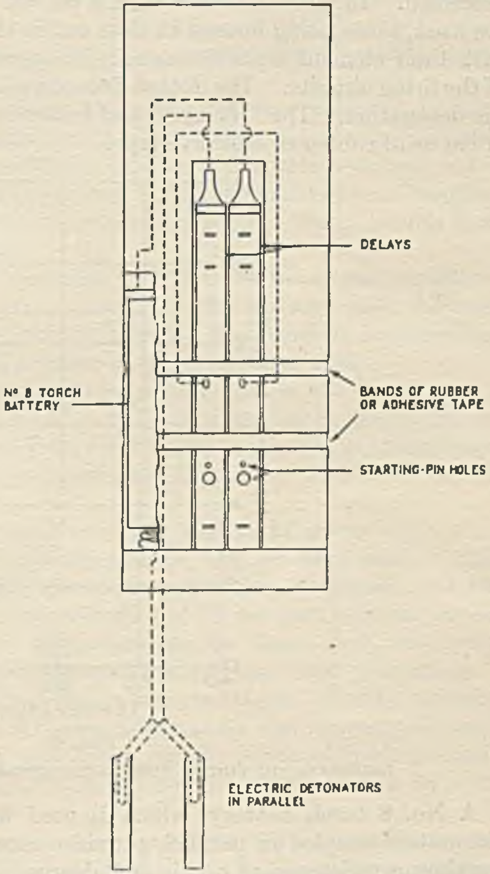


Fig. 3.

"DELAY" BOMB FIRING CIRCUIT (DIAGRAMMATIC).

Provided the device is handled with the element end downwards, it can be dropped on to a hard surface from a height of several feet after withdrawal of the starting-pin without risk of premature fracturing. If dropped with the element uppermost, however, the mass of the striker assembly transmits to the element, on impact, a tensile shock which is liable to cause instant or premature fracturing.

The device has been adapted to oilwell shooting by using the watch time-bomb mechanism case, the canister and pressure-tight bomb-case already described. In place of each watch, a pair of " delays," connected in series, are used, these being housed in slots cut in the side of the mechanism case, with their element ends downwards, as shown in Fig. 3, which shows one of the firing circuits. The dotted lines show how the device is wired up with the detonators. The " delays " and batteries are held in position by means of bands of rubber or adhesive tape.

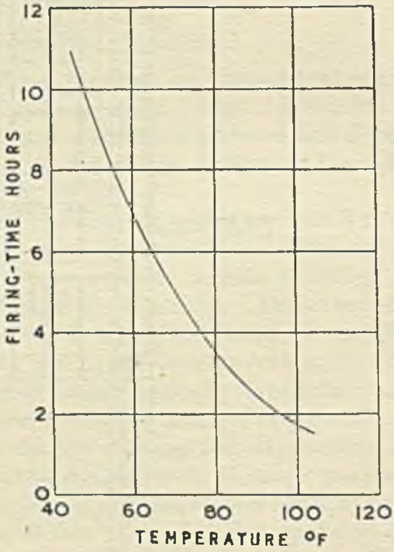


FIG. 4.

DECREASE OF FIRING TIME WITH INCREASE OF TEMPERATURE.

A No. 8 torch battery, which is used for firing each pair of electric detonators coupled in parallel, provides ample voltage for overcoming the maximum resistance of a pair of " delays " plus the internal resistance of the circuit.

By using a pair of " delays " all risk of premature firing is virtually eliminated, and by duplicating the circuits the chances of failure are rendered negligible.

(iii) *Effect of Temperature on Timing.*

The timing of the " delay " is subject to very considerable variation with temperature, and Fig. 4 shows this variation for the standard " 6-hour delay at 65° F."

The normal well-shooting depth for wells in the English fields has been about 2000 ft, the rock temperature at this depth varying from about 80° to 105° F. The actual temperature effect to which the bomb is subjected is partly dependent on the length of the period of circulation of drilling fluid during cleaning-out operations, as well as by the time elapsing between completion of circulation and lowering of the bomb into the well; moreover, the accuracy of the timing of the "delay" is subject to a small + or − variation. In practice, the firing time for this "delay" has varied between about 2 and 4 hours, and has afforded an ample margin for completing the bomb assembly, lowering it down the well, and feeding in the tamping material.

This type of time-bomb has answered its purpose entirely satisfactorily, and is still being used.

In order to speed up operations, the technique was modified both as regards the circulating fluid and the tamping. Instead of oil, bentonite water was used both before and after shooting. The hole was kept full of fluid to surface up to the time of shooting, and the amount of solid tamping was reduced to about 30 linear ft of crushed gypsum. Early results from this technique were encouraging.

The alteration in technique coincided with changes in general conditions owing to shooting taking place in another producing area with different sandstone development. The principal change in procedure included the shooting in certain wells of two or more of the producing sands.

The changes in conditions also included a reduction in the diameter of a number of the wells from 7¾ in to 5⅜ in or 5⅝ in, resulting in the maximum practicable charge being reduced from 400 to 300 or even 200 lb of explosive, and the maximum practicable concentration from 12 or 13 lb to 6 or 7 lb per foot.

The earlier technique, averaged over the results of seven wells shot, showed an improvement in oil production of 129 per cent and of fluid production 136 per cent, whilst the later technique, averaged over the results of thirty-four wells shot, showed 47 and 90 per cent respectively for oil and fluid. The aggregate improvement for these forty-one wells amounted to 61 per cent oil production and 93 per cent fluid production.

The bentonite fluid tamping has certain disadvantages. Firstly, cleaning out with bentonite water, even if the specific gravity and viscosity are kept down to the minimum required to circulate out the debris, is liable partially to mud-off the producing sand, or to increase its resistance to flow by mere loss of water to the formation.

Secondly, (*a*) it reduces to some extent the efficiency of detonation owing to compression and uneven redistribution of the air in the blasting gelatine; and (*b*) the back pressure due to the fluid head (particularly in a field which is de-pressured) exceeds the reservoir pressure and the debris may be forced back into the fissures, where it tends to form "bridges."

In view of this, the technique has been modified. The hole is cleaned out with oil circulation, but it is not bailed down until after the charge and time-bomb have been placed in position. For tamping, a solid plaster plug takes the place of the gravel or crushed gypsum and bentonite water to surface. It will be noted that this procedure reverts to solid tamping, low fluid back pressure at the moment of explosion, and cleaning out with oil circulation, but it is much more rapid as the result of modifications in application.

Details of this modified technique are:—

A pre-formed plug made by filling a 5-ft length of asbestos cement liner with plaster is first lowered and placed in position above the time-bomb. An " umbrella " attached to the bomb container prevents the plug from coming into contact with it.

Charges of freshly mixed plaster are then lowered in a dumping bailer provided with a glass disc, which is broken by means of a " dart " of suitable length. The first dump of plaster packs round the pre-formed plug and the subsequent dump builds up the plug to the requisite height of about 15 ft. After a lapse of 1½ hours, to allow the plaster to set, the oil in the hole is bailed down to a depth at which the pressure due to the remaining column is exceeded by the reservoir pressure.

For the purpose of carrying out those operations which must be performed after the placing of the time-bomb, a long " delay " time-bomb (7 days at 65° F.) of the same type as that described above is used. At average reservoir temperature, such a " delay " fires the charge within about 40 to 50 hours.

ACKNOWLEDGMENTS.

For permission to publish this paper, the author desires to express his thanks to the chairman and directors of the Anglo-Iranian Oil Company, Ltd.

The D'Arcy Exploration Company's shooting operations described in this paper were carried out under the supervision of D. Comins and R. K. Dickie.

Acknowledgments are due to R. E. Ward of I.C.I. (Explosives), Ltd., for his assistance; and to Colonel F. S. Macrae and L. Gouldstone of the Ministry of Supply, for their co-operation with the author in adapting the present timing device to well shooting.

THE INSTITUTE OF PETROLEUM.

A MEETING of the Institute of Petroleum was held at 26, Portland Place, London, W.1, on Wednesday, December 12, 1945, the President (Professor F. H. Garner) in the Chair.

A paper on "Some Problems Encountered during Well Shooting Operations in the Nottinghamshire Oilfield" was presented by Mr. J. F. Waters (see pp. 119–126).

DISCUSSION.

THE PRESIDENT said it was always interesting to have one operation described in such detail and Mr. Waters has covered all the various considerations involved. The time bomb arrangement, invented for an entirely different purpose, was particularly interesting.

He asked how the delay with this lead alloy element compared with a clock, in which presumably the effect of temperature was very much less.

MR. WATERS said that the effect of temperature on a watch was negligible within the limits of oil well shooting operations. If the temperature became very much higher it might affect its working. They had had no experience of that, however, and with the watch type of time bomb, were able to ignore the effect of temperature.

As to the accuracy of timing, although the minute hand was missing from the watch as used, they were able to set it with a fair degree of accuracy, to within perhaps 5 or 10 minutes.

With the "L" delay type of bomb, with a 6-hour delay, the temperature came into the problem so much that it was almost anybody's guess.

MR. R. R. TWEED said the author had indicated the general increase of production obtained as the result of the treatment described. Can he say what was the difference of production obtained in the harder and the softer formations respectively?

Also, what was the difference in the size or amount of explosives he would recommend as between the hard and the soft formations?

CAPTAIN D. COMINS said they had not the data which would enable them to answer those questions. The size and amount of explosives had not been varied in accordance with the hardness or softness of the formations; the process for shooting the lower sands was the same as for shooting the upper sand. Generally speaking the lower sands were softer than the upper sands. Normally only the upper sands were shot; but when the lower sands were also shot it had not been the practice, for reasons of economy, to test the increased production from each sand separately.

MR. L. C. STEVENS asked what was considered the minimum safe distance from the shoe at which a shot could be placed?

He also asked whether it was possible to make the " L " delay work at higher temperatures, such as 200° or 220° F.?

Thirdly, had any cases been experienced where there had been complete failure to detonate, and if so, what action was taken?

Fourthly, figures had been given for the initial increase of production immediately after the shot, and he would like to know to what extent that increase of production was sustained? Did the rate of decline after the shot continue the same as before, or was there an initial increase which, after a week or two, brought the production curve back to the old level?

Mr. Waters said the shot was kept about 20 to 30 ft below the casing shoe. But that distance could probably be reduced very considerably by the use of the solid plug. They had evidence that there was no movement at all of the plug itself, and he did not think there was any evidence of its disintegration by the shot; it seemed to withstand the shock very well.

The question of temperature was very interesting. With the standard spring fitted to the " delays ", if one drew out a set of graphs showing the variation of firing time with temperature, it looked as though the limiting temperature was about 150° F. He had discussed this subject with Mr. Gouldstone, of the Ministry of Supply, and had been assured that, although it would require a certain amount of experiment, a " delay " could be devised to work at quite high temperatures, of the order of 300° F. In the standard article as now manufactured, the delay was limited by the spring, which was more affected by high temperature than was the element itself.

None of these delays had failed so far and it seemed that the only possibility of failure was the failure of the pressure-tight case. If that failed for any reason, the shot would fail. The dependability of the " L " delays was quite extraordinary. He was told at the Ministry of Supply that they knew of no case, in the first three million of these " delays " that were turned out, either of failure to fire or of premature firing. That gives a very good idea of their dependability.

He asked Capt. Comins to deal with the question of the rate of decline of production after firing.

Captain Comins said he did not think one could state the minimum safe distance of the shot below the shoe. They had not placed it nearer than 19 ft. On the other hand, he did not think that 20 ft or even 40 ft was necessarily safe. It depended on the method of tamping.

With liquid tamping and/or inadequate solid tamping the shock waves were liable to affect the casing at any weak point, for example where for any reason it might be unsupported by cement. It was of course generally known that, when using liquid tamping only, it was unsafe to shoot with the liquid level down in the casing as damage was liable to occur at such level.

There had been one failure of a charge to detonate, but this was before time bombs were used and charges were being detonated by means of electrical leads from surface. In this case the charge was eventually detonated by cleaning out the gravel tamping to within 2 to 3 ft of the top of the charge and lowering a small secondary charge, 50 lb, which was fired by time bomb. That figure 2 to 3 feet was a useful figure to remember.

With regard to production increases after shooting the increases quoted were the sustained increases on the pump allowing for normal decline; except in the case of a few wells which were shot immediately on completion. In such cases the percentage increase was determined by comparison of the rate of rise of oil level in the hole, determined by float, before and after shooting as these were the only comparable figures.

Where wells had previously been on production and were shut down for a time preparatory to shooting, there would be a certain amount of temporary recovery which would give a false reading. This was ignored. If, on the other hand, a well which had not been on production was shot, the immediate increase of yield, measured the next day after the foam had subsided, should be a fairly good indication of the permanent increase—*i.e.*, the percentage improvement.

Brigadier Stokes expressed appreciation of the paper and asked, in regard to the inclusion of booster pellets in the charge, whether they were used for additional security, or were they necessary on grounds of reliability?

Mr. Waters said the expert opinion of the I.C.I. technical staff was accepted as to the use of the pellets, their type and the numbers in which they were used. He did not say that they themselves had evidence, but there existed ample evidence that the pellets did certainly improve the propagation of the explosion.

Mr. E. Thornton asked whether explosives other than blasting gelatine had been used and, if so, what sort of effects did they have?

Mr. Waters said that blasting gelatine was selected, not because it was the usual type of explosive to use, but because it was extremely efficient and a standard production. This polar blasting gelatine was extremely safe, it could be handled in all weathers, and was very powerful and it is a standard article of production. He did not think it could be improved upon for the particular job of oil well shooting.

Mr. G. W. Lepper said that although nitro-glycerine in the fluid form was used a great deal in the United States he believed there was a Home Office Regulation in Britain against the transport of liquid nitro-glycerine. For that reason, just after the war of 1914–18, when Messrs. S. Pearson & Sons were drilling for the Government in Derbyshire, they very laboriously washed out the nitro-glycerine from some dynamite and used it to shoot a well. He understood that the polar blasting gelatine which the D'Arcy Exploration Company had been using was the best solid equivalent of nitro-glycerine, and it was said to be very safe. He had been privileged to be present during some of these shooting operations. The petroleum licencees in Great Britain who wished to shoot their wells had first to obtain the permission of the Minister of Fuel and Power to use explosives. There was a little apprehension at first as to whether the casing might suffer, and the matter was discussed with I.C.I. Ltd., who had had some experience of shooting in water-wells. They said the effect with the casing filled with water was a little uncertain; a casing might rupture hundreds of feet above the shock point.

Having followed all the operations from the first shooting operation in Scotland by the Anglo-American Oil Company before the war, where the ordinary method of detonating by means of an electric cable was used, it had been very interesting to watch the very great improvements effected in technique. The D'Arcy Exploration Company had shot a large number of wells and may be said to have developed it to a fine art. There had not been a single accident. The only case which caused some embarrassment at the time was that in which the charge failed to explode because the firing cable was fractured.

From a knowledge of these operations, he thought the D'Arcy Exploration Company were to be congratulated on their perseverance, and on the very fine technique which they had now developed, in conjunction with I.C.I.

THE PRESIDENT asked what precautions were taken before lowering the mechanism. Obviously the most dangerous time was that when the electrical connections were made and the operator had a live bomb in his hand. He presumed that the wires were tested very carefully beforehand.

MR. WATERS said that the mechanism was tested for short-circuits very carefully.

With regard to precautions at the last moment when the pins are withdrawn, there was one feature of the "delay" which he had not mentioned, and that was that if it was dropped with the element end downwards the effect of dropping it was to lengthen the time of delay. What happened was that the mass of the striker head, the striker pin and the spring came down and actually had an annealing effect on the lead alloy element and increased the length of the delay. On the other hand, if the "delay" was dropped the other way up, *i.e.*, with the element at the top, it would fire immediately, or at any rate the length of time would be reduced. The make-up of the bomb took this into consideration, and the "delays" were installed with the element end downwards so that, even supposing a man was nervous and dropped the whole thing, it would not result in a premature functioning of the "delay".

MR. L. C. STEVENS asked how the bomb was lowered into the hole?

MR. WATERS said it was run on a Halliburton line in a 3 ft container, in which there was 10 lb or so of explosive, plus the priming charge in the bomb. It was lowered extremely carefully. Rough treatment would not have very much effect on the "delays", but one naturally exercised care in lowering.

MR. STEVENS asked how it was released?

MR. WATERS said it was released by means of a detaching hook which, so long as it was held in tension, remained right side up; but as soon as the tension was released, the top part, which was heavier than the bottom part, swung over and the hook became disconnected.

Captain Comins said there was nothing to add to the description which had been given of the technique, but a point which should be borne in mind by anybody going in for shooting was the importance of adhering to a very strict drill. The whole of the gear should be ready, inspected and tested, on the day before the shooting, and, with a little practice, a very accurate time programme could be prepared. Otherwise, darkness might come on or the shot explode, before tamping has been completed. This had never occurred in their operations.

From his experience of shooting he was absolutely convinced that solid tamping was far preferable to liquid, no matter what kind of solid tamping it was. The energy was absorbed where one wanted it absorbed and there was practically no reaction at all at surface: from the point of view of safety also it was much better than liquid tamping.

His second conviction was that it was essential to have the minimum back pressure on the formation when firing the shot. There were two reasons for reducing back pressure to the minimum, and he thought Mr. Waters mentioned both of them. One was that the debris of the explosion was swept into the hole more easily owing to the greater bottom hole differential pressure available. Indeed if the fluid back pressure was too high—higher than the reservoir pressure that is—fluid would be lost to the formation, thus tending to force the debris back into the drainage channels formed by the shot. The second reason was that it was understood that the efficiency of the charge was reduced by excessive fluid back pressure owing to compression of its air content.

Thirdly, he was convinced that at the time of firing the shot there should be no mud fluid or even bentonite water in the hole and the well should be cleaned out afterwards with oil circulation, to avoid the risk of mudding off spoiling or reducing the effect of the shot. Wells should preferably be cleaned out with oil before shooting, but in caving formations this may not be practicable consistently with safety in placing the charges.

He believed in placing the shots against the lower part of the sand perferably against the less permeable sections of the sand, because one only risked compacting it where that did not matter very much, and the fissures would extend upwards into the other more permeable sections, thus providing gravity drainage channels.

Further, he thought all shooting operations should be carried out during the very early life of the field, before the reservoir pressures were lowered by production. The advantage of doing that is: firstly, there was more differential pressure to bring the debris back and less loss of circulating fluid before and after shooting, which tended to obscure the results of shooting; secondly, there was far less caving trouble from shale bands than in wells which had been for some time on production.

The wells most responsive to shooting appeared to be those whose productivity was mainly dependent on fissuring and those which were originally drilled in with mud, the shooting having in these a corrective effect on the mudding off of potential capacity when originally drilled. Wells originally drilled in with mud showed an improvement in fluid production of 139 per cent as compared with 62 per cent for wells originally drilled in with oil.

With regard to economics, costs had varied from £350 to £500 per shot on the normal wells, where there was no particular difficulty with caving or cleaning out, or trouble with casing. On the other hand, as much as £1,000 or even £1,500 had had to be spent. Usually the more expensive jobs had been those shot in the way he had recommended, but the improvement had been very much greater than in other cases, and the total cost had been a great deal less than the cost of a new well. Thus it is worth while spending more time, trouble and money in order to achieve the improved results.

He did not think any discussion of this kind was complete without some reference to Paul Lewis, of the American Glycerine Company. When they first went in for shooting, with the technical assistance of I.C.I. (Explosives) Ltd., they studied Lewis' publications very carefully, and he would advise anyone else who goes in for shooting to do the same.

On the motion of THE PRESIDENT, a very hearty vote of thanks was according Mr. Waters for his interesting paper and his replies to the discussion.

MOLECULAR WEIGHTS OF VISCOUS HYDROCARBON OILS: CORRELATION OF DENSITY WITH VISCOSITIES.

By Alfred E. Hirschler.*

Synopsis.

Molecular weights of lubricant fractions have been correlated with kinematic viscosities at 100° and 210° F., using a modified Keith and Roess chart; and with the density at 25° C. and viscosity at 210° F. By combining these two charts a correlation between these four physical constants is developed whereby any two may be used to estimate values of the other two. Based on this chart, a simple equation has been developed for calculating the molecular weight from viscosity data, applicable to oils with viscosity indices between -50 and $+120$.

Using published data on lubricant fractions, and synthetic hydrocarbons in the lubricant range, these correlations are evaluated and compared with previously proposed correlations of molecular weights with viscosity data; the accuracy of the latter is shown to be quite dependent on the viscosity–temperature behaviour of the oils.

The data on synthetic hydrocarbons indicate that the viscosity–density correlations are much more sensitive to composition than the viscosity correlation; the latter is therefore recommended when two viscosities are available. Consideration of a large number of lubricant fractions indicates that the average composition is sufficiently uniform that the viscosity–density correlations will give satisfactory results in most cases; very naphthenic samples should, however, not be evaluated on the viscosity–density charts, unless they are especially prepared for this class of oils.

The correlation may be used to estimate vis_{100}, vis_{210} or density, given two of the three constants; the accuracy possible for oils of different origins is indicated.

Correlation of Molecular Weights of Lubricating Oils with Viscosity Data.

Introduction.

Several attempts have been made to correlate the molecular weights of the lubricant fractions of petroleum with viscosity data. Fenske, McCluer and Cannon [10] proposed the equation :

$$\text{Mol. Wt.} = \frac{32310 \log \dfrac{\text{S.U.S.}_{100}}{28}}{305 - \text{Visc. Index}} + 240 \quad . \quad . \quad . \quad (1)$$

where S.U.S._{100} is the viscosity in Saybolt Universal seconds at 100° F. This equation was recommended for the range 300–425 molecular weight and was believed accurate to ±2 per cent. Later Keith and Roess [18] published a chart correlating molecular weights with Saybolt viscosities at 100° and 210° F for the range 240–580 molecular weight. It was found that neither of the above correlations gave entirely satisfactory results when applied to data which have since become available, and it is the

---

* Sun Oil Company Experimental Division, Norwood, Pa.

purpose of this paper to describe the development of what are believed to be more accurate and reliable correlations based primarily on the more recent published data.

From the literature, a compilation was made of the available data pertaining to lubricant fractions which included viscosities at 100 and 210° F as well as experimental molecular weights. It was found that the various investigators had employed several different equations for the interconversion of kinematic and Saybolt viscosities, as well as various methods for calculation of the viscosity index. These quantities affect the calculated molecular weights, and it is therefore necessary, for the sake of consistency, to apply the same method of calculation to all the data. For interconversion of kinematic and Saybolt viscosities the A.S.T.M. Conversion Table * was adopted; and viscosity indices were calculated according to Dean, Bauer, and Berglund [6] as amplified in table form.† All data used in this paper were so calculated, and may differ from that in the original reference. Such differences are minor in the case of viscosities, and were found to have little effect on the molecular weights. Differences in viscosity index may be considerable, especially for the lighter oils. In most cases this was found to have a small adverse effect on the accuracy of equation.[1] The greatest difference in viscosity index was observed in the case of the fourteen oils described by Fenske, McCluer, and Cannon,[10] the majority of which were of low viscosity; but even in this case the average difference in calculated molecular weight was only 1 per cent.

Evaluation of Molecular Weight Data.

An examination of the available data [5, 10, 12, 18, 24, 26, 27, 37, 38] revealed that no viscosity–molecular weight correlation was possible which would give satisfactory agreement with all the data presented, thereby necessitating a choice of the most reliable values. The extensive molecular-weight data of Mair and co-workers [24, 26, 27] were obtained by means of an elaborate ebullioscopic apparatus described by Mair [23] and claimed to be accurate to ±1 per cent; Fenske, McCluer, and Cannon employed a thermal method based on the molal heat of vaporization; while the remainder employed cryoscopic methods. A variety of different solvents has been used in the cryoscopic determination of molecular weights of hydrocarbon oils, but there seems to be considerable disagreement among the various investigations as to the accuracy of the results obtained. Fenske *et al* [10] summarized the results of the earlier workers, and concluded that molecular weights of complex high-boiling hydrocarbon mixtures could not be determined by means of the cryoscopic method with an accuracy exceeding 5 per cent.

Rall and Smith [32] at the U.S. Bureau of Mines developed an elaborate apparatus for the cryoscopic determination of molecular weights, and sent samples of four oils to a number of co-operating laboratories in which research on petroleum products was being carried out, for a comparison

---

* Based on A.S.T.M. Standard Method for Conversion of Kinematic Viscosity to Saybolt Universal Viscosity (D 446–39).

† Standard Oil Co. circulars 30·50 and 30·52–30·55. A.S.T.M. method D 567–40T apparently is identical, but is less convenient to use and does not include oils of less than 40 Saybolt seconds at 210° F.

of the molecular weights obtained. Benzene was employed as the solvent by eleven laboratories.

Several years later Hanson and Bowman [14] developed an ebullioscopic apparatus and used it to determine the molecular weights of these same oils. For comparison they also determined the molecular weights cryoscopically. These results are summarized in Table I.

TABLE I.

Comparison of Molecular Weights of Lubricating Oils Obtained in Different Laboratories.

Sample.	Molecular weights.						
	Cryoscopic (benzene).				Ebullioscopic, Hanson and Bowman.		
	Rall and Smith.	Hanson and Bowman.	11 labs.		Benzene.	*cyclo*-Hexane.	Mean.
			Spread.	Mean.			
Oil 1	763	764	675–780	693	671	652	661
Oil 2	491	442	400–492	447	450	445	447
Oil 3	333	358	300–329	317	326	312	319
Oil 4	209	218	198–214	204	208	208·5	208

A rather wide spread between the results of the various laboratories is apparent. The values of Rall and Smith were higher than the mean of the results of the eleven co-operating laboratories in every case; this is also true for three of the four oils in the case of the cryoscopic determinations of Hanson and Bowman. Data were presented by Rall and Smith showing that impurities or moisture have a large adverse effect on molecular-weight determinations, and it was believed that this at least partly explains the discrepancies noted.

The above considerations suggest that much of the available cryoscopic data is of questionable accuracy. In view of the elaborate precautions taken, the ebullioscopic results of Mair and co-workers [24, 26, 27] are very probably the most accurate recorded in the literature. For this reason, and also because they are the most extensive, and cover the widest range of viscosities and viscosity–temperature characteristics, they were given paramount consideration in the setting up of a viscosity–molecular weight correlation. The principal objection to this procedure is that all of these fractions were derived from a single sample of crude.

Choice of Viscosity–Molecular Weight Correlation.

After consideration of several possible types of viscosity–molecular weight correlations, a modified form of the Keith and Roess chart was selected. Keith and Roess correlated molecular weights in terms of the slope of the line obtained when plotting viscosities on an A.S.T.M. viscosity–temperature chart. The relation used to express the slope of this line mathematically was the viscosity slope factor (V.S.F.) of Bell and Sharp,[2] which was obtained by superimposing on the A.S.T.M. chart (D341–32T) two linear scales; one vertically (H) and one horizontally (K), which might be in any convenient units. Since the ordinate scale of this chart was proportional to log log ($cS + 0{\cdot}8$), where cS is the kinematic viscosity expressed in centiStokes, Bell and Sharp represented H by the equation

$$H_t = 870 \log \log (cS + 0{\cdot}8) + 154 \quad . \quad . \quad . \quad . \quad (2)$$

where t is any temperature. The horizontal K scale was a linear scale chosen in such a manner that 210° F has a K value of 0 and 100° F a K value of 1·0. Then the slope of a line, or the viscosity slope factor is given by

$$\text{V.S.F.} = \frac{H_t - H_{t1}}{K_t - K_{t1}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where t and t_1 are any two temperatures. If these two temperatures be 100° F and 210° F, the viscosity slope factor is given simply by

$$\text{V.S.F.} = H_{100} - H_{210} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Bell and Sharp tabulated values of H as a function of the Saybolt viscosity. Revision of this table appeared advisable for the following reasons. First, in tabulating H in terms of the Saybolt viscosity, they used a conversion function different from that now adopted by the A.S.T.M. Committee. Secondly, the A.S.T.M. Viscosity–Temperature chart has been revised, and the ordinate scale of A.S.T.M. Standard D 341–39 is proportional to log log ($cS + 0{\cdot}6$) through the range 1·5–20,000,000 centiStokes.[1] During the past few years there has been a marked trend within the petroleum industry towards the use of kinematic rather than Saybolt viscosities, because of the greater accuracy of the former, especially in the case of lighter oils. Therefore it was believed more useful to set up the viscosity–molecular weight chart in terms of kinematic units, which has the additional advantage of being more closely related to the absolute unit of viscosity. A revised table of H values was therefore calculated from the equation

$$H = 870 \log \log (cS + 0{\cdot}6) + 154 \quad . \quad . \quad . \quad . \quad (5)$$

which differs from equation (2) only in the change of constant. Equations (3) and (4) are retained as the basis for calculation of the V.S.F. Values of H for kinematic viscosities from 2 to 109,000 centiStokes are listed in Table II. All H values and viscosity slope factors used in this paper were obtained from the revised table.

The H_{100} values obtained from Table II are 1–2 units smaller than the corresponding values of Bell and Sharp; whereas H_{210} may be 3–9 units less, depending on the viscosity. As a result, viscosity slope factors are from 2 to 8 units larger.

Derivation of Viscosity-Molecular Weight Correlation.

The modified Keith and Roess chart (Fig. 1) was developed in the following manner. The data were plotted as H_{100} versus molecular weight, and the points labelled with the viscosity at 210° F. Lines of constant viscosity at 210° F were drawn empirically at intervals by interpolation. It was found that these could not be represented by straight lines, as assumed by

TABLE II.

Tabulation of H *Function.* H = 870 log log (cS. + 0·6) + 154.

Kin. Vis. cS.	H.					Kin. Vis. cS.	H.				
	0.	0·2.	0·4.	0·6.	0·8.		0.	0·2.	0·4.	0·6.	0·8.
2	−178	−151	−126	−104	− 85	21	263	264	265	266	267
3	− 67	− 52	− 38	− 25	− 13	22	269	270	271	272	273
4	− 1	9	19	28	36	23	274	275	276	277	278
5	44	52	59	66	73	24	279	280	281	281	282
6	79	85	90	96	101	25	283	284	285	286	287
7	106	111	116	120	124	26	288	289	289	290	291
8	128	132	136	140	144	27	292	293	294	294	295
9	147	151	154	157	160	28	296	297	298	298	299
10	163	166	169	172	175	29	300	301	301	302	303
11	178	180	183	185	188	30	304	304	305	306	306
12	190	192	195	197	199	31	307	308	308	309	310
13	201	203	206	208	210	32	310	311	312	312	313
14	211	213	215	217	219	33	314	314	315	316	316
15	221	222	224	226	227	34	317	317	318	319	319
16	229	231	232	234	235	35	320	320	321	322	322
17	237	238	240	241	243	36	323	323	324	324	325
18	244	245	247	248	249	37	326	326	327	327	328
19	251	252	253	255	256	38	328	329	329	330	331
20	257	258	259	261	262	39	331	332	332	333	333

Kin. Vis. cS.	H.									
	0.	1.	2.	3.	4.	5.	6.	7.	8.	9.
40	334	336	339	341	343	345	347	349	352	354
50	355	357	359	361	363	364	366	368	369	371
60	372	374	375	377	378	380	381	382	384	385
70	386	387	388	390	391	392	393	394	395	397
80	398	399	400	401	402	403	404	405	406	407
90	408	409	410	410	411	412	413	414	415	415
100	416	417	418	419	420	420	421	422	423	423
110	424	425	425	426	427	428	428	429	430	430
120	431	432	432	433	433	434	435	435	436	437
130	437	438	438	439	439	440	441	441	442	442
140	443	443	444	444	445	446	446	447	447	448
150	448	449	449	450	450	450	451	451	452	452
160	453	453	454	454	455	455	456	456	456	457
170	457	458	458	459	459	460	460	460	461	461
180	461	462	462	463	463	463	464	464	465	465
190	465	466	466	466	467	467	468	468	468	469

Kin. Vis. cS.	H.									
	0.	10.	20.	30.	40.	50.	60.	70.	80.	90.
200	469	473	476	479	482	485	487	490	492	495
300	497	499	501	503	505	507	509	511	512	514
400	515	517	518	520	521	523	524	525	527	528
500	529	530	531	533	534	535	536	537	538	539
600	540	541	542	543	544	545	546	547	547	548
700	549	550	551	551	552	553	554	554	555	556
800	557	557	558	559	559	560	561	562	562	563
900	563	564	565	565	566	566	567	567	568	569
	H.									
	0.	100.	200.	300.	400.	500.	600.	700.	800.	900.
1000	569	574	578	583	587	591	594	597	600	603
2000	605	608	610	612	614	616	618	620	621	623
3000	625	626	628	629	631	632	633	634	636	637
4000	638	639	640	641	642	643	644	645	646	647
5000	648	649	650	651	652	652	653	654	655	656
6000	656	657	658	658	659	660	660	661	662	662
7000	663	664	664	665	665	666	666	667	667	668
8000	668	669	670	670	671	671	671	672	672	673
9000	673	674	674	675	675	676	676	677	677	677
	H.									
	0.	1000.	2000.	3000.	4000.	5000.	6000.	7000.	8000.	9000.
10,000	678	681	684	688	691	694	696	699	701	703
20,000	705	707	709	711	712	714	715	717	718	719
30,000	720	722	723	724	725	726	727	728	729	730
40,000	731	732	732	733	734	735	736	736	737	738
50,000	739	739	740	741	741	742	743	743	744	744
60,000	745	746	746	747	747	748	748	749	749	750
70,000	750	751	751	752	752	753	753	753	754	754
80,000	755	755	756	756	756	757	757	758	758	758
90,000	759	759	759	760	760	760	761	761	761	762
100,000	762	762	763	763	763	764	764	764	764	765

Keith and Roess. Using equation (4), points of intersection of these lines of constant viscosity with lines of constant viscosity slope factor were determined for several values of the V.S.F. ranging from 150 to 450. The best smooth curve was drawn through these points to establish lines of constant viscosity slope factor. The process was then reversed, and from equation (4) lines of constant viscosity calculated, and drawn intersecting these lines of constant viscosity slope factor. The chart was revised to give better agreement with experiment by a repetition of the same method. The final chart was drawn from these adjusted lines of constant viscosity slope factor.

It was found possible to represent the greater part of the viscosity correlation rather accurately by means of the equation

$$\text{Mol. Wt.} = 180 + S(H_{100} + 60) \quad . \quad . \quad . \quad . \quad (6)$$

where S is a function of the viscosity slope factor. Values of S are given in Table III for all unit values of the V.S.F. from 190 to 319.

TABLE III.

Values of S *Functions for Use in Calculation of Molecular Weights using Equation* 6.

Visc. slope factor, H100–H210.	*S* function.									
	0.	1.	2.	3.	4.	5.	6.	7.	8.	9.
190	1·214	1·204	1·194	1·184	1·173	1·163	1·152	1·141	1·131	1·120
200	1·109	1·099	1·088	1·078	1·067	1·056	1·046	1·035	1·025	1·015
210	1·005	0·995	0·985	0·975	0·965	0·956	0·946	0·936	0·927	0·917
220	0·908	0·899	0·889	0·880	0·870	0·861	0·852	0·843	0·834	0·824
230	0·815	0·806	0·797	0·788	0·779	0·771	0·762	0·754	0·746	0·737
240	0·729	0·721	0·713	0·705	0·696	0·689	0·681	0·673	0·665	0·657
250	0·649	0·642	0·634	0·626	0·618	0·611	0·603	0·596	0·589	0·581
260	0·574	0·567	0·560	0·552	0·545	0·538	0·532	0·525	0·518	0·512
270	0·506	0·500	0·493	0·487	0·481	0·475	0·469	0·464	0·458	0·452
280	0·446	0·440	0·435	0·429	0·424	0·419	0·414	0·409	0·404	0·399
290	0·394	0·390	0·385	0·381	0·376	0·372	0·368	0·364	0·360	0·356
300	0·352	0·348	0·345	0·341	0·338	0·334	0·330	0·327	0·324	0·320
310	0·317	0·314	0·310	0·308	0·304	0·301	0·298	0·295	0·292	0·289

For oils with viscosity slope factors between 220 and 310, S is given to a good approximation by the equation

$$S = 4{\cdot}146 - 1{\cdot}733 \log (\text{V.S.F.} - 145) \quad . \quad . \quad . \quad (7)$$

For oils with viscosities at 210° F less than 30 centiStokes, this range includes all oils from —40 to 100 V.I., which is the major part of the useful range of equation (6). However, combination of equations (6) and (7) results in a molecular-weight equation which is rather complicated; the use of Table III reduces the number of constants by three and eliminates the use of a table of logarithms.

Accuracy of Mol. Wts. Calculated by Fig. 1 *and previous Correlations.*

A tabulation was prepared listing the molecular weights of all oils as calculated by equation (1), the Keith and Roess chart,* the viscosity correlation of Fig. 1; and for the data of Mair and co-workers also by equation (6); together with the percentage deviations from the experimental

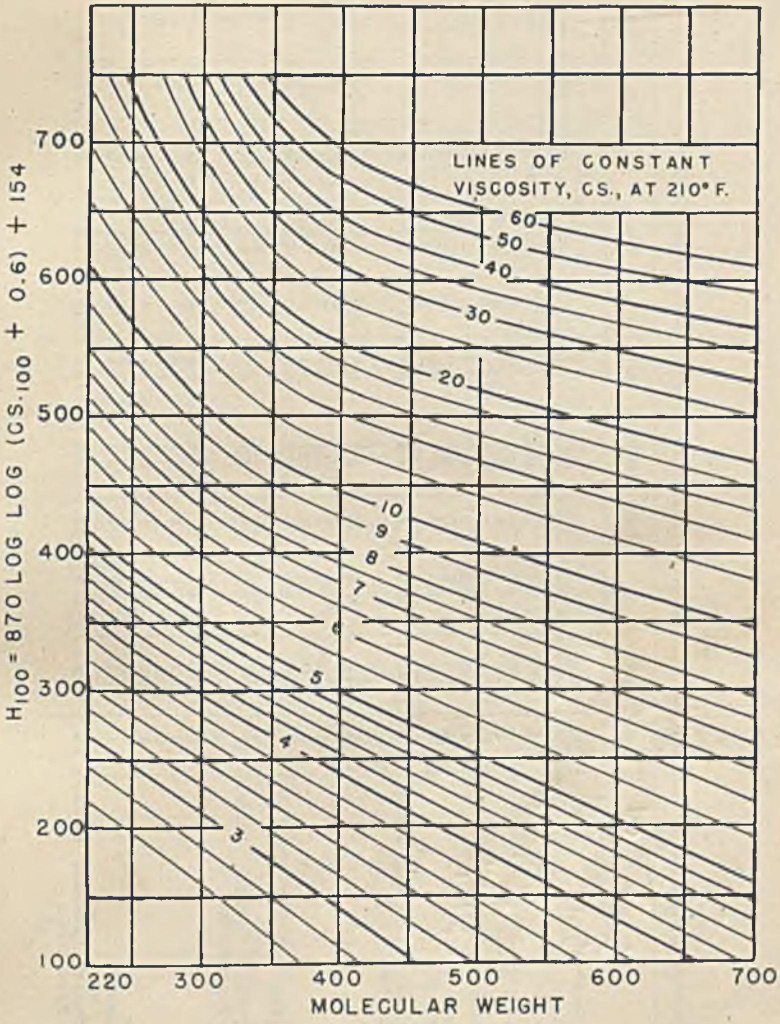


FIG. 1.

CORRELATION OF MOLECULAR WEIGHTS OF LUBRICATING OILS WITH VISCOSITIES AT 100° F AND 210° F.

---

* With the exception of oils whose molecular weights were listed in the paper of Keith and Roess,[18] the molecular weights by the Keith and Roess chart were obtained from a large-scale reproduction of it prepared by measuring the points of intersection of the lines with the aid of a magnifying glass and scale, and plotting these on graph paper. The chart so obtained gave molecular weights agreeing on the average to within ± 2 units with the values listed by Keith and Roess, which is sufficiently precise for purposes of comparison. The original of Fig. 1 was approximately 50 × 70 cm.

TABLE IV.

Statistical Evaluation of Methods for Calculation of Molecular Weights from Viscosity Data.

Range of VSF.	Source of data.	Fenske eqn.			Keith and Roess chart.			Fig. 1.			Eqn. 6.		
		No. of oils.	Aver. dev., per cent.	Dev. of aver., per cent.	No. of oils.	Aver. dev., per cent.	Dev. of aver., per cent.	No. of oils.	Aver. dev., per cent.	Dev. of aver., per cent.	No. of oils.	Aver. dev., per cent.	Dev. of aver., per cent.
221–240	Mair *et al*	—	—	—	4	12·1	−12·1	4	0·93	− 0·48	4	1·2	− 0·40
	Varteressian	5	19·7	−19·7	5	10·1	+10·1	5	1·9	+ 0·36	5	1·9	+ 1·2
	Keith and Roess	2	17·3	−17·3	2	0·85	+ 0·35	2	7·1	+ 7·1	2	8·1	+ 8·1
	Davis and McAllister	2	8·2	− 8·2	9	4·6	− 0·04	9	12·3	+12·3	9	12·9	+12·9
	Von Fuchs and Anderson	2	3·5	− 2·6	2	8·1	+ 8·1	2	22·1	+22·1	—	—	—
	Fenske [*]	—	—	—	—	—	—	1	7·7	+ 7·7	—	—	—
	Synthetic hydrocarbons : [*] Mikeska, Landa, Schiessler, Neyman-Pilat	1	10·5	−10·5	4	9·4	− 9·4	13	8·7	+ 8·4	—	—	—
241–260	Mair *et al*	10	12·4	−12·4	20	8·8	− 8·8	20	1·7	− 0·28	20	1·9	− 0·30
	Varteressian	5	11·7	−11·7	5	7·5	+ 7·5	5	2·9	+ 0·04	5	2·6	− 0·58
	Fenske [10]	2	0·40	+ 0·2	2	2·4	+ 2·4	2	10·9	+10·9	2	11·2	+11·2
	Keith and Roess	6	7·0	− 4·4	8	1·7	− 1·4	9	7·5	+ 7·5	10	9·5	+ 9·5
	Davis and McAllister	5	3·8	− 3·7	6	4·5	+ 4·2	6	12·1	+12·1	6	13·2	+13·2
	Von Fuchs and Anderson	1	6·3	− 6·3	1	3·9	− 3·9	1	8·4	+ 8·4	—	—	—
	Fenske [*]	—	—	—	—	—	—	27	5·5	+ 5·5	—	—	—
	Synthetic hydrocarbons : [*] Mikeska, Landa, Cosby, Schiessler, Neyman-Pilat	17	12·7	−12·3	26	9·1	8·5	43	5·0	+ 0·2	—	—	—
1–280	Mair *et al*	21	4·7	− 4·7	24	5·2	− 5·2	24	1·2	+ 0·65	24	1·2	+ 0·55
	Varteressian	2	1·3	− 1·3	2	1·2	− 0·68	3	5·6	+ 5·6	3	6·2	+ 6·2
	Fenske [10]	6	2·4	− 2·4	6	1·4	− 1·1	6	4·1	+ 4·1	6	3·6	+ 3·6
	Keith and Roess	4	4·0	+ 0·87	4	3·1	+ 3·1	4	10·6	+10·6	4	7·7	+ 7·7
	Davis and McAllister	2	6·5	+ 6·5	2	3·8	+ 3·8	2	13·2	+13·2	2	13·0	+13·0
	Von Fuchs and Anderson	4	7·0	+ 7·0	4	5·4	+ 5·4	4	14·0	+14·0	—	—	—
	Fenske [*]	—	—	—	—	—	—	37	3·5	+ 2·7	—	—	—
	Synthetic hydrocarbons : [*] Mikeska, Landa, Cosby, Schiessler, Neyman-Pilat	13	10·8	−10·8	11	9·4	− 9·4	19	5·8	− 4·5	—	—	—
281–300	Mair *et al*	11	3·3	+ 2·7	12	5·4	− 5·4	14	1·2	− 0·58	14	1·5	− 0·30
	Varteressian	—	—	—	3	2·2	+ 2·2	3	6·7	+ 6·7	3	7·7	+ 7·7
	Fenske [10]	4	1·2	− 0·9	4	7·2	− 7·2	4	4·8	− 4·8	4	2·5	− 2·5
	Keith and Roess	—	—	—	5	1·8	+ 1·0	6	5·4	+ 5·4	6	6·8	+ 6·8
	Von Fuchs and Anderson	1	9·0	+ 9·0	1	5·5	+ 5·5	1	10·6	+10·6	—	—	—
	Fenske [*]	—	—	—	—	—	—	35	2·7	+ 2·3	—	—	—
	Synthetic hydrocarbons : Mikeska, Schiessler, Neyman-Pilat	1	1·3	+ 1·3	2	3·3	− 3·3	7	6·3	+ 0·3	—	—	—
301–320	Mair *et al*	13	7·3	+ 7·3	12	7·0	− 7·0	13	0·89	− 0·19	13	1·3	+ 0·48
	Varteressian	—	—	—	—	—	—	2	2·1	+ 2·1	2	5·1	+ 5·1
	Fenske [10]	2	2·2	− 2·2	2	5·6	− 1·7	2	5·9	− 5·9	2	4·2	− 4·2
	Keith and Roess	12	10·4	+10·4	13	2·8	− 1·1	13	3·6	+ 3·6	13	4·9	+ 4·9
	Fenske [*]	—	—	—	—	—	—	11	4·2	+ 2·8	—	—	—
	Synthetic hydrocarbons : Neyman-Pilat	3	7·2	− 0·4	2	7·5	− 7·5	3	11·7	−11·7	—	—	—
321–350	Mair *et al*	18	9·5	+ 4·6	16	16·2	−16·2	18	2·0	− 1·1	18	2·3	− 1·1
	Keith and Roess	1	12·4	+12·4	1	8·1	+ 8·1	1	0·9	+ 0·93	1	2·5	+ 2·5
	Synthetic hydrocarbons : Neyman-Pilat	1	1·7	− 1·7	1	14·3	−14·3	1	15·6	−15·6	—	—	—
351–400	Mair *et al*	8	5·6	+ 2·4	11	>32·9	−32·9	11	0·55	− 0·13	11	3·0	− 2·4
Totals	Petroleum cuts	149	7·28	− 0·65	186	8·06	− 5·3	307	3·81	+ 3·04	189	4·20	− 2·75
	Synthetic hydrocarbons	36	10·9	−10·0	46	9·01	− 8·68	86	6·2	− 0·19	—	—	—
	All oils	185	7·98	− 1·94	232	8·26	− 5·98	393	4·34	+ 2·34	—	—	—

[*] *iso*Paraffins omitted.

molecular weights. Shortly after this paper was first presented,* Fenske and collaborators [9] published data on 113 lubricating-oil fractions derived from six crudes of varying types. Molecular weights of these cuts have been calculated from viscosity data using Fig. 1; calculation of the molecular weights using equations (1) and (6) or the chart of Keith and Roess has not been attempted.

In order to better compare the accuracy of these four methods for calculating molecular weights, the oils were grouped according to the V.S.F., and the percentage deviations from the experimental molecular weights averaged for all oils within each group. In order to show the absolute accuracy of each method, as well as to determine a tendency of any method to consistently err in the direction of either too large or too small molecular weights, the averages were taken both without regard to the sign of the deviation (aver. dev.), and also by taking the sign into account (dev. of aver.). Because of the large difference observed, the data of each investigator were for the most part thus averaged separately. The results of this statistical comparison are given in Table IV, and in Figs. 2, 3, and 4.

Figs. 2 and 3 graphically compare the accuracy of the four methods of calculating the molecular weight for the data of Mair *et al.* The average percentage deviation for a given range of V.S.F. is plotted at the mid-point of the range. It is strikingly apparent that the accuracy of equation (1) or of the Keith and Roess chart is dependent on the viscosity-temperature behaviour of the oil being considered. Fig. 1 correlates the molecular weights (data of Mair *et al*) to an average accuracy of slightly more than 1 per cent, which is very satisfactory, since the uncertainty in the molecular weight determinations was stated to be ±1 per cent.

From Figs. 2 and 3 it is evident that equation 6 represents Fig. 1 quite closely for oils with viscosity slope factors up to 300, and is reasonably accurate even for oils of very high V.S.F. Nevertheless, equation (6) is not recommended for use with oils whose V.S.F. exceeds 310, since for oils of certain ranges of viscosity the error might be considerable. However, practically all commercial lubricating oils fall within the range 200–310 V.S.F., since a V.S.F. of 310 corresponds to viscosity indices of about −50 to −150, depending on the viscosity, while a V.S.F. of 200 corresponds to viscosity indices of 110–160.

The correspondence between the molecular weight calculated from Fig. 1 and the experimental values (deviation of average) is shown in Fig. 4 as a function of the V.S.F. for all investigators listing sufficient data. The small figure opposite each point is the number of oils averaged in that particular range of V.S.F. It is apparent that there is a wide divergence between the data of the various investigators. There are two possible explanations for this : (*a*) Fig. 1 is not applicable to oils from a wide variety of sources; or (*b*) certain of the molecular weight data is considerably in error. The second possibility is considered the more probable from the evidence given below, although it would be very desirable to have additional accurate molecular-weight data on oils from a variety of sources.

---

* Paper presented before the Petroleum Division of the American Chemical Society, Memphis, Tenn., April, 1942.

In Table V the accuracy of the viscosity-molecular weight correlation for oils derived from six divergent crude types is indicated, using the recent data of Fenske and collaborators.[9] These data are the more interesting since they appeared subsequent to the development of the correlation, and consequently the correlation can in no way be biased in favour of this

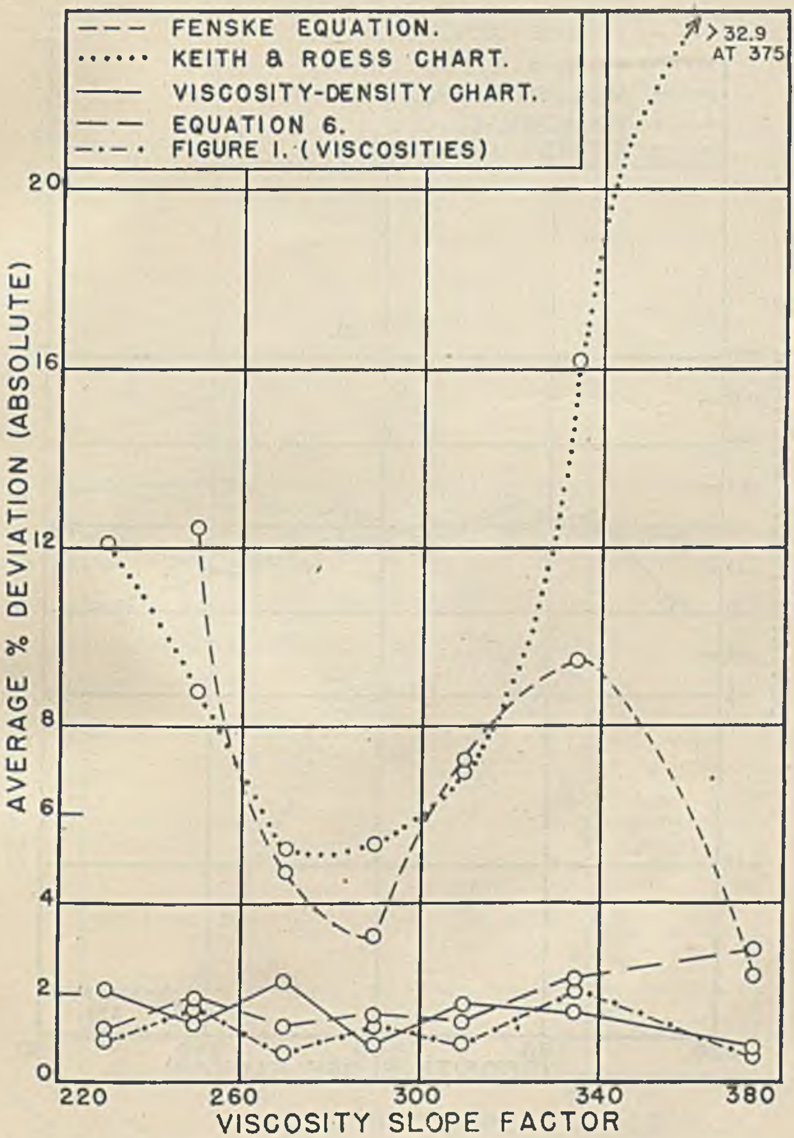


FIG. 2.

RELATIVE ACCURACY OF METHODS FOR CALCULATION OF MOLECULAR WEIGHT (DATA OF MAIR).

particular data. In every case but that of Mid-Continent No. 2 the average deviation of the calculated molecular weight is within the estimated

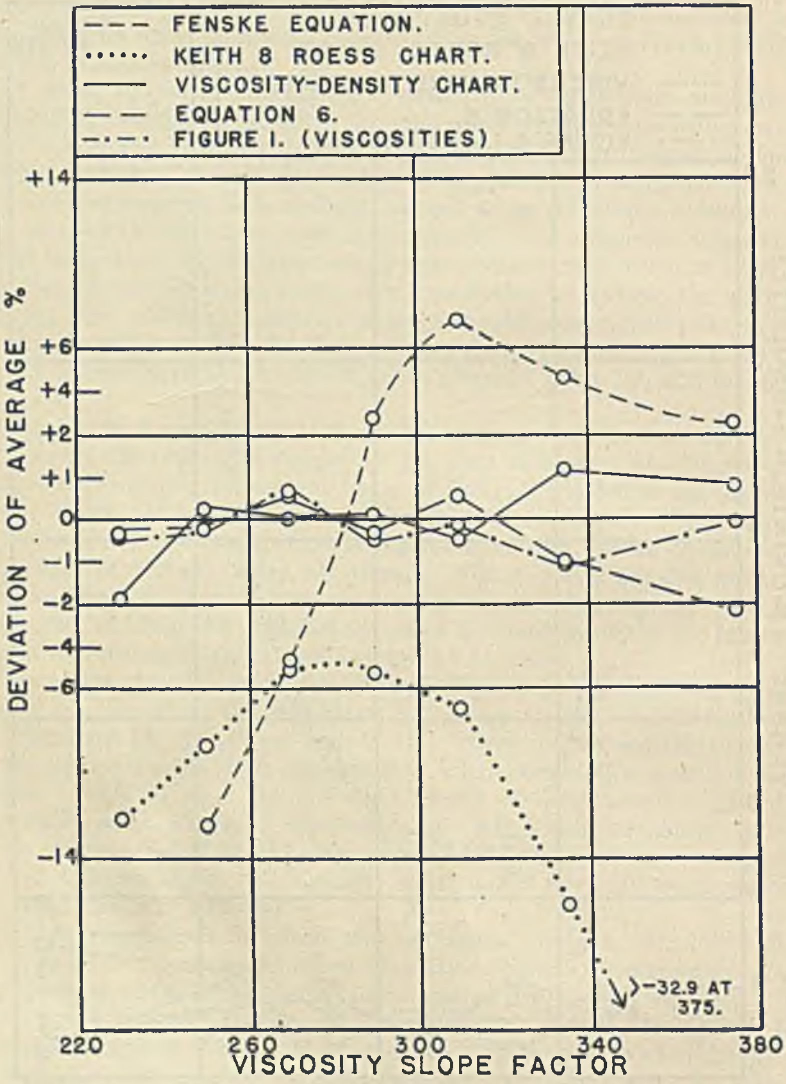


Fig. 3.

RELATIVE ACCURACY OF METHODS FOR CALCULATION OF MOLECULAR WEIGHT (DATA OF MAIR).

precision of the experimental molecular weight determinations, which was stated to be 4 to 5 per cent.

For all the data of Davis and McAllister,[5] whose samples were derived from Pennsylvania crudes, Fig. 1 gives rise to calculated molecular weights consistently much larger (approx. 12 per cent.) than the experimental values. However, Fig. 1 is in very good agreement with most of the data

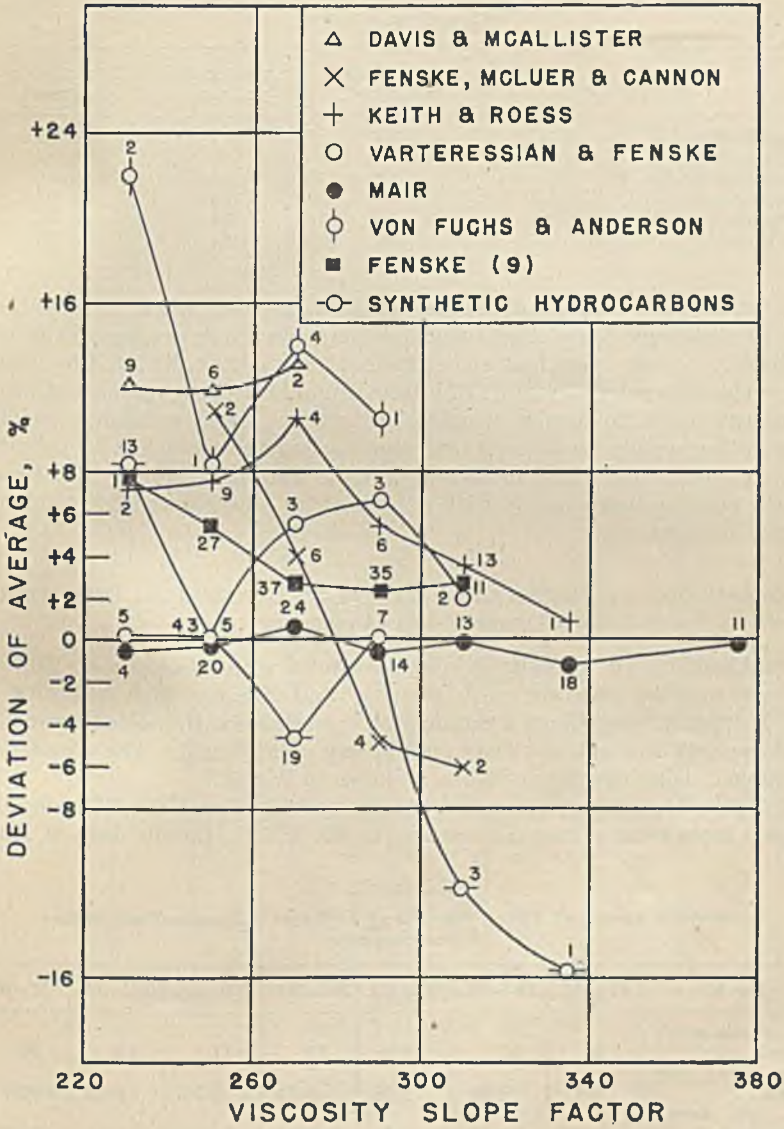


Fig. 4.

AGREEMENT OF VISCOSITY CORRELATION OF FIGURE 1 WITH DATA OF DIFFERENT INVESTIGATORS.

of Varteressian, Fenske, and Smith,[37] also derived from Pennsylvania crude; and with the Pennsylvania oils of Fenske.[9]

TABLE V.

Accuracy of Viscosity–Molecular Weight Correlation for Oils Derived from Various Crude Sources.

(Data of Fenske [3].)

Source of oil.	No. of oils averaged.	Aver. dev., per cent.	Dev. of aver., per cent.
Pennsylvania	23	4·7	+3·7
Rodessa	16	1·4	+1·1
Mid-Continent No. 1 . . .	19	3·7	+2·9
Mid-Continent No. 2 . . .	19	6·3	+6·3
California	17	4·1	+3·2
Gulf Coast	19	2·4	+2·4

Varteressian, Fenske, and Smith [37] refer to the derivation of a modified form of Keith and Roess chart, which, so far as we are aware, has never been published. These investigators list molecular weights calculated by means of this chart for a large number of lubricating-oil fractions, on most of which no experimental molecular weights are given; these molecular weights agree rather well in most cases with those calculated from Fig. 1. For ten of the eighteen oils whose molecular weights were determined, Fig. 1 gave results agreeing more closely with experiments; and showed less tendency toward large errors.

CORRELATION OF MOLECULAR WEIGHTS OF LUBRICATING OILS WITH DENSITY AND VISCOSITY.

Combinations of viscosity-gravity constant with viscosity at 210° F, viscosity-gravity constant with density, and density with viscosity at 210° F appeared capable of a rather good correlation with molecular weight. Of these only the last was examined in any great detail. The correlation developed, using the data of Mair, is shown in Fig. 5.*

In Table VI, the percentage deviations from the experimental molecular weights have been averaged according to the V.S.F., for the data of Mair.

TABLE VI.

Average Accuracy of Fig. 5 for Oils of Different Viscosity–Temperature Characteristics.

V.S.F.	221–40.	241–60.	261–80.	281–300.	301–20.	321–50.	351–400.
No. of oils averaged . .	4	17	19	12	11	13	10
Aver. dev., per cent. . .	2·1	1·30	2·28	0·83	1·76	1·58	0·77
Dev. of aver., per cent. .	−1·9	+0·18	+0·05	+0·08	−0·51	+1·14	+0·77

The data on the fifteen hydrogenated oils have not been included for reasons explained below.

---

* After completing this work it was found that a similar correlation of Engler viscosity at 50° C., density and molecular weight had been published by Kadmer.[17]

These averages have also been plotted in Figs. 2 and 3. It can be seen that, excluding the hydrogenated oils, the results are rather accurate, though somewhat less so than those from Fig. 1.

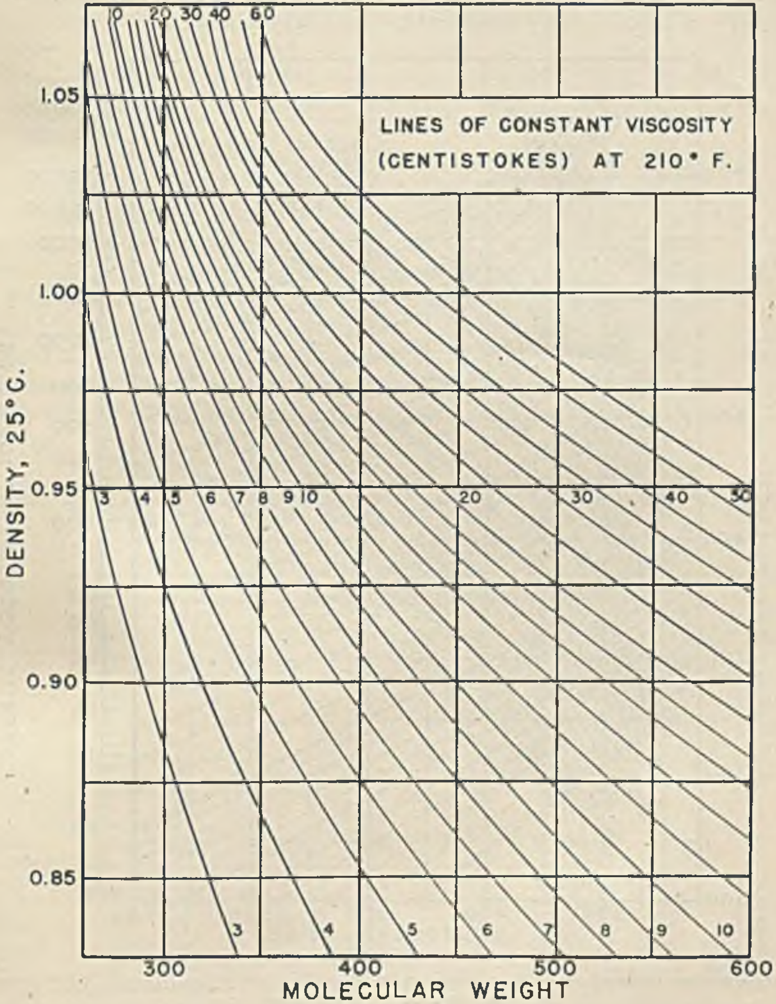


Fig. 5.

CORRELATION OF MOLECULAR WEIGHTS OF LUBRICATING OILS WITH DENSITY AND VISCOSITY AT 210° F.

Correlation of Vis_{100}, Vis_{210}, *Density and Molecular Weight. Calculation of Viscosities, Density and Viscosity Index.*

Fig. 5 and Fig. 1 may be combined in one correlation. This has been done, with minor modification; the result is Fig. 6. This chart correlates viscosities at 100° F. and 210° F, and density at 25° C, with the molecular weight. Any two of these four physical constants may be used to calculate approximate values of the other two. Molecular weights are less easy to determine experimentally than the other constants, and will therefore not often be useful in estimating viscosities or density. However, it is of some theoretical interest to note that given molecular weight and density, the viscosity of an oil at any temperature may be estimated.

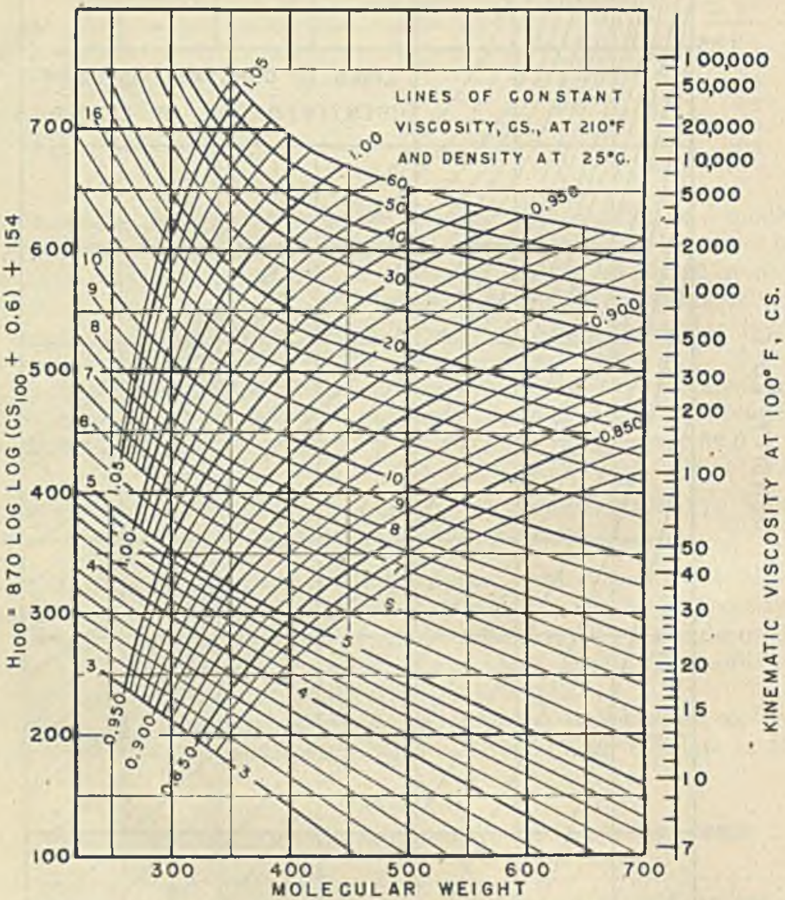


FIG. 6.

COMBINED CORRELATION OF MOLECULAR WEIGHTS OF LUBRICATING OILS WITH VISCOSITIES AND DENSITY.

Several correlations of viscosity and density data have been previously proposed—namely, the viscosity-gravity constants at 100° F and 210° F of Hill and Coats,[16] the gravity index system of McCluer and Fenske,[28] the relation of viscosity and gravity to the U.O.P. characterization factor given by Watson, Nelson, and Murphy [42] and the Viscosity–Temperature Zone–Gravity classification of oils of Larson and Schwaderer.[21] In all but the last of these, the relation as given is indirect. No data indicating the accuracy with which viscosities or density could be estimated are given by Larson.

The accuracy with which viscosities, densities, or molecular weights may be estimated by the use of Fig. 6 is indicated in Table VII for oils derived from a variety of crude types. It is worthy of note that the accuracy for the estimation of viscosity or density is greatest for the Pennsylvania oils, even though the correlation was derived primarily from data on a Mid-Continent oil. This is probably the result of the less complex nature (smaller number of rings per molecule) of the Pennsylvania oils. The greatest deviations are observed for the California and Gulf Coast oils.

Estimation of the viscosity at 210° F is consistently more accurate than the estimation of the 100° F viscosity. This is probably in part the result of the much greater range of viscosity covered at 100° F. With the exception of the data of Mair, calculation of the molecular weight from viscosity and density is slightly more accurate when the viscosity at 210° F is used. Comparison of Table VII with Table V for the data of Fenske,[9] indicates that, in general, the viscosity correlation gives better results than the combination of viscosity with density for calculation of molecular weights; however the reverse is true in the case of Mid-Continent No. 2 and the Pennsylvania oil.

TABLE VII.

Accuracy of Fig. 6 for Estimation of Viscosities and Density, and for Calculation of Molecular Weights from Density and One Viscosity.

Source of oil.	No. of samples averaged.	Reference.	Vis. at 210° F. from V_{100}–density, aver. dev., per cent.	Vis. at 100° F. from V_{210}–density, aver. dev., per cent.	Density from V_{100}–V_{210}, aver. dev., g./ml.	Mol. wt. from V_{210}–density, aver. dev., per cent.	Mol. wt. from V_{100}–density, aver. dev., per cent.
Oklahoma . .	88	24, 26, 27	2·6	4·4	0·005	2·5	2·2
Pennsylvania .	35	37	1·1	1·8	0·002	—	—
" .	23	9	0·7	0·7	0·001	3·4	3·7
Rodessa . .	16	9	2·5	3·7	0·006	1·6	2·2
Mid-Continent :							
No. 1 . .	17	9	2·2	3·5	0·004	5·1	5·7
No. 2 . .	19	9	0·9	1·2	0·003	5·9	5·9
California . .	17	9	6·6	9·4	0·011	7·8	9·7
Gulf Coast .	19	9	5·3	7·2	0·009	5·9	7·8

Approximate values for V.S.F. may be obtained from the density or molecular weight and either the 100° F or 210° F viscosity by first calculating the unknown viscosity, and making use of the proper tables.

Limitations of Density Correlations, and their Further Evaluation.

While Fig. 5 and the density correlations of Fig. 6 give reasonably good results for the lubricant fractions considered in Tables VI and VII, they possess some limitations not applicable to Fig. 1. The calculated molecular weights of the fifteen hydrogenated oils of Mair, Willingham, and Streiff[27] are for the most part considerably higher than the experimental values, the extent of the deviation increasing roughly with the aromatic content of the original oil, and thus with the percentage of hydro-aromatic rings in the hydrogenated samples. Some of the samples of Mair and Schicktanz [24] are aromatic-free, and thus consist of molecules containing naphthene rings and paraffin chains, as do the hydrogenated oils. Specific refraction data indicate that the hydrogenated oils have a greater number of rings per molecule than the extracted cuts, three to four rings per molecule for most of the hydrogenated oils as compared to one to two for the latter. For the one hydrogenated oil with less than two rings per molecule, agreement with Fig. 5 is nearly perfect.

It will be shown later in the discussion of synthetic hydrocarbons that, while Fig. 1 gives rather good results for a variety of hydrocarbon types, the viscosity–density correlations of Fig. 5 and Fig. 6 are quite sensitive to composition, as has been indicated by the results for the hydrogenated oils. The correlation of viscosities with density and the viscosity–density–molecular weight correlations are therefore quite empirical; their validity for petroleum fractions must rest upon a reasonably close similarity in average composition for cuts derived from various sources. The accuracy of molecular weights calculated from density and viscosity is the problem of main interest; however, the available data do not cover a sufficiently wide cross-section of oils to establish well the general applicability of the viscosity–density correlations to petroleum fractions in view of the wide deviations for the synthetic hydrocarbons. It was therefore considered desirable to further evaluate the viscosity–density correlation by an indirect method.

For a sample whose experimental density, and that calculated from viscosities by means of Fig. 6 are identical, the molecular weights calculated from viscosities or from either viscosity and the density will also be identical. If the calculated density is too low, molecular weights calculated from density and viscosity will be less than those calculated from viscosities; if the calculated density is too large, they will be greater. The viscosity molecular weights, being relatively insensitive to composition, may be taken as approximately correct; and hence the accuracy of the viscosity–density–molecular weight correlations can be assessed in terms of the accuracy of the correlation of viscosities with density.

Table VIII summarizes data for a large number of petroleum fractions of diverse origins. In the majority of cases the agreement is very satisfactory; however, in several instances deviations much larger than the average are observed. A negative deviation in the calculated density indicates an above-average aromaticity; a positive deviation, on the other hand, indicates an above-average amount of polynuclear naphthenes. (See discussion of synthetic hydrocarbons.) The poorest agreement was observed for the extract fractions derived from a Van Zandt, Texas crude; for a number of these, negative deviations exceeding 0·02 g/ml were observed. Distillate cuts from this crude also exhibit abnormal negative deviation. This crude is therefore characterized as very aromatic. The raffinate fractions from this crude, however, were in rather good agreement with the correlation.

In several cases, larger than normal positive deviations were also observed, namely for the California and Gulf Coast cuts of Fenske [9] and the Sugarland

TABLE VIII.

Accuracy of Viscosity–Density Correlation for Petroleum Fractions.

Source of Oils.	Treatment.	No. of oils.	No. of oils for which error in calc'd. density is <0·006 g/ml.	Aver. dev., g/ml.	Dev. of aver., g/ml.	Reference.
Oklahoma	Extracts, distilled and re-extracted	129	90	0·0051	−0·00003	26
,,	Raffinates, distilled and re-extracted	27	24	0·0041	+0·0033	24
Pennsylvania	Vacuum distillation	23	23	0·0014	−0·0010	9
Rodessa	,, ,,	16	10	0·0064	−0·0064	9
Mid-Continent No. 1	,, ,,	19	13	0·0045	+0·0037	9
,, No. 2	,, ,,	19	18	0·0027	−0·0008	9
California	,, ,,	17	3	0·0111	+0·0111	9
Gulf Coast	,, ,,	19	9	0·0089	+0·0086	9
Bosco, La.	Solvent extracts	23	22	0·0017	−0·0011	9
,,	Distillates	12	9	0·0051	−0·0047	9
,,	Raffinates, distilled	12	12	0·0018	−0·0013	9
,,	Extract, distilled	11	4	0·0075	−0·0073	9
Sugarland (Gulf Coast)	Vacuum distillation	20	6	0·0105	+0·0103	15
Van Zandt (Texas)	,, ,,	20	0	0·0117	−0·0117	3
,, ,,	Distillates, solvent extracts	84	14	0·0140	−0·0137	3
,, ,,	Distillates, solvent raffinates	52	40	0·0050	−0·0046	3
Various	Various	90	53	0·0050	−0·0016	28
,,	Extracts, raffinates	14	7	0·0059	+0·0004	18
Pennsylvania	Distillation, extraction	19	13	0·0060	−0·0060	5
Various [a]	Vacuum distillation	14	6	0·0070	+0·0070	10
Various	Commercial cuts	10	10	0·0025	−0·0001	35
Pennsylvania	Extraction, distillation	16	15	0·0021	−0·0010	11
Various	Commercial cuts	6	4	0·0052	+0·0010	29
Unknown	Unknown	10	7	0·0070	+0·0012	7
Totals, all oils		682	412	0·0065	−0·0023	—
Totals, excluding Van Zandt		526	358	0·0053	+0·00013	—

(Gulf Coast) cuts of Hersh.[15] These crudes are therefore indicated to be more than ordinarily naphthenic, especially the fractions of higher molecular weight.

Because almost one fourth of the total number of oils listed in Table VIII are derived from the Van Zandt crude, which showed the largest deviations, averages were also computed for all oils excepting those from the Van Zandt crude. Of the 526 oils in this group, for 358 or 68 per cent, the calculated density was in error by 0·006 g/ml or less, the average error being about 0·005 g/ml. The deviation of the average is only 0·00013 g/ml, indicating that the correlation represents a good average for petroleum fractions obtained from varied sources, though it was based on fractions from an Oklahoma crude. The agreement with the correlation is in fact considerably better than might have been anticipated on the basis of the pure compound data, and indicates a really remarkable degree of uniformity in the average composition of lubricant fractions from various origins. The average deviation from the correlation of 0·005 g/ml in density corresponds to about 1–3 per cent difference in molecular weights calculated from viscosities or from viscosity and density. Because of the angle between the lines of constant viscosity at 210° F and the lines of constant density in Fig. 6, the molecular weight calculated from density and viscosity at 210° F always deviates less from the value calculated from viscosities than the molecular weight calculated from density and viscosity at 100° F.

Data are given by Watson[42] on several cuts from a residuum derived from a cracked Mid-Continent gas oil. Several of these deviate rather widely from the density-viscosity correlation, the maximum error in calculated density being −0·057 g/ml.

Physical properties of a considerable number of synthetic lubricating oils prepared by polymerization of a series of olefins are reported by Sullivan.[36] In nearly all cases the calculated densities were much too high, in one case by as much as +0·095 g/ml. However the polymer of *cyclo*hexene, the only cyclic olefin included, deviated by −0·073 g/ml. The polymers of cracked distillates were in much better agreement than those of the low molecular-weight olefins.

The foregoing facts indicate that the viscosity–density correlations will be satisfactory for naturally occurring petroleum fractions of diverse origin, but should not be applied to cracked products or synthetic oils. Caution should be exercised in applying these correlations to petroleum fractions likely to contain an unusual concentration of either polycyclic aromatics or polycyclic naphthenes, such as certain highly aromatic extracts, naphthenic white oils of high molecular weight, or hydrogenated products from highly aromatic extracts. Fractions with molecular weights exceeding 375 derived from Gulf Coast or California crudes may also be expected to deviate.

The data of Fenske[9] for California and Gulf Coast oils and the data of Mair for hydrogenated aromatic extracts have shown that for the very naphthenic oils molecular weights obtained from viscosities are more accurate than those from viscosity and density. Except for highly aromatic fractions, it is probably best not to employ the density for the calculation of molecular weight if the density calculated from the viscosities by means of Fig. 6 differs by more than 0·0100 g/ml from the experimental value.

For highly aromatic extracts, the molecular weights calculated from viscosity and density appear to be fairly accurate in spite of the large deviations of polycyclic aromatics from the correlation. To a large extent, this appears to be the result of the crowding of the density lines in the region of high density, which causes the molecular weight to be less sensitive to density deviations. Thus, for an oil of high density the experimental density may deviate from the correlation by as much as 0·02 g/ml without giving rise to a difference of more than 4 or 5 per cent in the molecular weights calculated from viscosities or from viscosity and density. In addition, unless the extract is derived from a cut rather homogeneous with respect to molecular weight, polycyclic naphthenes will tend to be concentrated along with the aromatics;[25] the deviations for these types of hydrocarbons being in opposite directions, they will tend to neutralize each other. For the viscosity–density correlations the sensitivity for calculation of molecular weight is greatest in the region of high density and low molecular weight; on the other hand, because of the scarcity of data, the viscosity correlation is largely an extrapolation in this region. This extrapolation is somewhat uncertain due to the curvature of the constant viscosity lines in this area. For extracts of neutral oils exceeding 1·0 g/ml in density there is some indication that molecular weights calculated from viscosity and density may be more accurate than those calculated from viscosities alone. This may not be true for residua from severe cracking operations. More molecular weight data are needed on high-density oils which deviate from the viscosity–density correlation.

Conversion of Density at 25° *C to Density* 20/4 *or Specific Gravity* 60/60.

The correlation was developed on the basis of the density at 25° C due to the fact that the data used were given at that temperature. It is realized that the density at 20° C or the specific gravity 60/60 are more often of interest to petroleum chemists than the density at 25°. It can be shown from the temperature coefficients of density given by Lipkin and Kurtz [22] that for oils with molecular weights between 250 and 700 the density at 20° C may be obtained from that at 25° C simply by adding 0·003, with a maximum error of 0·0003; similarly the specific gravity at 60/60 is obtained from the density at 25° C by adding 0·007 with a maximum error of 0·0004. The accuracy of the correlation is not sufficient to require greater precision in the temperature coefficient.

Application of Viscosity Correlation to Synthetic Hydrocarbons.

Within the past few years a number of pure hydrocarbons in the lubricating-oil range have been synthesized, and it appeared of interest to determine whether viscosity–molecular weight correlations developed for lubricating oils could be extended to these pure hydrocarbons. The deviations of the calculated molecular weights from the theoretical ones are summarized in Table IV. The data on *iso*paraffins have not been included in these averages. For some recent data [33, 34] molecular weights have not been calculated by the Fenske equation or the chart of Keith and Roess. For a number of hydrocarbons prepared by Mikeska, the viscosities at 100° F could not be measured, and extrapolated values were given. It was found that on the whole discrepancies between calculated and theoretical molecular weights were larger for this group than for the remainder. Since it was believed that errors in extrapolation of the viscosity might be at least partly responsible, it was felt best to include only those hydrocarbons whose viscosities at 100° F were experimentally determined.

An examination of Table IV shows that for the great majority of the pure hydrocarbons the viscosity correlation of Fig. 1 gives molecular weights more accurately than equation (1) or the Keith and Roess chart.[18] The latter two correlations lead to molecular weights which are rather consistently too low. The molecular weights from Fig. 1 are not as accurate as for the majority of lubricating oils, but the deviations are divided rather equally between positive and negative.

It is of considerable interest to examine the effect of the structure of the hydrocarbon upon the degree of agreement with Fig. 1. In Table IX the hydrocarbons are averaged according to the type of ring structure. A rather wide variety of hydrocarbon types is represented, for most of which the calculated molecular weights are in reasonably good agreement with the theoretical ones.

Table X shows the effect of the percentage of ring carbon atoms on the accuracy of molecular weights calculated from viscosities. The naphthenes and aromatics fall in two distinct groups; for the former, with increase in the percentage of ring-carbon atoms, the deviation of the average becomes more positive, whereas for the aromatics the deviations become

TABLE IX.

Accuracy of Viscsity–Molecular Weight Correlation for Pure Hydrocarbons.

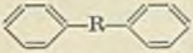
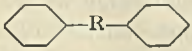
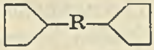
Ring structure exclusive of side chain.	No. of compounds.	Code No.	Aver. dev., per cent.	Dev. of aver., per cent.
	19	Mikeska 1, 3, 4–7; PSC 9, 52, 10, 68, 79–82, 87, 99, 101, 103; Neyman Pilat 2.	7·0	− 0·8
	10	Mikeska 17, 18, 20, 22, 23, 25, 27–29; Neyman Pilat C.	3·3	− 1·6
	1	Mikeska 41.	10·8	+10·8
	13	Mikeska 47, 48, 50, 51; PSC 12, 13, 18, 116; Neyman Pilat 6.	6·1	− 5·1
Three aromatic rings, separated.	2	PSC 89, 119.	6·4	− 6·4
	1	PSC 16	10·8	+10·8
	4	Mikeska 33–36.	3·9	+ 3·9
	14	Mikeska 12; PSC 60, 69, 75–78, 88, 91, 100, 102, 104; Neyman Pilat, 3, 4.	7·0	− 0·7
	4	Mikeska 38, 39; PSC 62.	11·5	+10·3
	1	Mikeska 46	3·0	+3·0
	7	Mikeska 52; PSC 11, 19, 65; Neyman Pilat 7; Landa-Evans 2.	4·6	− 1·2
Three-six-membered rings.	3	PSC 90, 115; Neyman Pilat 5.	7·5	+ 7·0
	1	PSC 108.	18	+18
	4	PSC 64, 74, 110, 117	9·2	− 1·5
	1	PSC 15	11·3	+11·3
	1	PSC 111.	2·6	+ 2·6
Three five-membered rings.	2	PSC 112, 113.	13·3	+13·3

TABLE X.

Effect of Percentage of Rings on Accuracy of Molecular Weight Calculated from Viscosities.

	100 per cent. chain.	Rings and Chain.						100 per cent. ring, naphthene.
		Percentage of ring carbon atoms.						
		14–34.		35–39.		60–80.		
		Aromatics.	Naphthenes.	Aromatics.	Naphthenes.	Aromatics.	Naphthenes.	
No. of hydrocarbons averaged . . .	21	24	21	20	12	2	5	1
Aver. dev., per cent. .	11·2	6·2	7·0	5·5	6·8	6·4	9·8	31
Dev. of aver., per cent. .	−10·1	−1·2	+0·5	−3·0	+3·4	−6·4	+9·5	+31

more negative. Except for highly refined stocks petroleum cuts usually contain both aromatic and naphthene rings; for such a mixture, the deviation should be less than for a pure hydrocarbon containing only one type of ring.

For naturally occurring distillate fractions, the percentage of rings ranges from 20–30 per cent for a Pennsylvania oil, to 50–60 per cent for a California oil.[9] Within that range the deviation of the average for the pure hydrocarbons is rather small.

A rather marked exception to the general agreement for most of the pure hydrocarbon types is observed in the case of *iso*paraffins; the calculated molecular weights being considerably and consistently too low. The viscosity–molecular weight correlation is thus not applicable to *iso*paraffins. There does not appear to be any valid evidence for the existence of *iso*paraffins in wax-free lubricating oils even of Pennsylvania origin,[25, 39] and even if they do exist, they are certainly present in relatively small amounts. For that reason, the data on *iso*paraffins were not included in the statistical averages in Table IV, thus restricting the comparison to synthetic hydrocarbons of types which might be present in petroleum in significant amounts.

The deviation of the average for the viscosity correlation of Fig. 1 so calculated for the synthetic oils is also plotted versus the V.S.F. in Fig. 3, for comparison with the petroleum cuts. For the most part the choice of the data of Mair in setting up the viscosity–molecular weight correlation is supported by the results for the synthetic hydrocarbons; however, some of the newer data appearing since the development of this correlation indicate that perhaps a revision downward of about 2 per cent in molecular weight for oils between 220 and 250 V.S.F. might be desirable. Additional accurate molecular weight data for petroleum cuts in this range are needed.

The fact that position isomerism has a definite and regular effect upon the accuracy of the viscosity-molecular weight correlation is shown by the results presented graphically in Fig. 7, for a series of phenyl eicosanes, *cyclo*hexyl eicosanes, and *n*-butyl docosanes. The similarity in the shape of the curves is very striking. The effect of conversion of the aromatic ring to a naphthene ring is well brought out by comparing the curves for the phenyl and *cyclo*hexyl eicosanes; the calculated molecular weights of the aromatics are consistently lower.

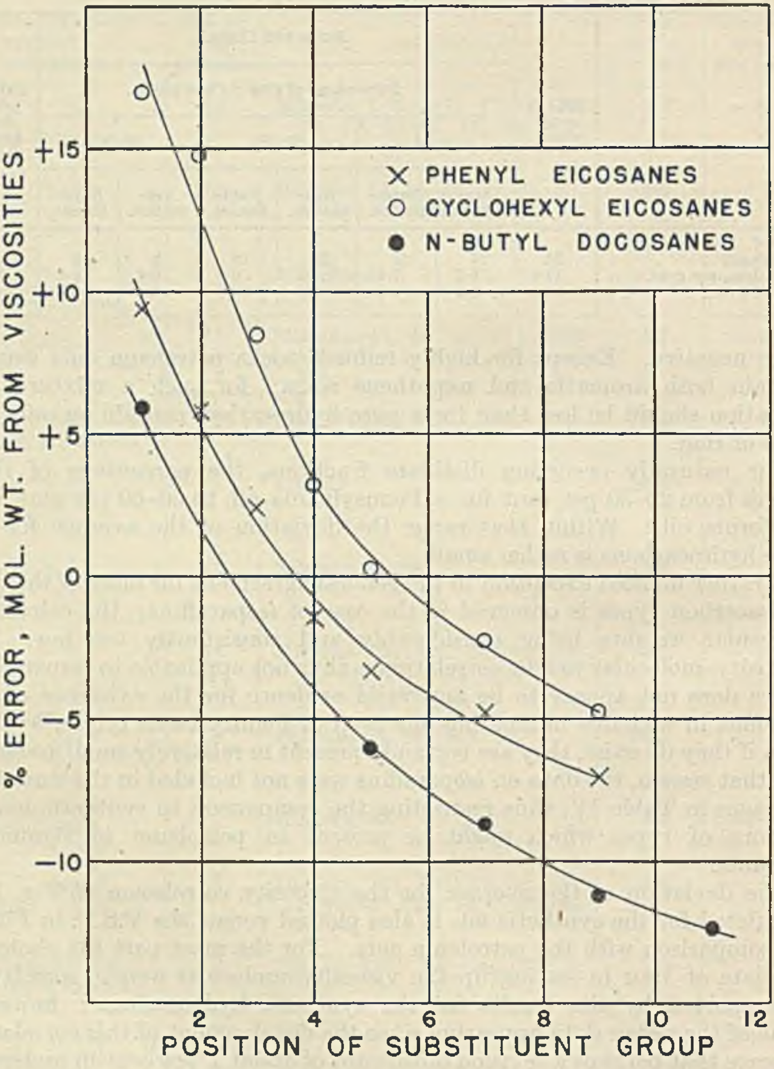


FIG. 7.

EFFECT OF POSITION ISOMERISM ON ACCURACY OF VISCOSITY MOLECULAR WEIGHTS.

VISCOSITY–DENSITY CORRELATIONS AND SYNTHETIC HYDROCARBONS.

Although with the exception of *iso*paraffins and hydrocarbons of more than about 70 weight per cent rings, Fig. 1 may be applied to synthetic hydrocarbons with reasonably good results, the same is not true for Fig. 5, or for the density correlations of Fig. 6. Hydrocarbons containing one or two naphthene rings are in fair agreement; for the rest, the calculated molecular weights are considerably in error. These deviations from the density correlations follow a rather consistent pattern which is closely related to the molecular structure. This may be correlated in terms of the ratio of the actual 210° F viscosity of a given synthetic hydrocarbon to the 210° F viscosity calculated from Fig. 5 using the theoretical molecular weight and the density. For convenience we may term this quantity the viscosity ratio; the denominator is approximately the viscosity of a petroleum oil of the same molecular weight and density as the synthetic hydrocarbon.

For *iso*paraffins, the average viscosity ratio is about 0·89, with values ranging from 0·80 to 0·95. In general, the higher values are for compounds whose branch is near one end of the molecule, while the low values are for molecules whose branch is near the centre. For naphthenes with six-membered rings, the monocyclic compounds average 1·02, the dicyclic hydrocarbons 1·12, and the tricyclic ones 1·75. Data on naphthenes with five-membered rings are rather scanty; four monocyclic compounds average 0·94; one dicyclic 0·95, and two tricyclic ones 0·94, while for one hydrocarbon consisting of four rings with no side chains, the viscosity ratio is 1·06. These data are sufficient to indicate that *cyclo*pentene derivatives have consistently lower viscosity ratios than the *cyclo*hexane compounds. Monocyclic aromatics, on the other hand, average about 0·83, dicyclic aromatics 0·64, and tricyclic aromatics 0·30. Tetralin derivatives have an average viscosity ratio of 0·84, which is almost exactly midway between the values for the dicyclic six-ring naphthenes and the dicyclic aromatics.

Similar viscosity ratios were calculated for the fifteen hydrogenated oils of Mair. When these viscosity ratios were plotted versus the average number of rings per molecule, a smooth curve could be drawn through the points; from this curve viscosity ratios at 2, 3, 4 and 4·5 rings per molecule were found to be 0·99, 1·11, 1·62, and 2·7 respectively. These values appear to be definitely lower than for the synthetic hydrocarbons with an equal number of six-membered rings; this may be the result of the presence of some five-membered rings in the hydrogenated oils, or possibly a greater degree of branching in the paraffinic side chains.

The above facts indicate that the viscosity–density correlations are relatively sensitive to composition. In terms of molecular weight, if the viscosity ratio is less than one, the calculated molecular weight is too low; the opposite is true if the viscosity ratio exceeds unity. The largest deviations in viscosity ratio are observed for the polycyclic aromatics and the polycyclic naphthenes; in the former case the calculated molecular weights are too low; in the latter, they are too high.

For those fractions covered in Table VIII which showed the greatest deviations from the correlation, "viscosity ratios" were calculated, employing the molecular weight calculated from viscosities when no experimental value was available. For a large majority of the nearly 800 naturally occurring petroleum fractions which have been examined to date, the "viscosity ratios" were found to be in the range 0·90–1·10; the extremes were 0·63 and 1·42.

Cracked products, as one would expect, may contain a higher proportion of aromatic rings than naturally occurring petroleum fractions.

For the cracked residua described by Watson [42] the lowest viscosity ratio was found to be 0·48.

The low viscosity ratios of polycyclic aromatics might be interpreted as an indication that for highly aromatic extracts, viscosity–density–molecular weight correlations would be unsuitable. Actually, the data now available (mostly that of Mair) indicate that the calculated molecular weights are fairly accurate. In large part, this is due to the fact that the error in molecular weight corresponding to a given viscosity ratio decreases rather considerably as the density is increased (see Fig. 5). Because of their high densities, the calculated molecular weights of polycyclic aromatics will tend to be more accurate than those of polycyclic naphthenes. More data on extract fractions are needed to properly assess the accuracy of the correlation for highly aromatic cuts.

Data for Construction of Correlations. Alternative Methods of Plotting.

Data is given in Tables XI and XII from which the correlations of Fig. 1 and 6 may be constructed by anyone desiring to make use of them. Space would not permit inclusion in Table XII of the data necessary for construction of all the constant viscosity lines of Fig. 1; however, these may be readily interpolated by drawing several lines of constant V.S.F. ranging in value from 200 to 450 V.S.F. through the constant viscosity lines given in Table XI, using equation (4) for this purpose. From these lines of constant V.S.F., the interpolations are easily made by again employing equation (4).

TABLE XI.

Data Necessary for Construction of Viscosity–Molecular Weight Correlation of Figures 1 and 6.

Viscosity, 210° F., cS.	Molecular weight.						
	250.	300.	350.	400.	500.	600.	700.
	H_{100}.	H_{100}.	H_{100}.	H_{100}.	H_{100}.	H_{100}.	H_{100}.
2·6	198	159	119	—	—	—	—
3	247	212	177	141	—	—	—
3·6	302	269	237	206	—	—	—
4	331	299	269	240	184	—	—
5	392	355	325	299	251	206	—
6	441	399	367	343	299	257	—
7	480	433	400	377	336	297	—
8	512	463	427	403	364	328	295
10	567	510	470	445	409	375	345
12	612	547	502	476	441	409	380
14	650	577	529	502	467	437	409
17	699	615	561	531	496	468	441
20	740	646	586	554	520	493	466
25	—	690	621	586	550	524	500
30	—	722	648	610	574	549	526
40	—	—	689	646	609	586	566
50	—	—	719	673	634	611	592
60	—	—	741	695	654	631	611

There are several alternative methods for plotting the correlation of Fig. 6 which offer advantages for certain purposes or are of interest. The use of

TABLE XII.

Data Necessary for Construction of Density Lines of Fig. 6 or Viscosity–Density–Molecular Weight Correlation.

(Fig. 5.)

Viscosity, 210° F, cS.	Density, 25° C.												
	0·83	0·85	0·87	0·89	0·91	0·93	0·95	0·97	0·99	1·01	1·03	1·05	1·07
	Mol. wt.	Mol. wt.	Mol. wt.	Mol. wt.	Mol. wt.	Mol. wt.	Mol. wt.	Mol. wt.	Mol. wt.	Mol. wt.	Mol. wt.	Mol. wt.	Mol. wt.
3	338	323	308	294	282	270	261	253	245	—	—	—	—
4	388	367	347	328	311	295	281	271	261	253	246	240	—
5	430	404	379	356	335	316	299	285	274	265	257	250	—
6	469	437	409	382	357	335	315	300	286	275	266	258	252
8	535	495	460	427	395	360	342	321	305	291	279	271	263
10	593	546	505	466	427	393	363	339	320	304	289	280	272
14	683	625	577	528	479	430	398	367	343	322	305	293·	284
20	—	710	656	597	539	487	437	398	369	343	322	306	297
30	—	—	—	678	613	551	490	442	403	369	342	324	313
40	—	—	—	—	667	600	533	480	432	389	358	338	325
60	—	—	—	—	—	668	597	540	480	421	382	360	—

density as one co-ordinate makes possible the use of interchangeable scales, such as d_4^{20}, specific gravity 60/60 or A.P.I. gravity. If H_{100} is selected for the ordinate and the density or gravity as the abscissa, the lines of constant viscosity at 210° F are almost straight and nearly parallel; furthermore, if they are drawn as H_{210}, they become practically evenly spaced. Since both density and molecular weight are being correlated with viscosities, lines of constant molecular volume may be readily drawn; it is of considerable theoretical interest that on this H_{100}-density plot the lines of constant molecular volume are almost straight and nearly parallel lines. Lines of constant molecular volume may also be drawn on Fig. 6; in this case also they are practically straight lines, in contrast to the constant density lines. These relations show the close connection between molecular volume and viscosity–temperature coefficients.

SUMMARY.

Correlations have been developed whereby molecular weights of lubricant fractions can be calculated from viscosities at 100° F and 210° F, or from either viscosity and the density. Using available published data, these correlations are evaluated and compared with earlier molecular-weight correlations; the accuracy of the latter is shown to be a function of the viscosity–temperature behaviour of a given oil.

The agreement of these correlations with data on synthetic hydrocarbons in the lubricant range is discussed. In general, most hydrocarbon types are in approximate agreement with the Vis_{100}–Vis_{210} correlation; the viscosity–density correlations, on the other hand, are much more sensitive to composition, and both polycyclic naphthenes and polycyclic aromatics exhibit large deviations, but in opposite directions. Use of the viscosity correlation is therefore to be preferred when data are available; however, for many oils the usual inspection data include only one viscosity. Consideration of more than 700 lubricant fractions indicates that the average composition is sufficiently uniform that the viscosity–density correlations

will give satisfactory results provided highly naphthenic fractions, cracked products, and synthetic oils are avoided.

An equation is proposed, which rather accurately represents the Vis_{100}–Vis_{210} correlation for oils with viscosity indices between about −50 and 110.

The correlation of Vis_{100}, Vis_{210}, and density may be used to estimate any one of these three constants, given the other two.

ACKNOWLEDGMENT.

Acknowledgment is hereby given to Dr. J. H. Bruun for guidance during the course of this work, to Mr. S. S. Kurtz, Jr., for many helpful suggestions in regard to the preparation of this manuscript, and to Mr. J. S. Sweely for assistance in working up the data for publication.

Literature cited.

[1] Anderson, R. P., and Geniesse, J. C. Private communication.
[2] Bell, T. G., and Sharp, L. H. *Oil Gas J.*, 1933, **32** (13), 13–16.
[3] Cannon, M. R., and Fenske, M. R. *Industr. Engng. Chem.*, 1939, **31**, 643–50.
[4] Cosby, J. N., and Sutherland, L. H. *Refiner*, 1941, **20**, 471–80.
[5] Davis, G. H. B., and McAllister, E. N. *Industr. Engng. Chem.*, 1930, **22**, 1326.
[6] Dean, E. W., Bauer, A. D., and Berglund, J. H. *Ibid.*, 1940, **32**, 102–7.
[7] Dornte, R. W., and Ferguson, C. V. *Ibid.*, 1936, **28**, 863–6; Dornte, R. W., Ferguson, C. V., and Hoskins, C. P. *Ibid.*, 1936, 1342–5.
[8] Evans, E. B. *J. Inst. Petrol. Tech.*, 1938, **24**, 321–37, 537–53.
[9] Fenske, M. R., Carnahan, F. L., Breston, J. N., Caser, A. H., and Rescorla, A. R. *Industr. Engng. Chem.*, 1942, **34**, 638–46.
[10] Fenske, M. R., McCluer, W. B., and Cannon, M. R. *Ibid.*, 1934, **26**, 976–80.
[11] Fenske, M. R., Stevenson, C. E., Lawson, N. D., Herbolsheimer, G., and Koch, E. F. *Ibid.*, 1941, **33**, 516–24.
[12] Fitzsimons, O., and Thiele, E. W. *Industr. Engng. Chem. Anal.*, 1935, 11–14.
[13] Goheen, G. E. *J. Amer. chem. Soc.*, 1941, **63**, 744–49.
[14] Hanson, W. E., and Bowman, J. R. *Industr. Engng. Chem. Anal.*, 1939, **11**, 440–2.
[15] Hersh, R. E., Fisher, E. K., and Fenske, M. R. *Industr. Engng. Chem.*, 1935, **27**, 1441–6.
[16] Hill, J. B., and Coats, H. B. *Ibid.*, 1938, **20**, 641–4.
[17] Kadmer, E. H., *Oel u. Kohle*, 1938, **14**, 1–7.
[18] Keith, J. R., and Roess, L. C. *Industr. Engng. Chem.*, 1937, **29**, 460–4.
[19] Landa, S., and Cech, J. *Collection Czechoslov. Chem. Communications*, 1934, **6**, 423–32.
[20] Landa, S., Cech, J., and Sliva, V. *Ibid.*, 1933, **5**, 204–10.
[21] Larson, C. M., and Schwaderer, W. C. *Oil Gas J.*, 1934, **33** (5), 10, 63.
[22] Lipkin, M. R., and Kurtz, S. S., Jr. *Industr. Engng. Chem. Anal.*, 1941, **13**, 291–5.
[23] Mair, B. J. *Bur. Stand. J. Res., Wash.*, 1935, **14**, 345–57.
[24] Mair, B. J., and Schicktanz, S. T. *Ibid.*, 1936, **17**, 909–22.
[25] Mair, B. J., and Willingham, C. B. *Ibid.*, 1936, **17**, 923–42.
[26] Mair, B. J., and Willingham, C. B. *Ibid.*, 1938, **21**, 535–63.
[27] Mair, B. J., Willingham, C. B., and Streiff, A. J. *Ibid.*, 1938, **21**, 565–80.
[28] McCluer, W. B., and Fenske, M. R. *Industr. Engng. Chem.*, 1932, **24**, 1371–4.
[29] McNab, J. G., Winning, W. C., Baldwin, B. G., and Miller, F. L. *J. Soc. aut. Engrs.*, 1941, **49**, 309–25.
[30] Mikeska, L. A. *Industr. Engng. Chem.*, 1936, **28**, 970–84.
[31] Neyman-Pilat, E., and Pilat, S. *Ibid.*, 1941, **33**, 1382–90.
[32] Rall, H. T., and Smith, H. M. *Industr. Engng. Chem. Anal.*, 1936, **8**, 324–30.
[33] Schiessler, R. W., Clarke, D. G., Rowland, C. S., Sloatman, W. S., and Herr, C. H. *Refiner*, 1943, **22**, 390–409.
[34] Schiessler, R. W., Cosby, J. N., Clarke, D. G., Rowland, C. S., Sloatman, W. S., and Herr, C. H. *Ibid.*, 1942, **21**, 393–400.
[35] Suess, F. A., Baldwin, H. C., Jones, W. A., and Lincoln, B. H. *Ibid.*, 1942, **21**, 51–62.

[36] Sullivan, F. W., Jr., Voorhees, V., Neeley, A. W., and Shankland, R. V. *Industr. Engng. Chem.*, 1931, **23**, 604–11.
[37] Varteressian, K. A., Fenske, M. R., and Smith, H. S. Paper presented before the Petroleum Division, American Chemical Society, Baltimore, April 3–7, 1939.
[38] Von Fuchs, G. H., and Anderson, A. P. *Industr. Engng. Chem.*, 1937, **29**, 319–25.
[39] Vlugter, J. C., Waterman, H. I., and Van Westen, H. A. *J. Inst. Petrol. Tech.*, 1932, **18**, 735–50.
[40] Vlugter, J. C., Waterman, H. I., and Van Westen, H. A. *Ibid.*, 1935, **21**, 661–76.
[41] Waterman, H. I., and Leendertse, J. J. *J. Inst. Petrol. Tech.*, 1939, **25**, 89–99.
[42] Watson, K. M., Nelson, E. F., and Murphy, G. B. *Industr. Engng. Chem.*, 1935, **27**, 1460–4.

THE BLENDING OCTANE NUMBERS OF 2:5-DIMETHYLFURAN.

By Hugh B. Nisbet.

Summary.

Following a review of the theory of knocking combustions and the influence of the chemical nature of the fuel thereon, inductive reasoning suggests that 2 : 5-dimethylfuran should have high-blending octane numbers in admixture with basis fuels of low octane number. The results of engine tests confirm this.

The phenomenon of knock in a spark-ignition engine is now generally recognized as the audible sound which accompanies the combustion of the latter part of the fuel–air charge in the cylinder at such a speed that the burning of the gas takes place in practically its own volume. Flame speeds of the rate of true detonation waves may be reached. Higher engine temperature and pressures than normal are thus produced, with consequent overheating of the engine and resultant loss of power. Moreover, substantial agreement has been reached that knock is brought about by conditions which obtain in the fuel–air mixture just prior to its combustion. By thermal decomposition and partial oxidation, the hydrocarbon molecules give rise to radicals which are chain carriers. These radicals are capable of initiating chain reactions in which the carrier may regenerate itself or may generate a greater number of chain carrying radicals by the process of chain branching. The chain of reactions can be broken by destruction of carriers by contact with solid surfaces or with other molecules or radicals in the gaseous phase. When the rate of destruction of the chain carriers is greater than the rate of their formation, the combustion reaction can be kept within limits, while if the rate of formation of chain carriers greatly exceeds the rate of destruction, the mixture may inflame spontaneously and the flame speed may be that of a detonating wave. In a normal explosion in the cylinder the spark creates a flame which passes through the fuel–air charge at an almost uniform and fairly low speed, while in a knocking explosion the formation of a large number of chain carriers in the unconsumed fuel–air mixture in front of the flame causes detonation of the latter part of the charge in front of the initial flame.

The factors which influence profoundly the possibility of knocking explosions have been divided into : (*a*) engine, and (*b*) fuel factors.[1] Among the engine factors conducive to knocking are increase in compression ratio, spark advance, and supercharging : among those which inhibit knocking are decrease in distance of flame travel, increased turbulence, spark retard, and increased ratio of surface to volume of the combustion chamber, particularly in the knocking zone. Increase of engine temperature is generally conducive to knock, but may lessen knock under certain conditions.[2] Most important among the fuel factors is the chemical constitution of the fuel—*i.e.*, the types of hydrocarbon and other organic molecules present in the motor spirit. Other fuel factors include the composition of the fuel–air mixture and the presence or absence of a knock inhibitor such as lead tetraethyl.

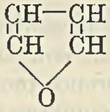
The anti-knock value of any particular fuel is measured by its octane number determined under standard conditions in comparison with *iso*-octane and *n*-heptane mixtures or secondary reference fuels. The octane number gives a measure of the highest usuable compression ratio or the critical compression ratio (C.C.R.) for the fuel under test. It has been pointed out, however, that the octane scale is not a uniform measure of knock resistance, since a change of one unit represents a much smaller change in C.C.R. for low octane numbers than for high octane numbers. In spite of this lack of uniformity in the octane-number scale, which appears to call for a more rational method of rating fuels, it is still used as the means of comparing different motor spirits.

Intensive research on the molecular configurations which give rise to high octane numbers has brought to light numerous compounds of high motor fuel value. Among these are substances such as *iso*octane itself, triptane, and the aromatic hydrocarbon benzene. At the same time the following rules have been formulated for the effect of molecular constitution on octane number : (*a*) *iso*paraffins have higher values than *n*-paraffins and the value is higher the more condensed the structure ; (*b*) the longer the carbon chains in the molecule the lower the octane number ; (*c*) the formation of olefines by the introduction of a double bond into the molecule increases the value, and the more central the double bond the higher the value ; (*d*) cyclization of the paraffin molecule to *cyclo*paraffin increases the octane number ; (*e*) the introduction of double bonds into *cyclo*paraffin molecules raises the value ; (*f*) aromatics generally have high octane numbers.

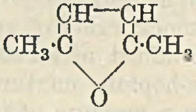
When materials of high octane number are blended with fuels of low value, the octane number of the blend cannot, in general, be calculated by the mixture rule, for the effect of the high antiknock fuel is not always linear with concentration. The blending octane number, calculated by the formula of Garner, Evans, Sprake, and Broom,[3] can be used to indicate the value of the blending agent, but this value applies only to the particular blend under examination, for it varies with the character of the basis fuel and the percentage of the blending agent added. The rules for the development of high-blending octane numbers by varying the molecular configurations are, within these limits, however, the same as those given above for octane numbers.[4] The limiting factors must always be clearly stated, for it is possible for a blending agent to show a high blending value when in admixture with a basis fuel of low octane number, and to show no abnormal value when blended in the same proportions with a basis fuel of high initial octane number.

The search for materials which have high-blending octane numbers when mixed with basis fuels of low octane number is warranted by the fact that blending with, say, 10 to 30 per cent of blending agent will produce a fuel with an octane number considerably higher than the proportion of the additive would indicate if the value were calculated by the simple mixture rule.

It has already been shown [5] that the combination of a conjugated double-bond system with an ether linkage as found in the molecule of furan (I) gives a blending agent which, added to fuels of low octane number,



(I.)



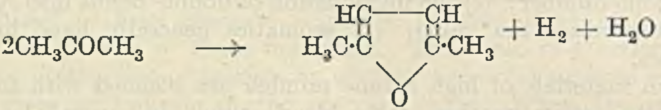
(II.)

has very high-blending octane numbers. This substance, however, suffers from the disadvantage that it is very volatile (b.pt. 31° C/745 mm), and the present investigation deals with a study of 2 : 5-dimethylfuran (II) which falls into the normal motor spirit range as regards boiling point (92·5–94° C/758 mm). This latter compound might be expected to show even higher values than furan, for the substitution of two hydrogen atoms by methyl groups is equivalent to centralising the molecule.

2 : 5-Dimethylfuran can be prepared by removal of a molecule of water from acetonylacetone (III) by distillation with anhydrous zinc chloride.[6]

(III.) (II.)

The preliminary tests were made on a sample so prepared. Dimethylfuran is manufactured by the pyrolysis of acetone (IV) by exposing to a temperature of 700° C, for 0·15 sec.[7] The later engine tests were conducted on a commercial sample which was purified by distillation in a G.L.C. silvered vacuum jacketted fractionating column.[8] The physical properties (some taken from the literature) of the compound are listed in Table I.



(IV.) (II.)

TABLE I.

Physical Properties of 2 : 5-Dimethylfuran.

B.pt. ° C/mm	92·5–94/758 *
Sp. gr. 17·7/4°	0·90264 [9]
20·1/4°	0·8883 [10]
18·3/4°	0·90888 *
Refractive index $n_D^{17\cdot7°}$	1·44270 [11]
Calorific value (gross)	8328
Cals. 15°/g (air)	8325 Av. 8320 *†
Const. vol.	8307

* Values determined on sample.
† Calorimetric method of B.S.S. 1016/1942 using gelatine capsules of known C.V. to hold liquid.

The samples used were freshly distilled to remove any gum before engine tests were made.

Octane numbers were determined by the C.F.R. Motor Method on blends of dimethylfuran using the following as basis fuels :

Fuel A . . . Octane number 40·5
„ B . . . „ „ 56·0
„ C . . . „ „ 99·8 (commercial *iso*octane)

Blending octane numbers were calculated using the formula of Garner *et al.*[3] The results are given in Table II. The values show that dimethylfuran has very high-blending octane numbers when added in small percentages to fuels of low octane number, but that the relative rise in octane number of the blends decreases with increasing proportions of blending agent. Blended with a fuel of initial high octane number—*e.g.*, *iso*octane —dimethylfuran possesses no advantage as a blending agent. Indeed, it lowers the octane number in the blend.

TABLE II.

Blending Octane Numbers of Blends containing 2 : 5-Dimethylfuran.

Basis fuel.		Blends with 10% dimethylfuran.		Blends with 20% dimethylfuran.		Blends with 30% dimethylfuran.	
	Octane number.	Octane number of blend.	Blending octane number of additive.	Octane number of blend.	Blending octane number of additive.	Octane number of blend.	Blending octane number of additive.
A	40·5	57·0	205	69	183	76·3	160
B	56·0	69·5	191	76·8	160	81	139
C	98·8	97·2	83	—	—	—	—

Substances which behave in this way have been shown to have negative lead susceptibilities (= increase in C.C.R. for 1 c.c. lead tetraethyl per gal) in that when treated with lead tetraethyl the tendency to knock increases.[12] Jost and Müffling [13] have indicated that lead susceptibilities can be calculater from reaction kinetic data. No information as to the lead susceptibility of dimethylfuran can yet be given, but Table III gives the values for the octane numbers of some of the blends examined above further doped with lead tetraethyl.

TABLE III.

Octane Numbers of Blends containing 2 : 5-Dimethylfuran and Lead Tetraethyl.

Basis fuel.			Dimethylfuran, % in blend.	Octane number of undoped blend.	Doped blend.	
	Octane number.	% in blend.			TEL, cc per gal.	Octane number.
A	40·5	90	10	57·0	3·6	75·3
B	56·0	90	10	69·5	3·6	83·9
B	56·0	70	30	81	5·0	~91

The octane number of unblended 2 : 5-dimethylfuran, owing to lack of material, could be determined only approximately. The value so found was 90. A further report on this and on the lead susceptibility of this substance will be made when further supplies are available.

The vapour pressures (Reid) for some of the blends are given in Table IV.

TABLE IV.

Vapour Pressures (Reid) for some Blends containing 2 : 5-Dimethylfuran.

Basis fuel.		Dimethylfuran, % in blend.	Vapour pressure, lb/sq. in/100° F.
	% in blend.		
A	80	20	2·8
A	70	30	2·9
B	80	20	3·4

The author desires to thank the Governors of the Heriot Watt College and Scottish Oils, Ltd., for facilities.

References.

[1] B. Lewis, "The Experimental Side of Combustion Research in Engines," in "Frontiers in Chemistry," Vol. II, p. 205.

[2] Dumanois, *Ann. combustibles Liquides*, 1934, **1**, 143; Lewis, *loc. cit.*

[3] F. H. Garner, E. B. Evans, C. H. Sprake, and W. E. J. Broom, *Proc. World Petroleum Congress*, 1933; and Nash and Howes, "Motor Fuel Preparation and Application," II, 340.

[4] H. B. Nisbet, *Journ. Inst. Petrol.*, 1941, **27**, 293.

[5] H. B. Nisbet, *loc. cit.*

[6] Dietrich and Paal, *Berichte d. Deutsch. Chem.*, **20**, 1085.

[7] U.S. Pat. 2,098,592. *Chem. Abstr.*, 1938, 195.

[8] Gooderham, *J. Soc. Chem. Ind.*, 1935, **54**, 297T.

[9] Nasini and Carrara, *Gazz. chim. ital.*, **24** (I), 271.

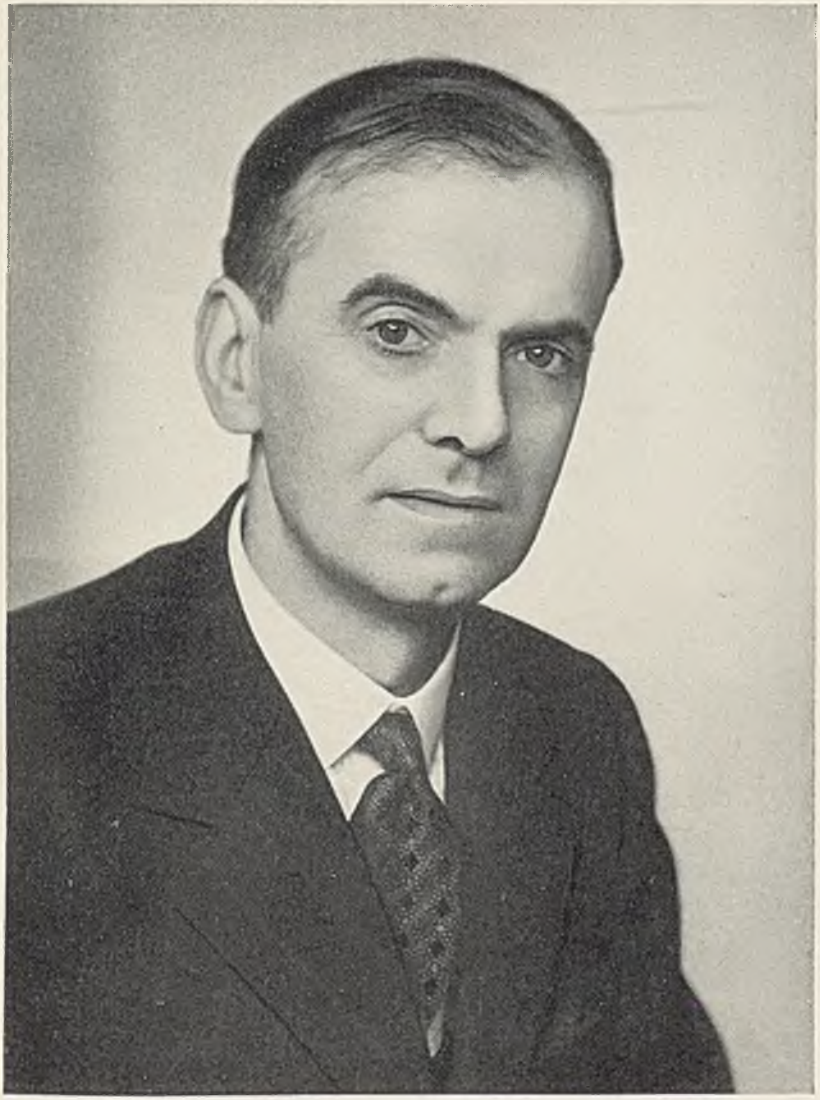
[10] v. Auwers, *Annalen*, **408**, 271.

[11] Nasini and Carrara, *loc. cit.*

[12] Lovell, Campbell, and Boyd, *Ind. Eng. Chem.*, 1935, **27**, 593; *Chem. Rev.*, 1938, **22**, 169.

[13] Jost and Müffling, *Z. Elektrochemie*, 1939, **45**, 93.

Heriot Watt College,
Edinburgh.
31*st July*, 1945.



Professor F. H. Garner., O.B.E., Ph.D., F.R.I.C.

President, 1944–46.

Professor F. H. Garner vacated the Chair in March 1946 after two years of arduous and self-sacrificing work as President of the Institute. The two years of his term of office, coinciding as they did with the most strenuous years of the War in which petroleum played so vital a part, were most difficult. During these two years considerable progress has been made in the reorganization of the Institute to meet the problems of the future, and Professor Garner has quietly and unostentatiously upheld the best traditions of the Institute throughout this period.

Members of the Institute will be gratified to learn that he has now taken full responsibility for the publications of the Institute as Honorary Editor in succession to Dr. A. E. Dunstan, who resigned from that office at the end of 1945. Since 1937 he has been Honorary Associate Editor.

[*To face p.* 166