THE INSTITUTE OF PETROLEUM.

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MR. J. S. JACKSON, Vice-President, occupied the Chair and the following paper was presented by Dr A. H. Nissan.

VISCOMETRY OF SOAP-IN-HYDROCARBON SYSTEMS.

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INTRODUCTION.

WHEN metallic soaps of fatty or naphthenic acids are mixed with hydrocarbons and either mechanically or thermally treated to give solutions, it is possible to obtain practically all degrees of subdivision of the soap, from the ultimate molecular solution yielding a low-viscosity liquid on the one hand, to a swollen, opaque, soft solid on the other. The factors governing the properties of the final product are very many, but chief amongst them are :—(1) The nature of the metallic ion ; (2) the nature of the acid ; (3) the extent of saponification of a multibasic acid or multivalent metallic ion ; (4) the co-ordinated complexes loosely attached to the soap ; (5) the crystallographic system of the undissolved soap ; (6) the nature of the solvent ; (7) the presence of other substances besides soap and solvent which act as peptizers, coagulators, accelerators, retarders, etc. ; (8) the mechanical, thermal, electrical and similar processing of the mixture ; (9) the age of the product. These several items will not be discussed here ; they are listed in order to illustrate the complexity of the systems obtained and the multiplicity of factors involved. Having obtained a particular solution of soap in a particular hydrocarbon by following any given set of procedures and precautions, it is desired to investigate the viscosity characteristics of the solution. The purposes of the present paper is to discuss certain of the available methods and their limitations, and in general to study them in the light of recent experience carried over three to four years experimental and theoretical investigation.

Properties of matter can, in general, be studied either qualitatively or quantitatively, or both. It is therefore instructive to discuss these systems by both methods in order that as much information as possible may be obtained. Before doing so it is as well to state that whilst the investigations envisage soaps in hydrocarbons in general, actually only divalent and trivalent metallic soaps of naphthenic and fatty acids, containing twelve and more C atoms dissolved in light hydrocarbon fractions—*e.g.*, benzene, *cyclo*hexane, petrol, and light naphthas—have been studied experimentally in this work.

The literature does not contain a great deal of work on the viscometry of soap–hydrocarbon systems, particularly for low-molecular-weight hydrocarbons. Freundlich and Röder [1] report some experiments on

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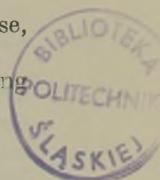
calcium naphthenate in white spirit.   Ostwald and his school [2] made a study of metal soaps in benzene.   Amongst those who studied the visco-metry of greases, where high-molecular-weight hydrocarbons are used as continuous phase, may be mentioned Bulkley and Bitner,[3] Arveson,[4] Blott and Samuel,[5] Varentzov,[5a] and Gallay and Puddington.[5b]

In the present work capillary viscometry of soaps in solution in low-molecular-weight hydrocarbons was studied in particular detail, and certain aspects of rotary and of falling sphere viscometers were found of interest in understanding the rheological behaviour of such systems. These experiments and their results will be described first, followed by a brief discussion of the rheology of these systems.

Capillary Viscometry.

The viscometers used were of two sizes : The smaller size could accom-modate tubes from capillary dimensions up to $\frac{1}{4}$ in. in diameter and the larger " viscometer " could be used with any size tube or pipe up to several inches in diameter, if necessary.   Actually, it was found that pipes with upper limit of 1-in. diameter were ample for all the fluids studied here, as peculiarities shown by these fluids disappear with larger diameters than 1 in. The two viscometers were recently described briefly.[6]   Fig. 1 is a photo-graph of the laboratory viscometer and Fig. 2 is of the large-scale version. The lettering in both figures correspond, as both were built on the same general plan, differing only in scale.   The laboratory viscometer was, however, temperature-controlled, whilst the large one was not.

Referring to Fig. 1, the colloid was kept in one of the two water-jacketed reservoirs V_1.   The two reservoirs were connected by a water-jacketed capillary tube, held inside an iron tube by means of two packing glands, one at each end.   The glass capillary projected into the reservoir and presented a sharp-end entry.   The iron pipe was connected to the reservoir by means of a 2-in. union.   The section of the capillary which was not water jacketed was insulated by cotton wool.

Flow was induced by means of high-pressure nitrogen, saturated with the solvent, which was applied to the reservoir containing the soap–hydrocarbon colloidal solution.   The nitrogen, obtained from the cylinder shown via a reducing valve, was stabilized by being connected to the two cylinders shown in the background ; further stabilization of the inlet pressure was obtained at low pressure by either (a) opening the valve shown below the gauge to allow a small leak, (b) by connecting this valve to a mercury " bubbler."   The nitrogen gas was then led through manifold M to one of the two small steel cylinders, shown in the foreground, con-taining a small quantity of the solvent.   As the temperature of all this work was standardized at 20° C., it was easy to keep these cylinders and the reservoirs at the same temperatures.   (At other temperatures, the vapour-saturation cylinders should be kept in the bath.)   Thus, drying of the fluid was prevented even when work extended over several weeks   The pressure of the gas was measured by a frequently calibrated Budenberg gauge for high pressures and by mercury or water manometers for low pressures.

As the fluid entered the second reservoir it displaced the solvent-saturated air or nitrogen into the second vapour-saturation cylinder, and from thence into flowmeter manifold N.   The flowmeter was a glass
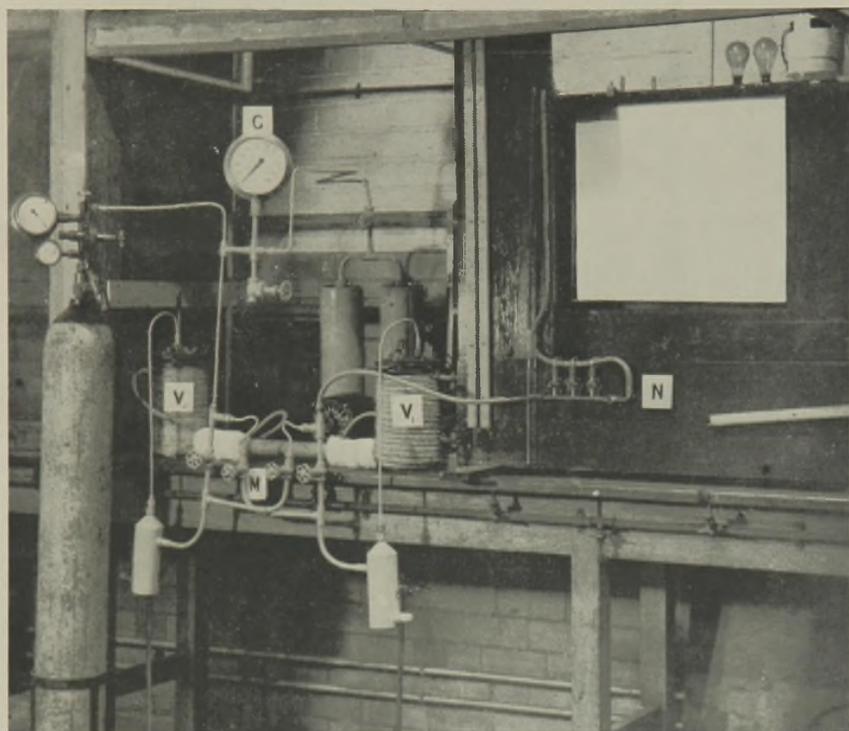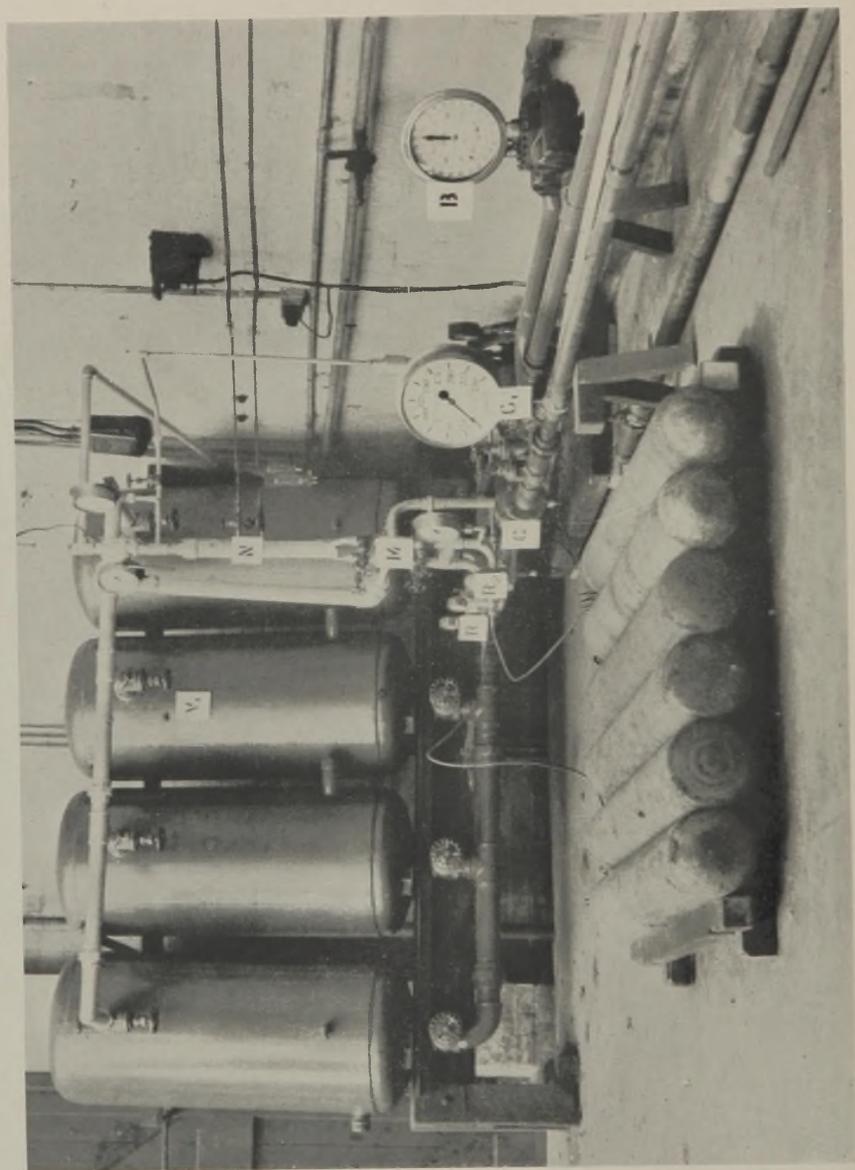
Fig. 1.

Fig. 2

capillary totally immersed in the water bath and the pressure drop across the flowmeter capillary was measured, using one or other of the taps shown to connect it to one of several manometers, ranging from an inclined toluene-manometer used for low rates of flow to a vertical one containing mercury for high rates of flow. The calibration and accuracy of this flowmeter was discussed in some detail previously.[7] The present work confirmed that the accuracy attained was ± 0.5 per cent.

Temperature control of the apparatus was obtained by circulating water through the jackets by means of a small gear-pump with suction from the tank shown. The temperature control system and uniformity of temperature obtained with this bath have been described in detail in the same paper.[7] The bath temperature was accurately controlled and maintained to $\pm 0.01°$ C.; the temperature of the fluid was probably maintained to better than $\pm 0.1°$ C.

In Fig. 2, referring to the larger apparatus, the following differences will be noted. R_1 and R_2 are two reducing valves working in parallel to supply the high-pressure nitrogen. N is an orifice built according to the B.S.I. specifications BS. 1042 (1943) and calibrated by means of water, using a Brodi meter B as calibrating meter, and also weighing the water discharged per second, and by means of air, nitrogen, and petrol-saturated nitrogen using accurately calibrated gas-meters. The coefficients of discharge from all these tests agreed with that given by the B.S.I. Finally, it will be seen that gauge G_1 is attached to the flow-pipe itself and not to the reservoir. For each experimental pipe through which the solutions were made to flow, gauges were attached at set intervals by means of a pressure ring welded around the pipe. The inside of the pipe was connected to the chamber so formed by means of four small holes drilled into the pipe-wall. Thus the pressure drop in the pipe could be measured for different sections with two ensuing advantages :—

1. When a fluid showed on the one hand successive breakdown, or on the other hand hardening with shear stress or rate of shear strain, successive sections of the pipe showed a pressure drop per foot of pipe which continuously decreased or increased respectively. Whilst some work was done with such systems, in this paper only fluids showing constant pressure drop per foot along a pipe are discussed.

2. The pressure drop so measured is not complicated by entrance or exit pressure losses.

In both viscometers, flow could be reversed so that either side could be used as the fluid reservoir whilst the other side could be utilized to receive the fluid. The larger viscometer was used with steel pipes down to $\frac{1}{4}$ in. in diameter, whilst the small reservoir used glass tubes up to that diameter, so that results from one could be correlated with the other, except for the fact that the small viscometer was fully affected by inlet losses whilst the larger one was not. Therefore, it was necessary to evaluate these losses.

Entrance losses were measured in several ways :—(1) On the large viscometer, by means of pressure gauges before and after a contraction. These pressure losses were corrected for the viscous loss for the lead-in large pipe, and for the length of the small pipe from the entrance to the gauge-point, by measuring the loss per unit length of the same pipe at the same rate; (2) on the small viscometers from measurements of pressure with tubes of

the same diameter but different length at the same value of rates of flow and calculating pressure loss at zero length; (3) by measurements of pressure losses in sharp-edged orifices at different rates of flow; (4) by measurements of losses in nozzles of short lead-in lengths and applying corrections.

Fig. 3 shows the results obtained with a peptized solution of aluminium stearate in gasoline. Entrance losses in simple fluids are due to two sources in the main, (1) kinetic energy losses, (2) Couette losses. The kinetic energy loss is analysed into the following components (see Barr [8] and Goldstein [9] for a full discussion) :—(a) $\frac{1}{2}\rho v^2$, due to the increase in kinetic energy of a particle along a stream-tube in accord with Bernoulli's theorem; (b) $\frac{1}{2}\rho v^2$, due to the parabolic distribution of the velocity of the stream tubes with the radius of the tube in the fully developed flow pattern; (c) a

Fig. 3.

third loss in the " entrance length " estimated by Boussinesq [8 and 9] as $0.12\rho v^2$, by Schiller [8 and 9] as $0.08\rho v^2$, by Atkinson and Goldstein as $0.205\rho v^2$, by Riemann [8] as $(0.124+0.006)\rho v^2$, and by Langhaar [10] as $0.14\rho v^2$, where ρ = density of fluid; v = mean velocity in the pipe. Thus, the total entrance losses for simple fluids (adopting Langhaar's figure) are $1.14\rho v^2$. No similar estimates have been made for entrance length losses with such fluids as soap solutions in hydrocarbon. However, at low velocities the effect must be negligible, as it is proportional to v^2, and at high velocities these colloids approach parabolic distribution with almost constant viscosities. Therefore it was decided to try the latest (Langhaar) experimental value of $1.14\rho v^2$ for the K.E. correction at the entrance, as it approaches the mean of all workers. On Fig. 3, it is seen that the curves converge to the line of $1.14\rho v^2$ at high velocities. Fig. 4 shows that by subtracting $1.14\rho v^2$ from

Fig. 4.

the contraction loss on entrance into a pipe and plotting the resultant value against the criterion (v/D), which is a measure of the characteristic rate of shear in the system, a single curve results for all experiments independently of shape of entrance and method of evaluation. (Only a few typical points are plotted to avoid confusion; other points from Fig. 3 fall similarly on the curve of Fig. 4 to those shown.) The upper line is for a higher concentration of soap in gasoline peptized by the same method and compound.
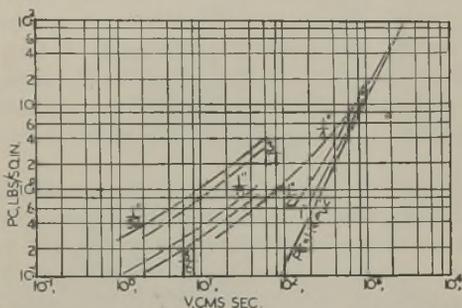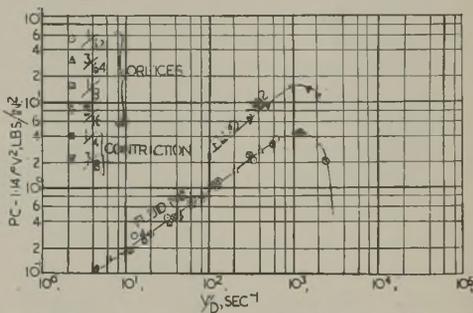
The Couette loss is usually ascribed to the convergence of the lines and consequent friction losses. It is a viscous loss—*i.e.*, function of (v/D) independent of dimensions of apparatus—and the curve in Fig. 4 may be mistaken for it. The Couette loss, however, amounts to friction drop in a pipe length of less than one diameter; results from Fig. 4 show a pressure drop in terms of number of diameters approaching 60 at the maximum. Hence, a new type of entrance loss in addition to the two mentioned above is encountered. It is considered that a new type of relaxation phenomenon is operative. Energy is lost at the entrance due to a tendency for the strained molecules to travel radially inwardly and backward in the " inlet length." The quantitative deductions from this explanation is left for another occasion. However, for practical viscometry, let

$$P_e = P_c - 1.14\rho v^2$$

then
$$P_e = f_1(v/D) \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where P_e = viscous pressure loss at entrance of a contraction, dynes/cm.^{2};
P_c = total pressure loss at entrance of a contraction, dynes/cm.^{2};
f_1 = function (type 1).

The pressure drop, P, in a pipe of length L and diameter D will, in general, follow the equation

$$P = (L/D)f_2(v/D) \qquad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\therefore \quad P_e = \frac{P}{(L/D)} \cdot \frac{f_1(v/D)}{f_2(v/D)}$$

$$= (P/L)f_3(v/D) \cdot D \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

or
$$\frac{P_e}{(P/L)} = nD \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where n is the number of diameters of pipe to which the entrance is equivalent in causing viscous pressure loss. For the same type of colloid —*i.e.*, relaxing in the same manner—this number of equivalent diameters should be independent of dimensions of apparatus and of concentration of colloid.

Fig. 5 shows the relationship of n calculated according to equation (4) with (v/D) for the two fluids of Fig. 4. Whether other colloids would give the same values of n at equal (v/D) cannot be stated without further knowledge whether the pheno-

v/D SEC^{-1}

FIG. 5.

mena taking place with soap–hydrocarbon systems take place with the other colloids.
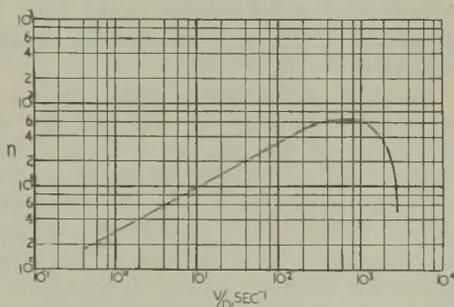
Thus the entrance losses for all shapes of entrance tested—*i.e.*, sharp-edge, conical, and bell-mouth reducers—are made up of approximately $1.14\rho v^2$, kinetic energy loss and a viscous loss equal to the loss encountered in the pipe for a length of nD at the same (v/D) value, shown later to be a measure of the rate of shear strain in the pipe.

The flow of soap–hydrocarbon colloidal systems in the pipe, beyond the " inlet length " varies in degrees of complexity by changing any of the factors enumerated in the first paragraph of this paper. It has already been stated that certain colloids gave a continuously decreasing value for P/L and that such systems are not considered in this paper. Again, some of these fluids showed a continuous change of viscosity with age, either thickening or breaking down. Whilst one such example will be reported later in the section dealing with falling sphere viscometry, only fluids relatively stable with age will be discussed in this section. Indeed, other complications will also be ignored. Certain high-viscosity colloids of soap in benzene, specially peptized, may show definite yield values, when tested by the viscometer, of several hundred dynes/sq. cm. Yet these materials were found to exhibit a level mirror-like surface on long standing, denying the existence of the yield value. The reason for the paradox is in the simultaneous possession of rigidity and a relaxation mechanism which is comparatively slow. Thus, in short-period tests the yield value is evident, with long periods the relaxation eliminates any effect of rigidity.

It is therefore intended to concentrate attention on the simplest types of these systems—*i.e.*, soaps of aluminium or calcium in hydrocarbon peptized by small quantities of, say, oleic acid, alcohol, pyridine, water, or similar compounds. Up to concentrations of, say, 5 gms. of soap per 100 c.c. of solvent, such systems will reveal a linear relationship between driving pressure and velocity for low values of pressure, or velocity, beyond which the linear relationship breaks down. At high rates of flow the systems will again show a linear (Newtonian) relationship. It is useful to discuss the relationship between " shearing stress " and " rate of shearing strain " rather than pressure and velocity.

In a circular pipe of uniform cross-section, the shearing stress at a point with radial distance r from the centre is $Pr/2L$, provided the flow in the pipe is in telescopic stream tubes and is derived independently of the distribution of the velocity in the pipe. Thus, if the value of r is chosen to be that of the pipe, the shearing stress $F = Pr/2L$ so calculated will be that at the wall.

Calculating the rate of shear strain at a corresponding point demands previous knowledge of the velocity distribution in the pipe, which knowledge is not available. It is therefore decided to use elementary dimensional analysis, which shows that for geometrically similar systems the criterion (v/D) is a measure of the rate of shear strain at corresponding points. Therefore, a plot of F *vs* (v/D) will, in effect, be a plot of the shearing stress *vs*, a multiple of the rate of shear strain at corresponding points for different tubes. It was seen in the study of inlet losses that, except for kinetic energy correction, which is negligible in the present discussion, the inlet loss at any value of (v/D) was equivalent to number of diameters added to the length. Thus for tubes of equal (L/D) ratios, the inlet loss at the same value of (v/D) can be considered as making them equivalent to tubes of (L'/D) ratios with L' being the same for all of them. Hence it is necessary to prepare plots of F *vs* (v/D) for tubes of equal (L/D) ratios in order that the characteristics of these materials may be studied, otherwise the tubes should all be corrected for inlet losses.

Fig. 6 shows such a plot for an aluminium soap solution in petrol. At low values, points not shown, a straight line obtains between F and (v/D) independently of the dimensions. However, as the rate of shear strain increases, the curves obtained for tubes of different diameters diverge from each other.

To understand the significance of this divergence it is necessary to refer to the assumption which is made to distinguish real simple viscous fluids from the ideal inviscid fluids of hydro- and aero-dynamics, namely that at solid–fluid interfaces of real simple fluids the relative velocity is zero— i.e., it is impossible for a fluid to " slip " on a solid surface. S. Goldstein [9] (pp. 676–80) gives a concise yet exhaustive discussion of this assumption, and reviews historically its development. At the present time it is fully accepted as being valid for all *simple* fluids (save gases and vapours at very low pressures, and similar systems possessing a mean free path for the molecules commensurable with the dimensions of the confining walls of the fluid). On a molecular basis, the forces responsible for the impossibility of slip are the short-distance attractions of the fluid molecules to those of the confining walls.

In dispersed systems the forces between the walls and the molecules of the continuous phase may be greater than the forces between the walls and the dispersed phase. If so, there would be a positive gradient of concentration of the dispersed phase as the distance from the wall increases—i.e., the layer next to the wall may be less viscous than the body of the system. Hence, on flow of the materials, phenomena similar to slip in outward character-
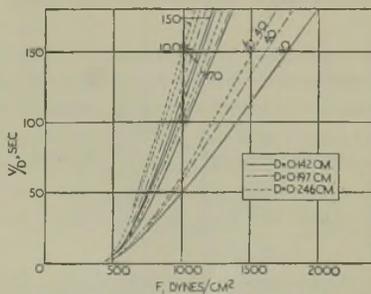

FIG. 6.

istics may be observed, although in fact there is no slip between the solid and the first molecular layer of the fluid. Even if no actual concentration gradients are produced, interfacial forces resulting merely in orientation of solvent or solute molecules at the interface will be sufficient to produce phenomena akin to " slip." Such phenomena have been observed by Scott-Blair,[11, 12] and others and are generally called σ-phenomena. If, on the other hand, the forces between the walls and the molecules of the continuous phase of a dispersed system are smaller than those between the wall and the dispersed phase the concentration gradient may be negative—in a direction from the surface to the centre of the fluid—and a superficial layer more viscous than the body may result. Such a state of affairs would give rise to what may be observed as surface *retardation*. Except that certain colloidal systems exhibit a superficial viscosity greater than the bulk viscosity on their interface with the air— e.g., the viscosity of air–liquid interface of a bubble of saponin water colloid is greater than the bulk viscosity giving " wrinkled bubbles " on deflation— no retarding layer has been explicitly reported for solid–liquid interface. In dispersed soap solutions in hydrocarbons such a phenomenon apparently takes place. The method for detection and independent evaluation of layer effects must be described here. The method is applicable only to

systems which do not show a breakdown, or build-up, of viscosity with shearing dependent on time.

When a fluid is forced to flow in a capillary, in a steady viscous regime it was shown that, in effect, a plot of v/D *vs* F for tubes of equal L/D ratio is a plot of the rate of shear strain *vs* shear stress except for a multiplier of the scales, and should, therefore, be a unique characteristic of the fluid and independent of the dimensions of the tube. If the fluid splits into two layers of different rheological characteristics, the shearing stress will still be given by $Pr/2L$, so long as flow is taking place in concentric layers —velocity distribution need neither be parabolic nor even known, provided it is not uniform. The rate of shear strain, s, on the other hand, will be given by :—

$$s = f\left(\frac{v}{D}, \frac{\mu_L r_L}{\mu_B r_B}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where the suffix L means layer and B, bulk. Therefore, for different tubes s need not be given by v/D only, but will be in addition a function of D, the diameter of the tube, since r_L will be independent of r_B and r, being governed solely by the natures of the wall and the flowing materials. Therefore, where slip or retardation takes place, a plot of v/D *vs* $Pr/2L$ for different tubes of the same L/D but of different D values will give a separate curve for such tubes. For slip F will be lower for smaller diameters at the same values of v/D, and for retardation layers it will be higher.

FIG. 7.

Fig. 7 gives typical curves of F *vs* $1/D$ at equal values of (v/D) for different tubes. $1/D$ is used instead of D in order that extrapolation to $D = \infty$ is made easy. The points shown for the smaller values of diameter were obtained from the small-scale viscometer without correcting for entrance loss; the points for the large-diameter tube were obtained from the large-scale apparatus after adding the entrance loss obtained from Fig. 4. As the entrance loss for constant values of (v/D) is the same for all tubes, it follows that the differences shown in F with change in $(1/D)$ are due to this layer effect and are not affected by inlet losses. It is noted that the curves tend to reach asymptotic values with increase in D (decrease in $(1/D)$), and that for pipes of more than $\frac{1}{2}$-in. diameter, the influence of the retardation layer is negligible.

A final point should be mentioned here in connexion with this pheno-menon :—the retarding layer effect may be either enhanced or even be solely due to the peculiar relaxation mechanism which gives rise to such high values to the inlet pressure losses. To appreciate this fact, a brief discussion of the relaxation mechanism is necessary.

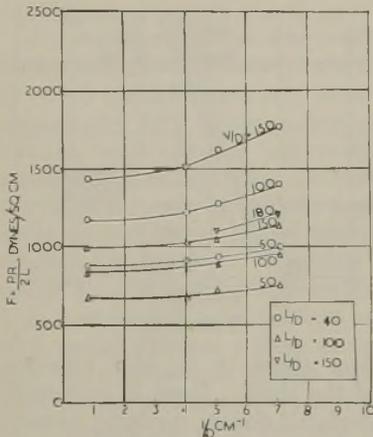In the kinetic theory of elasticity of long macromolecules like those of

rubber [13] it is postulated that the molecules assume random zigzag, coiled shapes with a certain distance between the ends being most preferred of all possible values between zero and the full extended length. With this most preferred " length " of molecule the entropy is a maximum; on straining the molecule into any other shape it is less. Thus, the strained molecules are in less " stable " forms than the unstrained. These assumptions are made in this paper also for the conditions of the macromolecules of associated soap molecules in a solvent. One additional assumption is, however, necessary. In the solid rubber, the strained molecules are relatively " fixed "—they relax with difficulty and probably only in minute steps. In solutions of rubber or soap in a hydrocarbon there is no such rigid fixity; the macromolecules can move bodily into regions of less strain and relax. It is therefore assumed that this process takes place. In a given time the strain in the molecules of a flowing solution will be the greater the greater the rate of shear strain, and in effect, it is postulated that these colloids will tend to develop *spontaneous secondary flow down the spatial gradients of the rates of strain*. This hypothesis explains certain characteristic features of the systems studied and is fortunately easily shown to be valid.

A glass disc was sealed at its centre to a glass rod and fixed in a horizontal plane, parallel to the bottom of a glass beaker and at a distance of less than a cm from the latter plane. The beaker was filled with solutions of rubber in benzene and of different solutions of calcium and aluminium soaps in light hydrocarbons peptized by small quantities of active compounds like xylenol, alcohols, cellosolve, etc. In each case, when the beaker was rotated at constant speed the following observations confirmed the validity of the hypothesis :—

(1) Small coloured particles showed macroscopic secondary radial flow inwards along the stationary surface, both above and below the glass disc. As the rate of shear strain increases with the radius the differential coefficient of the rate of shear strain with respect to the radius is negative, hence the secondary radial flow is negative as required. Quantitative study of this phenomenon confirmed that this secondary flow is not the hydraulic type generated by centrifugal forces along the moving surface, as there is greater hydrostatic pressure at the centre of the disc than at its periphery.

(2) At the intersection of the fluid surface with the central stationary rod there is a line of strained fluid. Above it, the fluid sticking to the rod is stationary. Therefore, there is a gradient of the rate of strain negative in an upward direction. Consequently the fluid spontaneously climbs up the rod to an appreciable height at a fairly high rate. The same phenomenon is observed when these materials are mixed by a stirrer on a rod. So rapid was the climbing rate on the rod in some of our experiments, as, for example, in making solutions of soap in benzene, that all stirrer rods were swelled at, or just above, the free surface, so that the climbing material is flung out by centrifugal force and returned into the fluid.

In the inlet of a pipe, it is therefore postulated that the tendency to move into regions of lower strain and then relax accounts for the high

losses encountered. Evaluation of the losses on this basis was made approximately, and the results were in fair agreements with measurements from other experiments.

As flow takes place in the pipe, beyond the inlet length, it is postulated that the strained molecules tend to flow inward. However, this flow cannot take place without other portions flowing outwards, to states of lower entropy. Therefore, the flow will take place on a molecular scale, the macromolecules displacing the hydrocarbon molecules and relaxing locally. The hydrocarbon molecule will tend to restore equilibrium in the concentration by diffusion. The net result is a loss of energy which is greater the greater the value of the local rate of shear strain—*i.e.*, it is higher on the periphery than at the centre of the pipe. In effect this is equivalent to layers of increasing viscosities as the radius increases. As this is a function of the radius, plots of (v/D) *vs* F for tubes of equal (L/D) values will not be independent of the radius of the tube, giving the appearance of a retarding layer.

The curves shown in Fig. 6 are typical of those soap–hydrocarbon systems possessing relatively low values of this relaxation effect. When the relaxation effect assumes higher values—as when calcium naphthenate of a particular pH is used in light hydrocarbon—the relaxation along the radius of the pipe can give peculiar thickening effects.

ROTATIONAL VISCOMETRY.

The principles governing the drag on one cylinder by another having relative motion to it, the space being filled by a soap solution in hydrocarbon, are the same as those described for the flow of these solutions in the pipe beyond the " inlet length." However, there is at least one advantage to be gained with the rotational viscometer over the capillary tube, and that is with the study of materials which show time-dependent changes in their viscosities on shearing. No such work was done in this investigation, but attention must be directed towards the work done by Green [14] and his collaborators using this type of instrument to study the laws of thixotropy of suspensoids.

Two other features of rotational viscometry of interest in connexion with these materials may be mentioned briefly :—(1) The rate of shear strain obtaining in the material between the inner and outer cylinder can be considered almost constant in comparison with the great variation in the values across a section of the material in a capillary viscometer under similar conditions of flow. Thus, there should be a very much smaller effect due to relaxation in rotational viscometry compared with capillary viscometry, in so far as the cylindrical portion of the apparatus is considered. The difference, however, is a matter of degree of magnitude only ; essentially similar phenomena take place in both types of viscometry.

(2) In studying simple viscous material by rotational viscometers, errors are encountered due to the drag on the flat ends of the stationary cylinder. These are termed " end effects," and efforts are usually made to eliminate them, either by shaping the ends, or by measuring the increase in torque when all conditions are varied except the length of the torque-measuring cylinder, and thus estimating the end-effects for zero length of immersion

and correcting for it.[8, 16].   From the studies reported here on the secondary flow across the flat ends of the stationary disc immersed in a rotating solution of soap in hydrocarbon, it would appear that end-effects for such systems may be quite large compared with those obtained with simple viscous materials.   It follows that it would be necessary to evaluate these effects experimentally for the conditions required, when accurate viscometry by the rotational method is undertaken.

Falling-Sphere Viscometry.

Falling-sphere viscometry affords the opportunity of testing materials in an unworked condition.   The three-dimensional problem of a falling sphere is much more complex than the flow in a tube, which, except for the secondary relaxation effect, is a problem of flow in a single dimension. The equations of falling-sphere viscometers will be discussed for simple fluids first and then empirical modifications will be introduced to fit them to the present systems.   It is found necessary to ignore such complications as the relaxation phenomenon, the retarding layer effect, etc.

The fundamental derivation of the equations of motion of a sphere in a fluid falling under an action of a force is that due to Stokes,[15, 18] who obtained :—

$$f = 6\pi r \mu v \qquad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where
$\quad f$ = force acting on sphere ;
$\quad r$ = radius of sphere ;
$\quad \mu$ = absolute viscosity of fluid ;
$\quad v$ = velocity of sphere.

Since for a sphere falling under gravity, f = weight of sphere in the fluid, Stokes' equation becomes :—

$$f = \tfrac{4}{3}\pi r^3 (\rho_1 - \rho_2) g = 6\pi r \mu v \quad . \quad . \quad . \quad . \quad (7)$$

where
$\quad \rho_1$ = density of sphere ;
$\quad \rho_2$ = density of fluid ;

or
$$\mu = \frac{2}{9} \frac{(\rho_1 - \rho_2) g r^2}{v} \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Oseen,[8, 15] re-derived Stokes' equation, taking into account certain terms which had been neglected by Stokes.   The effect of this is to introduce a correction when the Reynolds number $Re \left(= \dfrac{2vr\rho_2}{\mu} \right)$ is not negligible compared with unity.   The modified form obtained by Oseen is :—

$$f = 6\pi r \mu v (1 + \tfrac{3}{16} Re) \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Equations (6) and (9) both apply to a sphere falling in an infinitely extensive medium.   When the fluid is contained in a vessel of finite width but infinite length, corrections have to be applied for the effect of the wall on the velocity of the sphere.

Several corrections have been proposed (see Barr [8]), the best being that

by Faxen, who, working with Oseen's system of equations, arrived at the formula for an infinitely long cylinder of radius R,

$$f = 6\pi r\mu v \div \left[1 - 2\cdot104\left(\frac{r}{R}\right) + 2\cdot09\left(\frac{r}{R}\right)^3 - 0\cdot95\left(\frac{r}{R}\right)^5 \right] \quad . \quad (10)$$

which applies when $Re\left(\frac{r}{R}\right)^2$, $Re^2\left(\frac{r}{R}\right)$ and $\left(\frac{r}{R}\right)^6$ are negligible compared with unity.

From a consideration of numerous experimental data from different workers, it appears that the effect of the bottom of the cylindrical tube is negligible when the distance of the sphere from the end is comparable with the distance from the side walls.

In order to test the applicability of the various formulæ, a test was done using a lubricating oil with spheres of different diameters and densities. It was found that Faxen's formula gave a value of viscosity which was independent of the dimensions of the system, and which agreed with the
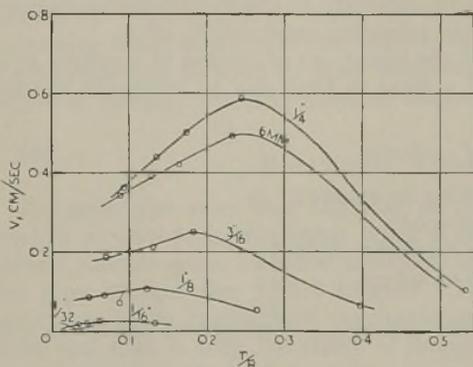

FIG. 8.

value obtained using an absolute capillary viscometer and a relative U-tube viscometer to the limits of the accuracy of the methods, which, for an oil of 6 poises, was 1 per cent. The only point to be noted in this connexion is that the density of steel spheres of the same diameter, ranging from $\frac{1}{32}$ in. up to $\frac{5}{8}$ in. in diameter, differed by as much as 0·5 per cent. from each other. Thus, it is advisable to determine the weight of individual balls and their volumes if highly accurate viscometry is desired for simple fluids; for complex colloids this error is small compared with the imperfection of knowledge of other factors.

The viscosity of soap solutions in hydrocarbons depends on the rate of shear strain, which itself is determined by the velocity and diameter of the sphere, and the diameter of the containing vessel.

The effect of the ratio r/R on the velocity of the sphere is two-fold. Firstly, as with a simple viscous fluid, an increase in r/R results in a retardation of the sphere. Secondly, an increase in r/R increases the rate of shear strain for the same velocity, thus changing the viscosity, which in turn results in an alteration in the velocity of the sphere. This effect is shown, in Fig. 8, for an aluminium stearate solution in petrol; the viscosity decreases with an increase in rate of shear strain, and the two effects are opposite. Up to a fairly large value for r/R, the effect of rate of shear strain is predominant and velocity increases with increased r/R. When r/R is increased further, the retarding effect of the wall (and probably of the layer at the interfaces) becomes predominant, and velocity rapidly decreases. The solution represented in Fig. 9 has an increasing function

of viscosity with rate of shear strain, so that the two effects combine giving a continuously decreasing velocity with increasing r/R.

In order to correlate results obtained with different spheres in different containing tubes, it is necessary to calculate the viscosity and rate of shear strain for each ball, and plot the results as a curve of viscosity against rate, of shear strain. A complete mathematical analysis proved impossible, as such derivation requires knowledge of the relationship between viscosity and shear stress, or rate of shear strain, which is not available for these fluids. Equations by Powell and Eyring,[19] by Bondi,[20] and by Grunberg and Nissan,[21] involve variables of energies and molecular structure which are not usually known for colloidal systems; and hence these equations are not normally applicable directly. It was therefore decided to use Faxen's formula for calculating an apparent value of the viscosity. The use of this formula for the colloidal systems of soaps in hydrocarbons involves two assumptions:—

1. That the wall correction is the same for colloids as for simple viscous fluids.

2. That the viscosity calculated by the formula is the mean viscosity of the fluid sheared by the ball. Only when the variation of viscosity with the rate of shear strain obtaining is small

Fig. 9.

are these assumptions acceptable, as then probably the viscosity obtained by Faxen's formula will be the same as the mean obtained by calculating the viscosity at each point and averaging by integration over the whole space. However, as explained above, it is necessary to accept such assumptions until further knowledge of the viscometry laws for colloids of soaps in hydrocarbons becomes available.

For characterizing the rate of shear strain it was found that the simple term (v/r) was not sufficient; another term involving (r/R) or $(R - r)$ was necessary.

In order to obtain a mean value for rate of shear strain Faxen's derivation was studied, but it was found impracticable to obtain an expression for the mean rate of shear strain or for shear stress from his work. Therefore, simplified flow models were assumed, which were more amenable to simple mathematical treatment. From these models it was possible to derive expressions for mean shear stress, mean rates of shear strain, and for the mean viscosity corresponding to these values. The suitability of these models was judged by the following criteria.

(1) The calculated value for mean viscosity $(\bar{\mu})$ should reduce to Stokes' viscosity (μ_s) for simple viscous fluids when $r/R = 0$, or
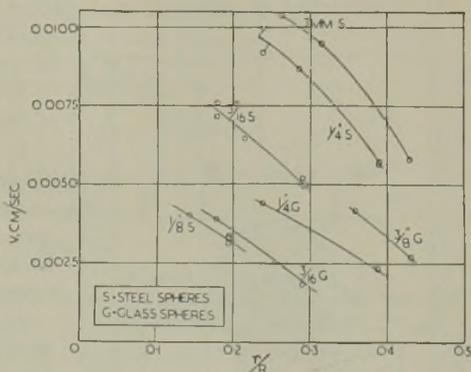
$$\lim_{r/R \longrightarrow 0} \bar{\mu} = \mu_s.$$

(2) The correction for the wall effect should be reasonably near that calculated by Faxen for practical values of r/R. Where these criteria fail, the model is considered to fail to represent the viscometric system.

If these two criteria are satisfied, then it is considered that the calculated values of viscosity, shear stress, and rate of shear strain are reasonably near the mean of the values actually occurring.

Several models were subjected to analysis, and the one giving the best results judged by the above criteria is as follows (see Fig. 10) :—

(1) The sphere is assumed stationary in a cylindrical tube, the fluid flowing along the tube and round the ball.

(2) The velocity distribution outside the planes AB and CD is assumed uniform and equal to the velocity v of the sphere in the experiment, i.e., the fluid is unstrained outside these planes.

(3) The velocity distribution in all planes between AB and CD is assumed parabolic (as for simple viscous flow in an annulus).
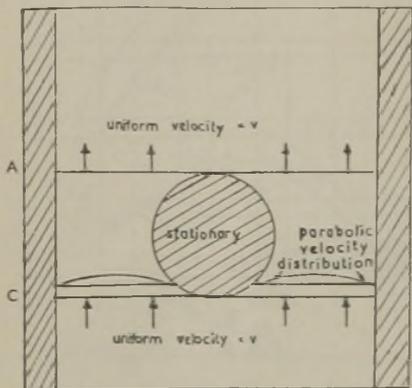
This model is different from fact in the following respects :—

FIG. 10.

1. No correction for kinetic energy effects is included. This omission is common to all derivations for falling-sphere systems, including Stokes–Ladenburg and Oseen–Faxen systems.

2. The actual velocity distribution round the sphere is not necessarily parabolic; probably it is sufficiently near to exclude large errors.

3. In practice the fluid in front of and behind the sphere is strained to a certain extent.

4. In practice, the sphere moves relative to the wall of the containing tube with a velocity v. In the model there is no relative velocity between sphere and wall.

The effects of 3 and 4 on the calculation of viscosity are opposite. The total effect of the differences between model and fact is apparently to render the model non-representative for values of r/R exceeding 0·25.

The formulæ obtained using the above model are :—

Mean rate of shear strain, $\overline{S}$, is given by

$$\overline{S} = \frac{3v}{r} \int_0^1 \frac{N^2}{N^2 - (y/r)[2 - (y/r)]N - [(y/r)(2 - y/r)]^{\frac{1}{2}}} \cdot d(y/r) \quad . \quad (11)$$

$$= 3\frac{v}{r}\phi_1(N)$$

Mean shear stress :—

$$\overline{F} = \frac{W}{2\pi r^2(N + 2)} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Mean viscosity :—

$$\overline{\mu} = \frac{\overline{F}}{\overline{S}} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (13)$$

In the above expressions $N = R/r$; W = weight of sphere in the fluid, *i.e.*, corrected for buoyancy.

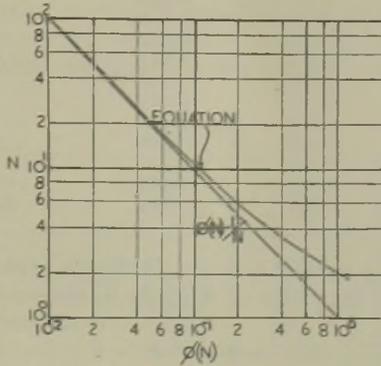The value of the integral in equation (11) is plotted against N in Fig. 11.

FIG. 11.

The derivation of these equations is not reproduced, since the method is fundamentally empirical in nature justified solely by results.

The two criteria discussed above can be applied as follows :—

1. Value of viscosity as N approaches infinity : It can be shown that as N approaches infinity, *i.e.*, r/R approaches zero, the value of the integral in equation (11) approaches $1/N$ (see Fig. 11) and $N + 2$ approaches N. Thus the limiting value of viscosity as $N \longrightarrow \infty$ becomes

$$\lim_{N \longrightarrow \infty} \mu = \frac{W}{2\pi r^2 N} \div \frac{3v}{r} \cdot \frac{1}{N}$$

or

$$\lim_{N \longrightarrow \infty} \mu = \frac{W}{6\pi r v}$$

This is Stokes' equation.

2. Value of wall correction : The factor by which the Stokes' viscosity must be multiplied to correct for the wall effect is, for the Faxen equation, K_F given by

$$K_F = \frac{N^5 - 2 \cdot 104 N^4 + 2 \cdot 09 N^2 - 0 \cdot 95}{N^5} \qquad . \qquad . \qquad . \qquad (14)$$

The correction from equation (13) above is K_M, given by

$$K_M = 1 \div (N + 2) \int_0^1 \frac{N^2 d(y/r)}{N^2 - (y/r)(2 - y/r)N - \sqrt{y/r(2 - y/r)}} . \qquad (15)$$

A comparison of the values of the two corrections at various values of

N is given in Table I. Both corrections approach unity as N approaches infinity.

<div align="center">TABLE I.</div>

N.	K_F.	K_M.	$\dfrac{K_M - K_F}{K_F} \times 100.$
2	0·179	0·243	$+36\cdot3$
2·5	0·285	0·322	$+13\cdot4$
3	0·376	0·393	$+\ \ 4\cdot52$
4	0·508	0·511	$+\ \ 0\cdot002$
5	0·597	0·589	$-\ \ 1\cdot34$
6	0·658	0·644	$-\ \ 2\cdot58$
8	0·739	0·715	$+\ \ 0\cdot27$
10	0·791	0·772	$-\ \ 2\cdot40$
13	0·840	0·818	$-\ \ 2\cdot62$
20	0·896	0·866	$-\ \ 3\cdot35$
25	0·916	0·898	$-\ \ 1\cdot97$
50	0·957	0·934	$-\ \ 2\cdot40$
100	0·980	0·980	Zero

Plots of K_F and K_M against r/R, i.e., $(1/N)$ are given in Fig. 12. It can be seen that for values of N above 4, reasonably good agreement is obtained between K_F and K_M, i.e., less than 5 per cent. differences. Therefore, equation (11) for mean rate of shear strain, and equation (12) for the mean shear stress, will be sufficiently correct for values of N greater than 4. Although it is possible to calculate a mean viscosity from equation (13) it is preferable to calculate the viscosity by Faxen's formula and utilize the equations derived here to calculate only the bases of comparison—i.e.,
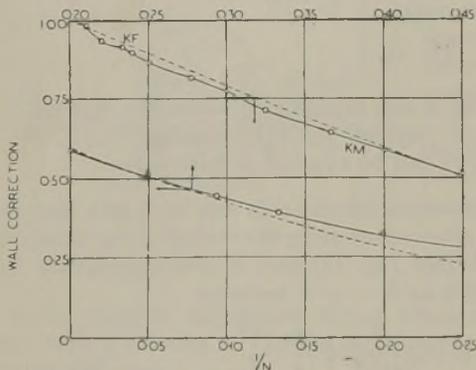

FIG. 12.

the stress and rates of strain ordinates—and not the criterion of comparison between two soap–hydrocarbon fluids, their viscosities.

Experiments were performed using two soap solutions in hydrocarbons with different viscosity–rate of shear-strain characteristics. The spheres used were steel ball-bearings of various sizes from $\frac{1}{32}$ in. upwards in dia., and accurately ground glass spheres of $\frac{3}{16}$, $\frac{1}{4}$ and $\frac{3}{8}$ in. dia. The containing vessels were glass cylinders varying in diameter from 1·2 cm to 6·9 cm. Lines between which to measure the time of fall of the spheres were marked on the cylinders at intervals of about 5 cm along their lengths, the total length of the cylinders being 40 to 50 cm. Temperature was controlled by immersing the containers in a tall water bath kept to within $\pm0\cdot1^\circ$ C. The tubes were maintained accurately vertical by fixing the whole apparatus, including the water bath, to a steel base-plate which could be adjusted by levelling screws. Before any measurements were made, it

was ascertained that the velocity of the sphere became constant after 5 cm of fall, and remained constant to within 5 cm of the bottom of the tube. For each sphere in each tube, several readings were taken and averaged.

It should be noted that the experimental error with these fluids was relatively high, as the materials were translucent and strong lighting was necessary which resulted in local heating, despite the water bath. Furthermore, the fluids were slightly heterogeneous, despite the care taken in preparation and storage.

All determinations with the first solution, which consisted of a colloidal dispersion of an aluminium soap in gasoline, were made on the same day. The results are summarized in Table II. The results marked with an asterisk are for N values less than 4, and so cannot be used with the above derivations.

TABLE II.

R, cm.	r, cm.	N.	v, cm./sec.	Faxen μ poises.	$\bar{S}$, sec.$^{-1}$ equ.[11]	F, dynes/cm.^{2} equ.[12]
0·6	0·0794	7·55	0·0190	365	0·102	42·3
	0·1588	3·79 *	0·0516	355	0·340	139·5
	0·238	2·52 *	0·0640	400	0·490	268
	0·300	2·00 *	0·126	227	1·293	383
	0·317	1·89 *	0·103	300	1·14	415
1·3	0·0794	16·35	0·0255	327	0·0646	22·0
	0·1588	8·21	0·107	260	0·263	79·2
	0·238	5·47	0·249	218	0·689	162·3
	0·300	4·33	0·493	150	1·449	242
	0·317	4·10	0·583	137	1·734	265
1·83	0·0794	23·00	0·0196	447	0·0323	16·2
	0·1588	11·51	0·0723	300	0·119	59·8
	0·238	7·70	0·210	270	0·371	125
	0·300	6·10	0·420	215	0·795	190
	0·317	5·75	0·504	197	0·973	209
2·35	0·0397	59·2	0·00574	405	0·0073	3·28
	0·0794	29·6	0·0182	485	0·0232	12·8
	0·1588	14·8	0·0934	355	0·119	48·1
	0·238	9·91	0·200	340	0·277	101·7
	0·300	7·82	0·391	258	0·536	156
	0·317	7·41	0·441	250	0·610	172
3·4	0·1588	21·45	0·0872	400	0·077	34·5
	0·238	14·28	0·186	385	0·164	74·5
	0·300	11·33	0·344	325	0·303	115
	0·317	10·70	0·362	318	0·319	127

Attempts to correlate the results by plotting viscosity against v/r were unsuccessful, as shown in Fig. 13. Though a curve is obtained for the different spheres in each tube, the curves for the different tubes do not coincide. A plot of Faxen viscosity against rate of shear strain from equation (11) gives a single curve for all spheres and tubes (Fig. 14). Experiments in which N was less than 4 give erratic results. Though there is still a spread in Fig. 14, this is probably no more than to be expected, due to the experimental difficulties encountered with the fluids and to the

H

neglect of the several factors of layer effect, yield values masked by relaxation, etc., in the simple treatment of the theory.

Thus it is considered that Fig. 14 represents a satisfactory correlation of
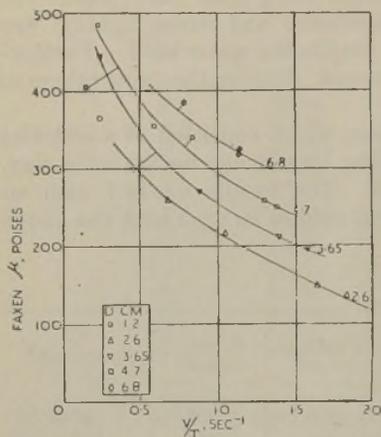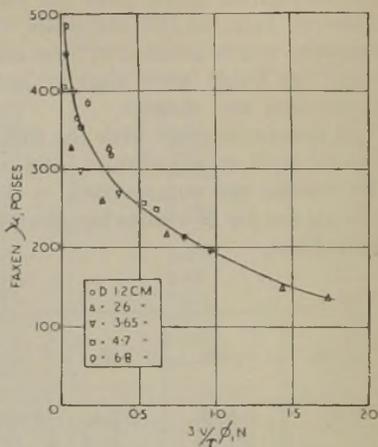

Fig. 13.

Fig. 14.

the results.   Fig. 15 shows the relation of viscosity to average shear stress, as calculated by equation (12).

A highly viscous, colloidal suspension of soap in petrol peptized differently from Fluid No. 1 was tried next.   Owing to its very high viscosity, with
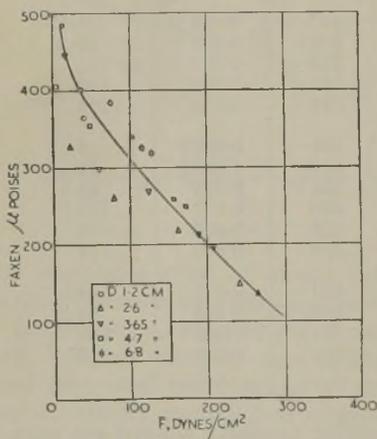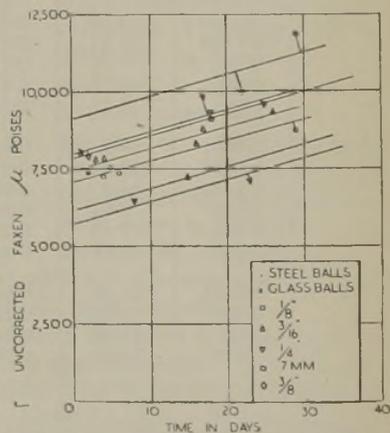

Fig. 15.

Fig. 16.

consequent low velocity of the falling sphere, experiments with this fluid were spread over a period of thirty-six days.   During this period, the viscosity increased steadily, owing to the fluid not being stable over such a period of time, rendering the comparison of the two fluids complicated. Correction of measurements for this increase in viscosity was possible, as

the change was found to be linear with time, this fact being checked by results taken with the same sphere and tube on the first, last, and intermediate days. Variation of viscosity with rate of shear strain for this material is relatively small, and thus a plot of viscosity *versus* time gives

TABLE III.

R, cm.	r, cm.	N.	V, cm./sec.	Faxen μ corrected to first day, poises.	$\bar{S}$ corrected to first day, sec.$^{-1}$.	$\bar{F}$, dynes/cm.^{2}.	Day of test.	
0·813	0·350	2·32	0·00578	7980	0·0340	412	1	
	0·317	2·56	0·00570	8070	0·0302	353		
	0·317	2·56	0·00560	7850	0·0301	353	2	
	0·238	3·43	0·00515	7290	0·0263	223		
	0·238	3·43	0·00487	7650	0·0251	223	3	
	0·238	3·43	0·00485	7600	0·0252	223	4	
	0·1588	5·13	0·00320	7050	0·0150	113		
	0·1588	5·13	0·00309	7280	0·0145	113	5	
	0·1588	5·13	0·00317	7030	0·0150	113	6	Steel spheres.
1·102	0·350	3·15	0·00781	7910	0·0361	346	25	
	0·317	3·49	0·00718	7910	0·0320	294		
	0·238	4·62	0·00526	7600	0·0220	183	26	
	0·1588	6·94	0·00309	6750	0·0119	90·1	29	
1·323	0·238	5·55	0·00663	7270	0·0205	160·5	16	
	0·238	5·55	0·00626	7670	0·0193	160·5	17	
	0·317	4·16	0·00820	8770	0·0268	262		
	0·317	4·16	0·00867	8080	0·0291	262	18	
	0·350	3·77	0·00991	7920	0·0343	309		
0·813	0·350	2·32	0·00445	8050	0·0343	412	36	
0·813	0·317	2·56	0·00216	6000	0·0123	139	8	
	0·238	3·43	0·00160	6250	0·00935	84·1	15	
1·102	0·476	2·32	0·00222	9850	0·0115	181	29	Glass spheres.
1·323	0·476	2·77	0·00358	8520	0·0139	164	22	
	0·238	5·58	0·00287	4340	0·0105	60·1	23	
	0·317	4·18	0·00345	5590	0·0128	100		

a straight line for each ball, almost independently of the containing tube used. By this means, the slope of the lines, and hence the viscosity correction for time, can be fixed fairly accurately. The plot is given in Fig. 16, and the results, corrected to the first day of measurements, are given in Table III.

Again it is found that no correlation is obtained by plotting viscosity

against v/r (see Fig. 17).   A plot of viscosity and rate of shear strain from equation (11) is given in Fig. 18.   It can be seen that a reasonable curve is obtained.   An important point is that the fact that viscosity increased
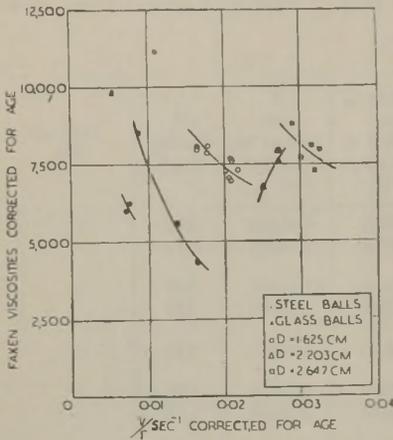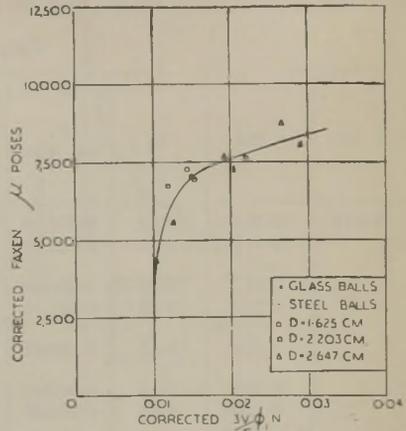

FIG. 17.   FIG. 18.

with shearing stress with this fluid is not indicated by any other plot. Points for which N is less than 4 were omitted.

Fig. 19 shows the relationship of viscosity with average shear stress as calculated by equation (12).

Whilst this discussion of falling-sphere viscometry in relation to such a

FIG. 19.

complex system as soap dispersions in hydrocarbons has only emphasized rather than solved the difficulties encountered in interpreting experiments, it is hoped that the empirical approach described will at least prove useful, as it has done here, in elucidating some of the viscosity characteristics of the fluids.

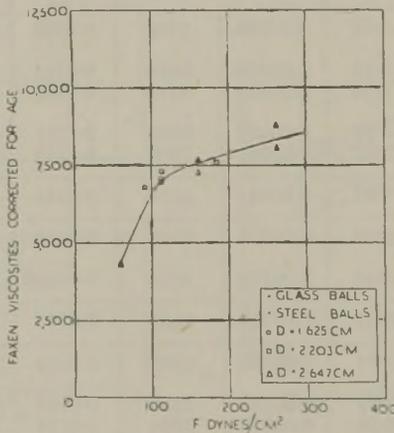## DIFFERENT VISCOSITIES FOR DIFFERENT TYPES OF RATES
OF STRAIN.

Following Lamb,[15] imagine three planes drawn through any point, perpendicularly to the 3 co-ordinate axes x, y, z, and consider the components of velocity u, v, w, in the three directions of a particle moving with velocity V. In the equations of motions derived in detail by Lamb, it will be seen that the components of stress are affected by three distinct " types " of rates of strain (the same as there are different types of strains in problems of elasticity), *i.e.*,

1. rate of bulk dilatation or of volumetric expansion and contraction : $\left(\dfrac{\partial u}{\partial x} + \dfrac{\partial v}{\partial y} + \dfrac{\partial w}{\partial z}\right)$;

2. rate of " compression " (or " tension ") : $\dfrac{\partial u}{\partial x}$;

3. rate of shear : $\left(\dfrac{\partial u}{\partial y} + \dfrac{\partial v}{\partial x}\right)$

and similarly for v and w. It is assumed that the effects on each component of stress is proportional to the corresponding rate of strain ; the constant of proportionality, being the " coefficient of viscosity," is further assumed to be the same for all three types of rates of strain shown.

For isotropic simple fluids this last assumption is reasonable and was justified, at least in so far as the equality of the viscosity coefficient for the second and third types of rates of strain are concerned, by Pochitino's work on pitch reported in full by Hatschek.[16] The dissipation of energy by dilatation has not been proved with accuracy to be consistent with the assumption that the viscosity ordinarily measured is responsible for " bulk viscosity." [17] It appears highly improbable that a material like a colloidal dispersion of soap in hydrocarbon, which gives optical anisotropy on flow, would possess only *one* coefficient of viscosity for rates of strain of all three types.   However, with capillary and Couette viscometers the third type of rate of strain is predominant, and results from the two systems of viscometry would be expected to agree after layer effect, end effects, etc., have been accounted for.   In falling-sphere viscometry both second and third types are operative.   It is therefore interesting to compare results obtained by capillary and falling-sphere viscometry.

It has already been stated that at low rates of shear these dispersions give a constant viscosity. Tests were therefore specially conducted at very low rates. The viscosity was found to be independent of dimensions of apparatus ; therefore layer effects were insignificant. Similarly the viscosity, using $\frac{1}{32}$ and $\frac{1}{16}$-in. dia. balls, was found to be the same, and, therefore, it appears that ordinary Newtonian laws of flow are operative. However, the viscosity for the soap dispersion by a capillary viscometer was 640 poises ; that by falling-sphere method was 240 poises. Tests on a rubber in benzene solution showed inequality again, but in a reversed order : capillary viscosity was 50 poises whilst falling sphere gave 120 poises. It appears therefore reasonable to assume that these colloids possess more than one " coefficient of viscosity." (This is not to say that

they necessarily possess three coefficients of viscosity along the three axes of space; they possess coefficients of viscosity differing with the type of rate of strain as a solid possesses different moduli of elasticity for the different types of strains even although it is isotropic in behaviour.)

CONCLUSIONS.

Summarizing the results of the study on viscometry of soap in hydrocarbon systems it appears that

1. These systems behave as if they possessed a retarding layer at the fluid–solid interface.

2. These fluids relax in a way which implies extra loss of energy to that encountered in other pseudo-plastic systems. This results in

(a) A high viscous-type energy loss at entrance into a pipe.

(b) Certain complications in the flow pattern of the stream lines and resultant pressure losses becoming significant in rotary and capillary viscometry.

3. These fluids, when of sufficiently high concentration, reveal a definite yield value and recoil on short-period experiments. Where long periods are involved the relaxation of (2) above may mask the rigidity implied by a yield value.

4. At low rates of flow, and when no yield value is evident, these fluids behave as if they were simple Newtonian liquids.

5. In the region of low rates of flow, viscosities obtained by capillary and falling-sphere methods are not the same for the same fluid.

6. It is not possible to calculate, a priori, an explicit expression to denote the mean, or a standard, value for the rate of shear strain in viscometric methods without previous knowledge of the relation existing between the viscosity and the rate of shear strain for the fluid. Such knowledge is not usually available for colloidal systems, but it is found that in capillary viscometry the expression (v/D) is sufficiently representative of the rate of shear strain obtaining at dynamically similar points of a pipe containing soap dispersions in hydrocarbons to enable us to study these fluids on a comparative basis. In falling-sphere viscometry, however, the equivalent expression (v/r) is not found to be so useful; the mean rate of shear strain appears to contain a function of N, the ratio of the diameter of the fall tube to that of the falling sphere, as well as (v/r). This function of N is given based on an empirical treatment of a simplified model of the system.

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    Edgbaston,
      Birmingham, 15.

UNITS AND SYMBOLS.

Units.

Throughout the paper all calculations were made with consistent units using c.g.s. systems, where practical units were quoted or shown on the graphs (*e.g.*, lbs/sq. in for pressure), these were converted after calculation by using appropriate conversion factors.   The units used were thus :—

lengths	cms
velocities	cm/sec
acceleration	cm/sec^2
pressures and stresses	dynes/cm^2
forces and weights	dynes
densities	gms/ml
viscosities	poises

Symbols.

D = diameter of pipe.

F = shearing stress at the wall of a pipe.

$\bar{F}$ = mean shearing stress.

f = force acting on a falling sphere.

f_1, f_2, f_3 = functions of type (1), (2), and (3) respectively.

g = gravity constant = 981 cms/sec^2.

K_F = wall correction in falling-sphere viscometry as given by Faxen.

K_M = wall correction in falling-sphere viscometry as given by equations developed from the model proposed in this paper.

L = length of pipe.

L' = equivalent length of pipe ;

= $L + nD$.

N = ratio of radius of fall tube to radius of falling sphere.

n = number of diameters of pipe to which the entrance is equivalent in causing viscous pressure loss.

P = pressure drop in a pipe.

P_c = total contraction loss at entry of a pipe, nozzle, orifice, etc.

P_s = viscous pressure loss at entrance to contraction.

R = radius of fall tube in falling-sphere viscometry.

R_s = Reynolds number.

r = radial distance of a point from the axis of a pipe in capillary viscometry ; radius of sphere in falling-sphere viscometry.

r_L = radial thickness of the layer at fluid–solid interface.

r_B = radial thickness of the bulk of the fluid in a pipe.

$\bar{S}$ = mean rate of shear strain.

s = rate of shear strain.

u, v, w = components of velocity of a moving portion of a fluid, taken along the three co-ordinate axes.

W = weight of falling sphere in the fluid, *i.e.*, corrected for buoyancy.

y = vertical distance measured upward from the base of falling sphere.

ρ_1 = density of falling sphere.

ρ_2, ρ = density of fluid.

μ, μ_B = viscosity of fluid in bulk.

μ_L = viscosity of the layer at the fluid–solid interface.

$\bar{\mu}$ = mean viscosity taken over the sheared fluid.

ϕ_1 = function.

References.

[1] Freundlich, H., and Röder, H. L.   *Trans. Faraday Soc.*, 1938, **34**, 308.

[2] For a Bibliography see Scott-Blair, G. W.   " Introduction to Industrial Rheology." London : J. & A. Churchill, Ltd., 1938, p. 81.

[3] Bulkley, R., and Bitner, F. G.   *J. Rheol.*, 1930, **1**, 269.

[4] Arveson, M. H.   *Industr. Engng. Chem.*, 1932, **24**, 71.

[5] Blott, J. F. T., and Samuel, D. L.   *Ibid.*, 1940, **32**, 68.

[5a] Varentzov, V. P.   *Petroleum*, 1946, **9**, 184, and following issues.

[5b] Gallay, W., and Puddington, I. E.   *Canad. J. Res.*, 1946, **24**, 73.

[6] Garner, F. H.   *J. Inst. Petrol.*, 1946, **32**, 256.

[7] Nissan, A. H.   *Ibid.*, 1942, **28**, 41.

[8] Barr, G.   " A Monograph of Viscometry."   Oxford : University Press, 1931.

[9] Goldstein, S.   " Modern Development in Fluid Dynamics," 2 vols.   London :
    Clarendon Press, 1938.
[10] Langhaar, H. L.   *J. Appl. Mech.*, 1942, **9**, A55.
[11] Scott-Blair, G. W.   " Introduction to Industrial Rheology."   London : J. & A.
    Churchill, Ltd., 1938.
[12] *Idem.*   " A Survey of General and Applied Rheology."   London : Sir Isaac Pit-
    man & Sons, Ltd., 1944.
[13] See Treloar, L. R. G.   " Reports on Progress in Physics," 1942–43, **9**, 113, for a
    summary and review of work by himself, by Guth, Kuhn, Mark, Wall and others
    on this theory and its results.   Later work justifies to a great extent the two
    assumptions made.
[14] Green, H., and Weltmann, R. N.   *Industr. Engng. Chem. Anal.*, 1946, **18**, 167, and
    other papers by the same authors and collaborators.
[15] Lamb, H.   " Hydrodynamics."   6th Edn.   Cambridge : University Press, 1932.
[16] Hatschek, E.   " The Viscosity of Liquids."   London : G. Bell & Sons, 1928.
[17] Reiner, M.   " Ten Lectures on Theoretical Rheology."   Jerusalem.   Rubin Mass.,
    1943, 51.
[18] Stokes, G. G.   " Mathematical and Physical Papers."   Cambridge : University
    Press, 1880, **3**, 10 and 56.
[19] Powell, R. E., and Eyring, H.   *Nature*, 1944, **154**, 427.
[20] Bondi, A.   *J. Appl. Phys.*, 1945, **16**, 539.
[21] Grunberg, L., and Nissan, A. H.   *Nature*, 1945, **156**, 241.

DISCUSSION.

THE CHAIRMAN (Mr J. S. Jackson) : This is one of the occasions on which we had hoped to have a specialist Chairman to guide and lead the discussion.   We invited Professor Andrade, but he has been indisposed recently, and is not yet sufficiently recovered to feel justified in taking part in outside meetings.

I do not feel qualified to offer any critical commentary, but it is obvious that the paper covers a painstaking and thorough investigation of a problem which is of very real interest to everybody in the oil industry.

DR E. W. J. MARDLES : The authors of the paper are to be congratulated on having presented such an excellent mass of experimental data, the collection of which must have occupied a long time and must have de-manded great care and patience, and on the excellent manner in which they have analysed the results.   Dr Nissan should also be congratulated on the clear manner in which he has described the work and the courage with which he has tried to give explanations.   Many hypotheses to explain the complex phenomena he has indicated are controversial, and it is this complexity and controversial character which make rheology so fascinating a study.   Whenever we delve into these phenomena we find something new.

The appearance of the sigma phenomenon is of particular interest. Reiner, Scott-Blair, Buckingham, and others have used the method to determine the effect of the length of a tube, and its diameter, on the apparent viscosity.   With colloidal solutions and non-Newtonian liquids, that phenomenon appears prominently, and it is rather to be expected, because the colloidal dispersions of the soaps are composed of asymmetric particles. During flow not only the particles but the aggregates of the particles become orientated along the slipstream and the viscosity will depend on the degree of orientation.

Dr Nissan mentioned the degree of wetting, or the cohesion between the

walls and the liquid. That is very important, for with a liquid such as a white spirit or a mineral oil, which has a very low contact angle with surfaces such as glass or metal, and if is added to it a small amount of soap, the contact angle increases considerably; ordinary grease is practically a solid, with the contact angle above 90°, so that with soap-thickened liquids one would expect slipping at the walls. The σ-phenomenon is due to these two factors—namely, the orientation of the particles and the aggregates during their passage through the pipe, and also the slip at the walls. The velocity gradient across the diameter is uneven.

Thixotropy due to orientation is very interesting. With rough irregular particles such as silica, and with asymmetric particles dispersed in a viscous oil, the behaviour is like that of a Newtonian liquid, but in hexane of low viscosity thixotropy can be observed. In the low-viscosity liquids orientation occurs more quickly and more extensively than in viscous media during the time of the measurement. By varying the viscosity of the medium, one can obtain all kinds of behaviours with colloidal or other suspensions.

Another matter of particular interest is the paradox mentioned, that although the soap-thickened systems may show definite yield values, when tested by the viscometer, of several hundred dynes/sq.cm, yet these materials were found to exhibit a level mirror-like surface on long standing, denying the existence of the yield value. The reason for the paradox is in the simultaneous possession of rigidity and a relaxation mechanism which is comparatively slow. The existence of yield values has been a matter of contention for the last twenty years or more and began when Bingham brought forward his equation, in which the yield value was deducted from the acting pressure or shearing stress. Although the existence of yield values was denied by some workers yet it appears now to be well established for many systems. Dr Nissan and his colleagues have shown that the time factor comes in. Time is one of the most important factors in rheological measurements. Some time ago the British Rheologists' Club published a table of rheological systems in which the three factors of stress, strain, and time were involved.

Have the authors of the paper considered the elastic properties of their systems? Dr Nissan mentioned that below the yield stress Newtonian flow was observed. With a soap-thickened oil in a concentric-cylinder viscometer using a small load, below the yield stress, there will be movement but if the load is removed, there will be movement back. We have observed elastic creep over 24 hours with a soap–oil system and after removal of the stress the almost complete return. Below the threshold of the yield stress systems are solid and not liquid, although with mechanical disturbance the yield value may decrease in value, a form of rigidity thixotropy.

A soap-thickened system consists of aggregates of particles of soap, and a part of the energy of mechanical disturbance temporarily breaks up the flocculation or the aggregation. The yield stress is really a summation of all the bonds and links in a three-dimensional structure and, when these are broken, the yield stress should fall.

Gallay and Puddington, in one of their papers, mentioned that if you take a soap fibril in a grease and pull it out with a micro needle and then let it go, it snaps back, possibly due to this elastic effect.

I should like to congratulate the authors on the fact that they have taken the trouble to use with the same system a large variety of viscometers. Judging by the literature, this practice has not been done very much. Usually the individual worker has one form of viscometer, in which he examines different systems ; the authors have made measurements on an engineering scale and used their own pressure-viscometers, also the rotating cylinder and the falling-sphere viscometers, checking up the results and comparing them. It is an admirable piece of work, and I think that if other rheologists were to use the same technique they would realise that the apparent viscosity and rheological behaviour they are recording are often characteristic of the particular instrument they have used. The use of various instruments does rule out discrepancies of this kind and that is why the results presented in the paper are so valuable.

I should like to say something about the falling-sphere with non-Newtonian systems, for the behaviour is extremely complex. Using a little higher concentration solutions of various soaps in organic liquids, we have found that the rate of fall depends on the depth. I do not think the authors found that result.

DR NISSAN : No. We measured the rate of fall across several portions, and it was uniform. We did not take it right to the bottom, but avoided the last 5 to 10 cm. Down the tube, for each 5 cm, the rate of fall was the same.

DR MARDLES : I was doing some work for Mr E. G. Ellis in connexion with his grease panel, and I dropped a 1-in steel ball, and a steel ruler end on, into a yellow lime-base grease. Both the ball and the ruler were of practically the same weight, but while the ruler slipped down to the bottom, the 1-in ball went just beneath the surface and stayed there. That is the kind of result we have been getting. If an automatic record is taken of the rate of fall of a ball through a suspension or colloidal system, it will be found that it seems to decelerate as it descends towards the bottom, and very often it does not reach the bottom. We have experimented by pushing discs into grease ; the discs go only to a certain depth and then stop. The heavier the disc, the more nearly it will approach the bottom. There are several explanations, but more experimental work is required before any complete and satisfactory explanation can be given.

The great difficulty I have experienced, and which all workers with these soap solutions have experienced, is due to the extraordinary complexity of the condition of the soap. This depends on how the system is prepared and on how it is treated subsequently. In a 1-gallon tin of grease there appear to be different consistencies in the various parts, possibly due to the asymmetry of the particles. As the tin is filled a sort of pattern may be woven according to how the particles lie. In one direction one may be " running with the grain " of the grease, and in another direction " across the grain," with a corresponding change in consistency. By adding a little water to greases or soap-thickened liquids, the system becomes more thixotropic ; the small soap particles become wet, and there is a different state of flocculation and aggregation. In addition there is ageing and hardening.

The whole problem of the rheology of soap-thickened liquids is highly

complex, and the only approach to a clear solution of the problem is to take one factor at a time, as the authors of this paper have done, and try to understand it.

DR NISSAN : Dr Mardles has added much to our knowledge, but on one or two points I would like to say a word.

The material shown in the graph did not appear to have a large yield value; the figures given were for more concentrated fluids. But that it did have a yield value was quite evident, because it possessed elastic recoil on rapid application and release of stress. Evidently the force was not sufficient to shear it permanently.

With regard to the Newtonian flow regime, it is difficult to know whether it was a truly Newtonian material—i.e., flowing with parabolic distribution of velocity in a tube—or whether it was flowing completely by step-wise elastic strain : relaxation, strain : relaxation, and so on. Such a mechanism of flow could probably give a pressure/velocity diagram which was linear. Parabolic distribution may or may not have been there; it is impossible to say which mechanism applied. It is to be noted that if the strain : relaxation steps were infinitesimal Newtonian flow would result as presumably viscous flow on a molecular scale is in discreet steps.

Coming to the σ-phenomenon, Dr Mardles has mentioned that it can be changed merely by the viscosity of the solvent. That is quite apparent from other work. In a paper by V. P. Varentzov,* are several curves (Fig. 20) which illustrate this point. In our systems, it will be remembered, there was a σ-phenomenon; I said it was in the opposite direction from the normal, that apparently the system was more viscous on the surface than in the bulk. Varentzov published his figures as showing no slip. But if the curves are examined and the effect of change in diameters followed it will be seen that there is generally a change in the rate of shear at constant stress—i.e., as the diameter gets smaller there is a higher rate of shear for the same shearing force. It should be noted that the scale of the graphs is highly condensed.

Another thing to be remembered is that the grease here was not a solution of soap, but rather it was actually micro-crystalline; and that illustrates the point made by Dr Mardles, that this σ-phenomenon is obtained ranging from positive to negative values and disappearing completely by changing the medium.

Referring to the falling-sphere viscosities, we checked several times for the change of rate of fall with depth; and for those materials which were relatively thin as compared with greases we confirmed that it was constant before we proceeded to study them. Furthermore, we chose materials which were non-thixotropic. In these systems the velocity was uniform, and, of course, these analyses will apply only to such systems, and not to the more complex ones such as Dr Mardles has discussed.

MR L. GRUNBERG : I think one of the more significant points in the paper is that the authors have laid emphasis on the importance of the rate of shear strain, as compared with the shear stress. If the literature on

* Symp. Visc. Liquids & Colloids, Acad. Sci. U.S.S.R., 1941, 1, 197–210; Petroleum, 1946, 9, 184, 206.

the subject is studied, it will be found that shear stress figures prominently, whereas the rate of shear strain usually takes second place ; that is because the rate of shear strain is very difficult to evaluate.　The authors' emphasis
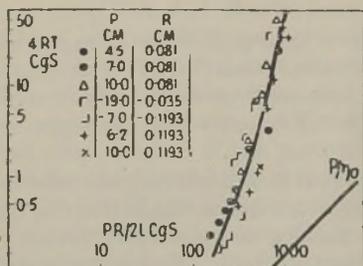

Fig. 5.—*Sodium grease* 5%, *t*=20°C.

Fig. 6.—*Aluminium grease* 10%, *t*=20°C.
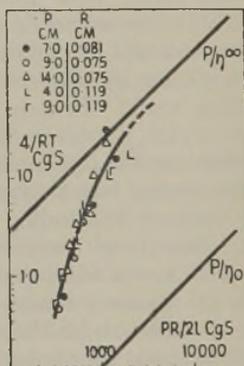
Fig. 7.—*Calcium grease* 10%, *t*=20°C.

Fig. 9.—*Calcium grease* 5%, *t*= − 20°C.

Fig. 10.—*Calcium grease* 10%, *t*= − 20°C.
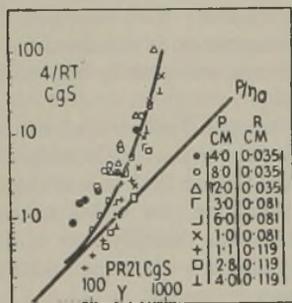
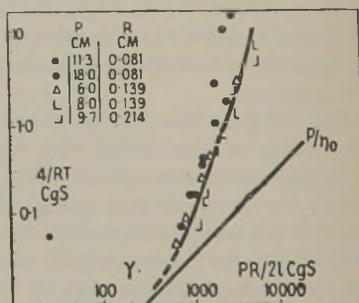Fig. 11.—*Aluminium grease* 5%, *t*= − 20°C.

FIG. 20.

of the rate of shear strain is one reason why their paper is a most important contribution.

The reference to the inverted σ-phenomenon recalls some work of D. P.

Barnard and R. E. Wilson,[*] who observed that with the Newtonian liquids containing polar molecules, the flow through capillaries decreased with time, owing to the formation of adsorbed layers on the wall of the capillary. That links up with some work which Dr Nissan and I did on the flow of solutions of sodium chloride and other substances in water.[†] We found, in using a capillary diameter of 10^{-4} cm, that there is a difference in the rate of flow (corrected for bulk viscosity) for the same pressure drop, if those different liquids are used; and at that time we could find no other explanation than that the concentration of solute in the boundary layer was different from that in the bulk of the liquid. I wonder whether that explanation, rather than the relaxation theory, expresses the results.

There is another matter on which I can bring some supporting evidence. Some time ago we made some experiments on the temperature rise and the behaviour of different oils in bearings.   We used a number of oils, including a diesel oil–aluminium stearate gel.   Whereas with ordinary oils we found a certain amount of leakage from a journal bearing, when we used the soap solution the end leakage increased beyond anything that could be expected; the solution was absolutely oozing out from the end of the shaft, and it was thrown out at a considerable speed by the rotation of the shaft.   From a reading of the paper it seems that that phenomenon probably arises from the circumstance that, whereas inside the journal bearing there is a high rate of shear, at the outside, i.e., at the end of the shaft, the rate of shear is practically nil.   There is a flow from the location of high rate of shear strain to a position of low rate of shear strain, giving rise to abnormal leakage.

Generally, I think the most significant sentence in the paper is that which appears at the end of the first paragraph, where the authors refer to studying certain of the available methods " in the light of recent experience carried over three to four years experimental and theoretical investigation."   That sentence is very significant because it indicates the pains and the labour which these workers had to suffer before they produced this paper, on which I should like to congratulate them.

Mr H. G. Spence : Do the authors consider that some of this enormous end effect may be due to flow at that point causing a change in the concentration at the different parts of the material, as compared with the concentration distribution prevailing in the normal part of a tube ?

Dr Nissan : In effect, yes; but probably it is a longer story, at least in our opinion, than that of a mere change of concentration.   If we define the change of concentration as being due to the molecules of the solute tending to move from the highly-sheared region to the un-sheared region, we shall obtain a gradient similar to that obtained by Perrin in his colloidal atmosphere, for instance.   It will be remembered that in Perrin's experiments on the settling of colloidal dispersions the density increases with depth because some of the colloid particles settle down, but the kinetic energy of the particles disperses them again, the colloidal particles behaving as though they were large molecules, thus a dynamic equilibrium is established.   In our experiments, there probably will be a uniform velocity across the entry

* Industr. Engng. Chem., 1922, 14, 683.
† J. Inst. Petrol., 1943, 29, 193.

of a pipe.   Just beyond the entry the boundary layer begins, a thickening boundary layer, as in Newtonian flow.   At the end of the so-called inlet length probably more than 98 per cent of the diameter is filled in with the boundary layer.   Inside the boundary layer there is no shear;   there is flow, but it is uniform.   Outside it, *i.e.*, between the boundary layer limit and the perimeter of the tube, there is fairly severe shear.   Consequently, there is a boundary across which molecules of solute tend to jump, and then they relax.   In doing that, energy is lost, equal to the product of n, which represents the number of molecules jumping, times E, the energy loss on jumping per molecule.   But n is probably an exponential function of E.

So that there is a change of concentration towards equilibrium, but it is a dynamic, and not a static, equilibrium.   The elastic solute particles tend to go to the centre, but thermal agitation and other factors throw them back in the relaxed condition.   Thus there is a continuous tendency for elastic solute particles to flow down the spatial gradients of rates of shear, revealing secondary flow—which Mr Grunberg has just mentioned as occurring in a journal—as well as this dynamic change of concentration.

THE CHAIRMAN : It seems to me that meetings such as this offer a splendid opportunity to have questions answered by the authors or by other experts in the audience.   It might be helpful therefore if we relaxed at this stage into a rather less formal discussion since the fear of publication sometimes hangs heavily over would-be contributors to these discussions.   The publication of such informal queries and answers can of course remain at the discretion of the individuals concerned.

DR E. W. J. MARDLES : I should like to ask how much the phenomenon of " spinnbarkeit," the property of the drawing out of the system into long threads, is concerned with the " climbing up the rotating pole " experiment. The property is pronounced with " spinnbar " systems.

DR NISSAN : The connexion, to our minds, is that " spinnbarkeit " is the outward appearance of this very phenomenon;   in other words, we believe this relaxation is responsible for " spinnbarkeit " of long elastic molecules.

The reason I say that is this : assume that a new surface is formed; in that surface at the moment of formation there is a very severe, though temporary, strain.   Consequently, if the relaxation theory is correct, there should be a tendency for the surface molecules to go inwards.   But if a molecule shows a tendency to go inwards in a liquid, it shows surface tension.   In other words, a newly-formed surface of solutions of elastic materials which relax by the mechanism we suggest should have a higher surface tension than an old static surface, if we are right in what we suggest. We measured the dynamic surface tension by means of conical expanding jets.   At some critical point in such an experiment, the kinetic energy is a measure of the dynamic surface tension, and we can calibrate the apparatus and method by means of ordinary liquids such as oil, water, and so on. The dynamic surface tension of these fluids is sometimes about 300 dynes/ cm, whereas surface tension is only of the order of 29 to 30 dynes/cm.

It is true that, when a thread of an ordinary liquid is drawn, when the

length approaches the circumference of the cylinder it forms into a drop. If the dynamic surface tension increases with shear, however, it will not break into drops, and a stable thread will be obtained. The more quickly that is done, the more the fluid is " spinnbar." If the thread is pulled slowly, it will break, but if it is pulled quickly it goes back and does not break.

So that the two phenomena are connected ; indeed, one gives rise to the other.

MR E. THORNTON : I am very grateful to the authors for thinking and writing so clearly on this subject that even a chemist can follow it with great interest. All this work is leading us into a further search for knowledge, and it will have valuable consequences. We should be grateful for that ; but the principal feature is that they have brought this border-line subject, which used to belong to the abstruse mathematician, to the notice of the chemist.

MR J. H. CARLILE : There is a small practical point I have come across in working on the type of system mentioned by the authors. In carrying out work on long term stability in this type of system I have found that the rate of change of viscosity with time seems to be affected by the bulk of the sample of material being stored, *i.e.*, comparing bulks of the order of a few cc. and of a few gallons, there is found in the smaller bulk a much greater change of viscosity over the same period.

DR NISSAN : In reply, I can only offer a guess rather than an explanation. The specific volume of the material is, of course, inversely proportional to a standard dimension of the volume for any given shape. If a cube of 1 cm side, and having an area of 6 cm², is taken the volume is 1 cm³. If that is cut into eight equal cubes, each with 0·5 cm sides, the specific surface is twice as much ; for a cube $\frac{1}{n}$ cm side the specific surface is

$$6 \left(\frac{1}{n}\right)^2 \div \left(\frac{1}{n}\right)^3 = 6n \text{ cm.}$$

So that, if a container is to have an effect on the material at all, it will have that effect initially at least through the surface of contact. Therefore, the greater the specific surface for that volume, the greater the contact effect.

However, that is purely a guess, in the absence of more detailed work to check it. But if this explanation is correct, it should be possible to get relatively simple check experiments whereby, for the same surface, there would be different volumes, or rather, different surface areas for the same volume. For instance, if solid material were put into a gallon of liquid, the surface for the same volume could be increased until the ratio of surface in contact with the material to its volume was the same as that of a smaller sample container. If the breakdown is limited by phenomena occurring at the surface—and not by, say, secondary reactions in the liquid—then the rate of breakdown should be the same in both volumes. From such

experiments it may be possible to work on a basis of a unit specific surface from which breakdown with different volumes may be evaluated.

VOTE OF THANKS.

THE CHAIRMAN : It is my pleasure to offer the very hearty thanks of all of us to Dr Nissan and his collaborators for their most interesting paper, which is quite fascinating even for those who are not specialists in the subject.   We do appreciate also the clear way, and the generous way, in which Dr Nissan has dealt with the discussion.

The vote of thanks was carried with enthusiasm.

SPECTROSCOPIC ANALYSIS: APPLICATION OF THE HYDROGEN DISCHARGE LAMP TO THE ANALYSIS OF MIXTURES OF C$_8$ AROMATIC HYDROCARBONS.

By R. R. Gordon, M.A., Ph.D.,* H. Powell, Ph.D.,* and J. Tadayyon, B.Sc.†

Summary.

1. Two methods of using the hydrogen discharge lamp employed by other workers are described and examples of the application given. It is shown that neither of these methods gives accurate analyses.

2. A third method has been developed which, by the use of a microphotometer, makes possible a quantitative measure of the absorption at any wavelength.

3. This method in its present stage of development is not so accurate as the Spekker method normally used, but reasons are given for the opinion that it may be made at least as accurate as the normal method.

4. The method using the microphotometer is not so rapid as the Spekker method for the analysis of isolated samples, but is more rapid when analyses are required on a series of samples whose composition and concentration are known approximately.

5. The accuracy obtained is shown by the analysis of nineteen synthetic mixtures to be approximately ± 5 per cent, i.e., 10 per cent ± 5 per cent or 90 per cent ± 5 per cent.

Introduction.

THE method of analysis used up to the present in the Research Department of the Anglo-Iranian Oil Company, Ltd., at Sunbury for mixtures of aromatic hydrocarbons has been fully described in a previous publication,[1] and employs a high-tension spark between tungsten steel electrodes as the source of ultra-violet radiation. The spectra resulting from this source appear on the photographic plate as a large number of separate lines, and it has been suggested that this source suffers from several disadvantages.

Some workers consider that the interpretation of the photographic plates obtained using the Spekker photometer and high-tension spark is a matter of great difficulty and that large errors may be made in analysis. One reason for this is that the ease of determining the " match point "—i.e., the point at which the two halves of each photograph have equal blackening —is influenced by the nature of the emission line at which equality occurs. In some cases this may be a sharply defined line giving the easiest match point to determine, but it may happen that the line is diffuse, in which case the determination is more difficult. This objection, however, does not appear to be very serious in view of the results quoted in our previous publication.‡

* Anglo-Iranian Oil Company, Ltd., Research Laboratories, Sunbury-on-Thames.
† The University, Birmingham.
‡ J. Inst. Petrol., 1945, 31, 428.

I

Another possible objection to the use of the high-tension spark as the source of radiation is that for a very narrow absorption band the peak of the band may fall between two emission lines. This leads to an error in the determination of the molecular extinction coefficient for the pure hydrocarbon at the wavelength of the peak. Since this coefficient is determined once only for a hydrocarbon at a given wavelength, and is used thereafter as a constant in the analysis, any error involved in its measurement will be reflected in all subsequent analyses. While the objection is certainly valid, its effect can be minimized by always using the same emission lines in analysis as those used in determining the molecular extinction coefficients.

Still another source of error to which the Spekker method of analysis may be liable arises from the fact that the chosen range of values of the variable aperture cannot be traversed in a continuous manner, but must be covered in steps. There is always the possibility that the match point may fall between two such values and must be interpolated by eye. It has been found that there is no advantage to be gained by taking the areas of the variable apertures close together, as it appears that the eye cannot pick out the match point from a slowly varying series of values with any greater accuracy than can be obtained by interpolating visually between steps of 0·05 in the optical densities. A photometric method, however, such as that described later, would have the advantage of allowing the optical density at a given wavelength to be determined in a continuous manner, thus eliminating the need for visual interpolation.

As a possible method of overcoming these objections the use of a hydrogen discharge lamp has been suggested, the spectrum obtained from this source being continuous.

Possible objections to this method might arise from the area of the source or non-uniformity of its intensity. These objections may be dealt with (a) by a specially small lamp, or (b) by the principles of the method used.

Two methods have been put forward by other workers for utilizing this source. These are :—

1. A straightforward photograph may be taken through a suitable thickness of a solution of the mixture in a non-absorbing solvent. Then by experience the probable constituents of the mixture may be identified from the positions of the absorption bands, and quantities may be estimated visually from the relative intensities of the bands.

2. Photographs may be taken of various thicknesses of the solution being examined, each photograph being recorded in close proximity to a photograph taken through a fixed thickness of a solution of known composition and concentration. By comparing the two sets of photographs and noting the relative thicknesses at which the bands due to the unknown solution have the same intensity as the corresponding bands due to the known solution, it is possible to " bracket " the concentrations of the components in the mixture.

Both these methods have disadvantages, method 1, for example, clearly requiring a large amount of previous experience. Further, the interpretation of the photographic plate is much more subjective than that of the Spekker photographs. Method 2, since it involves comparison with standard solutions of the pure components, would in time prove

expensive in these valuable materials.   It also involves a preliminary photograph by method 1 in order to identify the components so that the correct " standard " solution may be chosen.   Even when this is done there is no certainty that the standard solution will contain all the necessary components, as the preliminary photograph may miss small quantities (less than 10 per cent) of some of them.

To overcome these objections a third method of using the hydrogen lamp has been developed in this laboratory.

PRINCIPLE OF THE METHOD.

This consists in essence of taking a photograph through a known thickness of solution and measuring the intensity of absorption recorded on the photographic plate by means of a micro-photometer.   The use of this instrument as a means of measuring the relative intensities of emission lines is well known in metallurgical analysis by means of the spectrograph, but it does not appear to have received the same attention in absorption analysis using ultra-violet radiation.   The chief difficulty in the application of the microphotometer lies in the fact that the blackening of a photographic plate is a complicated function of time of exposure, type of plate, wavelength of radiation causing the blackening, the developer used, and the time and temperature of development.   To eliminate these difficulties, or reduce them to a minimum, it is essential that every plate be calibrated by means of a series of standard exposures, the intensities of radiation corresponding to these bearing known ratios to one another.   The most obvious method of doing this is to place the source of radiation at fixed distances from the entrant slit of the spectrograph, the relative intensities of radiation falling on the slit being calculated according to the inverse square law.   The slit width and time of exposure are kept constant for all positions of the source. This method, however, requires a large amount of space, and could not be employed owing to the design of our apparatus.

Another method is to keep the light source at a fixed distance from the slit and vary the width of the slit with constant exposure time.   The amount of radiant energy is dependent on two factors : intensity per unit area of slit and the area (the time factor having been eliminated by using a constant time of exposure).   Since in the present case the intensity of the lamp has been shown to be constant by experiment and the slit height is fixed, then the total energy is proportional to the slit width.

If, therefore, a series of exposures is made with slit widths varying in known steps, the resulting plate blackenings will be a function of the corresponding slit widths.

The plate blackening is expressed quantitatively as the density of blackening, which is defined as the logarithm of the ratio of the intensity of light transmitted by the clear (unexposed) plate to that transmitted by the exposed part.   This is usually expressed as $\log \frac{i_0}{i}$.   When using a micro-photometer the ratio $\frac{i_0}{i}$ is taken as the ratio of the galvanometer throws at these two points.

The procedure is then as follows :—

(*a*) Photographs are taken with fixed intensity of source and time of exposure through the cell filled with solvent, the slit widths having values of 50, 45, 40 . . . . 5, 2, and 1 units (the unit in this case is 0·0025 mm). These are the standard exposures.

(*b*) The slit width is fixed at 50 units, and the absorbing material, diluted with non-absorbing solvent to give a suitable plate blackening at the desired wavelength, is placed in the radiation path.

(*c*) A photograph is taken through this solution, the time of exposure being the same as with the solvent alone.

(*d*) The plate bearing a series of calibration spectra on solvent only,
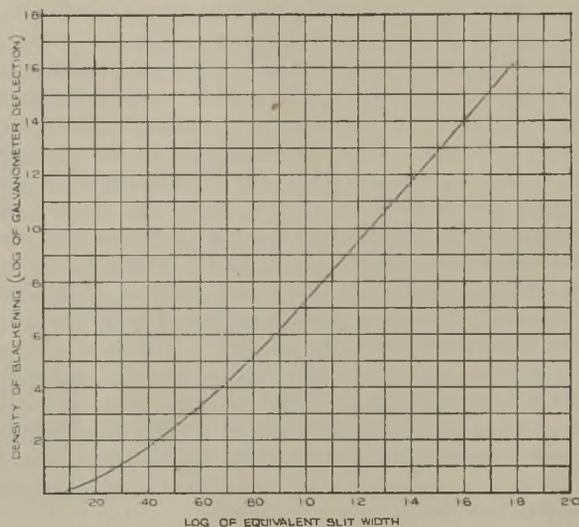
FIG. 1.

DENSITY OF BLACKENING *v.* LOG OF EQUIVALENT SLIT WIDTH.

and one absorption spectrum of the solution being analysed, is developed, fixed, washed, and dried.

(*e*) The plate blackenings on the developed plate are determined at the standard wavelengths selected for the analysis, by means of the microphotometer. From the standard exposures a calibration curve is drawn of blackening against log of slit width for each wavelength. An example of this is shown in Fig. 1.

(*f*) The plate blackening is determined at the standard wavelengths for the photograph taken through the solution, and the calibration curves for the appropriate wavelengths are used to convert density of blackening to effective exposure or slit width.

In determining plate blackening it is not essential in practice to make use of the clear plate deflection, since all measurements are by difference. The calibration curve may therefore be plotted against the logarithm of

the galvanometer deflections, thus reducing the amount of calculation required.

The optical density of the absorbing solution is defined as $\log \dfrac{I_0}{I}$, where I_0 and I are the intensities of the incident and transmitted radiation respectively.

The total energy of the radiation incident on the absorption cell containing the solution is $50k$, where k is the constant of proportionality between slit width and total energy, since the slit width was fixed at the arbitrary setting of fifty divisions.

Let the equivalent slit width at a given wavelength where absorption is occurring (obtained from the calibration curve) be A.

Then the equivalent total energy of the light transmitted by the solution is Ak.

The optical density is therefore given by :—

$$
\begin{aligned}
d &= \log \frac{50k}{Ak} \\
&= \log 50/A \\
&= \log 50 - \log A
\end{aligned}
$$

This explains the plotting of the calibration curve in terms of the logarithm of the slit width, in preference to the slit width itself.

Apparatus.

The apparatus used comprised a Hilger large, fully automatic quartz spectrograph, and a specially designed hydrogen discharge lamp. This spectrograph has approximately four times the dispersion of the medium spectrograph used in previous work, and required four photographic plates to cover the range of wavelengths covered by the medium spectrograph on a single plate. The range of wavelengths desired may be selected by a range indicator, all the necessary adjustments to maintain focus being made automatically.

The hydrogen lamp used was designed by Messrs. Adam Hilger, Ltd., to give a small source of uniform intensity over the luminous area. The lamp has a plane quartz end-plate, and is provided with a sealed-in palladium wire to maintain the pressure of hydrogen by diffusion. The normal method of introducing the hydrogen into the tube is to heat this wire with a small hydrogen flame. It has been found advantageous, in order to prevent back-diffusion of hydrogen, to cover the exposed wire with rubber tubing, which is then sealed with a screw clip. The lamp is run from a 4000-volt output transformer, the current in the secondary being maintained at 150 milliamps. Owing to the large amount of heat generated, it is necessary to provide water cooling with this lamp.

The microphotometer used in part of the work was a Casella instrument.

<div align="center">RESULTS.</div>

The results of analyses by the three methods discussed in the introduction are given below.

Method 1.   Direct Photograph.

An example of this method is shown in Fig. 2, which gives photographs of mixtures of *m*- and *p*-xylene.   The compositions of these mixtures are given in Table I reading from the top of Fig. 2.

<div align="center">TABLE I.</div>

Photograph.	Wt % of—		Total aromatics gm/l.
	p-xylene.	*m*-xylene.	
1	—	100·00	0·1723
2	19·60	80·40	0·1240
3	29·80	70·20	0·1245
4	40·21	59·79	0·1256
5	50·48	49·52	0·1242
6	60·15	39·85	0·1234
7	70·22	29·78	0·1239
8	80·23	19·77	0·1244
9	90·15	9·85	0·1249
10	100·00	—	0·0767

The absorption bands due to the individual components of these mixtures are indicated on Fig. 2, an absorbing layer of 2 cm of each solution being used.   On examination of the figure it is seen that all traces of *m*-xylene have disappeared in photograph No. 9.   This corresponds to 9·85 per cent wt *m*-xylene.   There is a certain loss of sensitivity by using a print instead of the original photographic plate, but even on the original the *m*-xylene could not be detected when present in amounts less than 8 per cent.

Similar photographs have been taken using mixtures of three and four components.   The general conclusion reached is that while such photographs may reveal the main constituents of a mixture, the method cannot be regarded as a quantitative method of analysis.   The example given in Fig. 2 is the simplest combination of the C_8 aromatics from the analytical point of view, since it gives two clear-cut, well-separated, and strong absorption bands due to the individual components.   The other C_8 aromatics give rise to bands which are overlapped to some extent by the remaining bands of *m*- and *p*-xylene shown in Fig. 2.   This leads to uncertainty in making an analysis particularly when the other components are present in small amounts.

### Method 2.   Comparison with " Standard " Solution.

This method is illustrated in Fig. 3.   Two solutions have been used, and it has been assumed that solution 1 (see below) is the unknown to be analysed, solution 2 having been made up using known concentrations of the components suggested by a preliminary photograph of solution 1 according to method 1.   The concentrations in solution 2 have been chosen

↑   ↑

m-xylene

p-xylene

Fɪɢ. 2.

MIXTURES OF *META-* AND *PARA*-XYLENES.

Direct photograph.
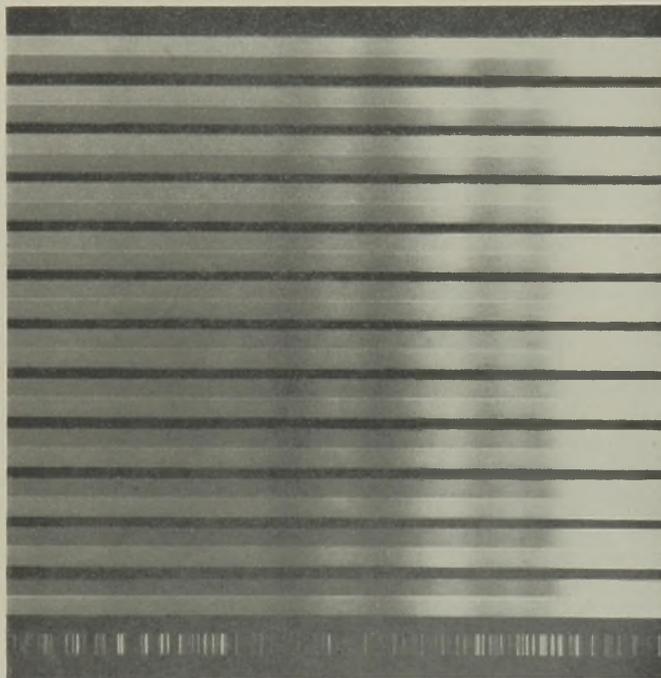
Solution No.	Thickness. mm.
2	2·25
1	3·00
2	2·50
1	3·00
2	2·75
1	3·00
2	3·00
1	3·00
2	3·25
1	3·00
2	3·50
1	3·00
2	3·75
1	3·00
2	4·00
1	3·00
2	4·25
1	3·00
2	4·50
1	3·00
2	4·75
1	3·00
2	5·00
1	3·00

Fɪɢ. 3.

MIXTURES OF C_8 AROMATICS.

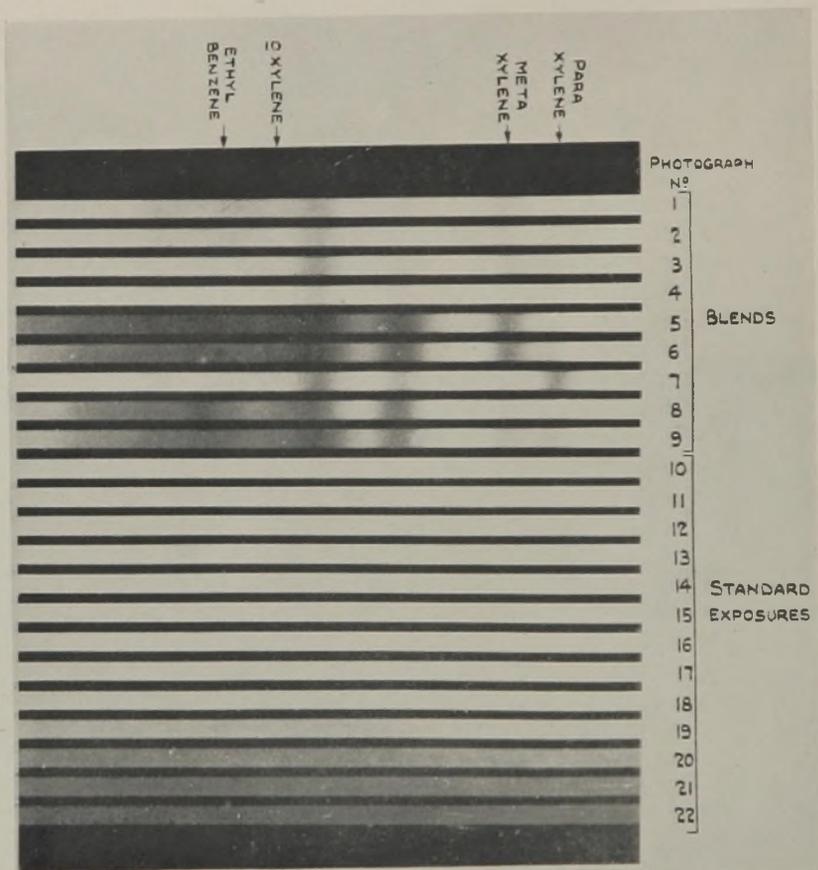Plate taken for comparison method.

[*To face p.* 108.

FIG. 4.
MIXTURES OF C_8 AROMATICS.
Plate taken for use with microphotometer.

to give a close approximation to those estimated for solution 1. An approximate thickness of solution 1 to give clear absorption bands was found by trial and error. A thickness of 3 mm was suitable in this case. A series of photographs was taken using a constant time of exposure (2 min) at this thickness, sufficient space being left between each pair of photographs to allow the interposition of a photograph of solution 2. These photographs of solution 2 were taken through thicknesses of 5·0, 4·75, 4·5, 4·25, 4·0, 3·75, 3·5, 3·25, 3·0, 2·75, 2·5, and 2·25 mm of solution. The resulting photograph shows a series of pairs of spectra somewhat similar to those obtained in the Spekker method of analysis.

The next step is to find from the photograph the thicknesses of solution 2 which show the same intensity of absorption as that obtained from solution 1, taking each maximum independently, and this is done by inspection. Then, since the concentration is inversely proportional to the thickness for a given intensity, it is a simple matter to obtain the concentrations of solution 1 from those of solution 2.

An experiment was made to test this method using a four-component mixture of C_8 aromatics. The actual compositions of solutions 1 and 2, expressed in terms of wt per cent on total aromatics, are given in the Table II, together with the composition of solution 1 as found using the method.

TABLE II.

				Composition, wt %.			
				m-Xylene.	p-Xylene.	o-Xylene.	Ethyl-benzene.
Solution 1.	Actual	.	.	40·37	13·0	19·94	26·66
	Found	.	.	35·5	14·0	25·0	25·5
Solution 2	.	.	.	34·64	14·34	25·55	25·47

The agreement between the actual and observed values in this case, while not particularly good, is better than that obtained from method 1. It is also to some extent fortuitous, in that the composition of solution 1 was in fact known, so that a close match solution could be made. Even with this advantage, the method is in no way comparable with the normal Spekker procedure, and is considerably more laborious and lengthy.

Method 3. In Conjunction with the Microphotometer.

Nineteen blends comprising two-, three-, and four-component mixtures of the three xylenes and ethylbenzene have been analysed by this method. An example of the photographs obtained is shown in Fig. 4. The composition and concentrations, both actual and observed, for the nineteen mixtures are given in Tables IV to VII.

One of the four-component blends (No. 3, Table VII, photograph No. 5, Fig. 4) has been selected as an example of the method. The standard exposures shown in the lower portion of the photograph (and numbered 10–22) were obtained using slit widths of 50, 45, 40, 30, 20, 12, 6, 5, 4, 3, 2, 1·5, and 1, and the 2 cm-cell filled with solvent, the exposure in each case being 2 minutes. The slit width was then fixed at 50, and a photograph

taken through a 2 cm thickness of the solution. On the microphotometer the galvanometer deflections given in Table III were obtained.

TABLE III.

Photograph No. (Fig. 4).	Contents of cell.	Slit width ($1 = 0.0025$ mm).	Galvanometer deflections (cm).			
			2745 Å.	2725 Å.	2708 Å.	2615 Å.
22	Solvent only	1	45·0	45·3	48·5	47·4
21	,,	1·5	41·3	42·7	44·0	43·7
20	,,	2	36·2	36·3	37·5	37·8
19	,,	3	26·5	26·6	28·8	28·5
18	,,	4	20·8	21·6	22·2	21·7
17	,,	5	16·5	17·4	17·7	18·3
16	,,	6	10·0	11·0	11·6	11·5
15	,,	12	6·2	6·4	6·7	6·95
14	,,	20	3·6	3·6	3·8	3·9
13	,,	30	2·3	2·25	2·45	2·5
12	,,	40	1·7	1·65	1·8	1·75
11	,,	45	1·5	1·4	1·5	1·5
10	,,	50	1·3	1·3	1·4	1·45
5	Blend 3 diluted to give suitable absorption	50	9·9	15·6	11·5	32·0

TABLE IV.

Results of Analysis of Mixtures containing m- *and* p-*Xylene.*

Blend No.	m-Xylene, wt %.		p-Xylene, wt %.		Total * aromatics, ratio obs/actual.
	Actual.	Obs.	Actual.	Obs.	
1	55·1	55·0	44·9	45·0	0·987
2	71·1	71·4	28·9	28·6	1·011
3	71·4	73·3	28·6	26·7	1·004
4	78·9	77·9	21·1	22·1	0·984
5	86·2	86·8	13·8	13·2	0·983

* Columns 2 and 4 of the above table are obtained from the known weights of aromatics added in making the mixture, the sum being taken as 100 per cent. Columns 3 and 5 are obtained by taking the sum of the observed weights of the individual aromatics as 100 per cent. Column 6 shows the ratio of the sum of the observed weights to the weight of aromatics added.

TABLE V.

Results of Analysis of Mixtures containing m-, p-*Xylene and Ethylbenzene.*

Blend No.	m-Xylene, wt %.		p-Xylene, wt %.		Ethylbenzene, wt %.		Total aromatics, ratio obs/actual.
	Actual.	Obs.	Actual.	Obs.	Actual.	Obs.	
1	33·6	29·8	14·8	15·1	51·6	55·1	1·003
2	38·4	39·3	23·2	21·4	38·4	39·3	1·022
3	45·9	48·7	9·4	9·4	44·7	41·9	0·964
4	53·2	59·6	12·2	12·0	34·6	28·4	0·986
5	74·2	75·7	13·7	10·4	12·1	13·9	0·981
6	83·0	77·2	10·7	11·8	6·3	11·0	1·015

From these figures a calibration curve is drawn for each wavelength relating logarithm of slit width and logarithm of galvanometer deflection (similar to Fig. 1). Using the deflections obtained when the solution is in the cell, the logarithms of the equivalent slit widths are found to be 0·899, 0·729, 0·869, and 0·429 at wavelengths 2745, 2725, 2708, and 2615 Å respectively.

The resulting optical densities are, therefore :—

$$2745 \text{ Å } \log 50 - 0 \cdot 899 = 0 \cdot 800$$
$$2725 \text{ Å } \log 50 - 0 \cdot 729 = 0 \cdot 970$$
$$2708 \text{ Å } \log 50 - 0 \cdot 869 = 0 \cdot 830$$
$$2615 \text{ Å } \log 50 - 0 \cdot 429 = 1 \cdot 270$$

From this point on the computation is similar to that given in a previous publication (*loc. cit.*) and the result is given in Table VII, blend 3.

TABLE VI.

Results of Analysis of Mixtures containing m-, p-, *and* o-*Xylene.*

Blend No.	m-Xylene, wt %.		p-Xylene, wt %.		o-Xylene, wt %.		Total aromatics, ratio obs/actual.
	Actual.	Obs.	Actual.	Obs.	Actual.	Obs.	
1	36·6	36·9	15·9	19·4	47·5	43·7	0·915
2	38·8	36·2	26·9	31·0	34·3	32·8	0·918
3	54·9	50·3	9·4	13·0	35·7	36·7	1·050
4	65·0	65·0	18·0	21·8	17·0	13·2	1·059

TABLE VII.

Results of Analysis of Mixtures containing m-, p-, o-*Xylene and Ethylbenzene.*

Blend No.	m-Xylene, wt %.		p-Xylene, wt %.		o-Xylene, wt %.		Ethylbenzene, wt %.		Total aromatics, ratio obs/ actual.
	Actual.	Obs.	Actual.	Obs.	Actual.	Obs.	Actual.	Obs.	
1	28·0	28·7	7·8	10·0	18·3	18·6	45·9	42·7	1·000
2	37·8	39·0	9·8	11·4	24·7	21·2	27·7	28·4	0·988
3	44·2	44·4	6·7	8·0	23·2	21·2	25·9	26·4	1·010
4	34·1	29·8	21·8	22·9	30·0	32·2	14·1	15·1	0·934

DISCUSSION.

This method using the microphotometer is reasonably accurate even in its present stage of development, and it is felt that it can be improved to give an accuracy at least as good as that obtained with the Spekker.

The reason for the somewhat erratic nature of the results given in Table VII lies in the difficulty of always measuring the absorption at the exact wavelengths required for analysis. In the Spekker method this is easy, by reason of the line nature of the spectrum, but with the hydrogen lamp no such indications of position on a wavelength basis are available.

The method adopted to determine the set wavelengths in the analyses discussed was to measure the distance between the various absorption peaks for the pure components and then, using a peak in the spectrum of the sample being analysed as a reference point, to obtain the other wavelengths by measurement using a vernier scale attached to the carriage of the micro-photometer. It has been found, however, that this method is not of sufficient accuracy because the absorption peaks are not sharp enough to give a well-defined reference datum. To overcome this difficulty altera-tions are being made to the microphotometer, which will allow a definite wavelength in an iron arc adjacent to the absorption spectrum to be located by visual inspection with a magnifying eyepiece fitted with cross-wires. It is essential in this method to have the iron arc photograph very close to the absorption spectrum, and also that the plateholder is not moved between exposing on the absorption spectrum and photographing the arc. This can be accomplished by the use of a Hartman diaphragm consisting of a sliding metal plate with " staggered " holes, which can be disposed so that only part of the slit is illuminated through a given hole. The plate-holder then remains in a set position for both exposures.

Another improvement proposed is to dry the photographic plates in a dust-free atmosphere, since minute particles of dust occurring at a wave-length required for analysis may give rise to erroneous galvanometer deflections.

The method described above is not so rapid as the Spekker method for the analysis of isolated samples, but if a series of samples of closely similar composition is to be analysed, then it would be quicker. The total time taken for the analysis of nine blends, each of four components, including taking the photographs for standardizing purposes, is about twelve hours, compared with about eighteen hours for the Spekker, assuming a single operator in both cases. The comparison, however, is much less favourable for a smaller number of blends, and this is particularly so if the approximate composition is not known beforehand.

We are aware that there are other ways of using the hydrogen discharge lamp in absorption analysis, the best known being the photo-electric method as used in the Beckman Spectrophotometer. The work described in this paper, however, shows how this source may be used with the standard photographic apparatus in use in Great Britain.

ACKNOWLEDGEMENTS.

SECOND REPORT ON TESTS FOR SOIL STABILIZATION. BY THE SOIL STABILIZATION PANEL OF STANDARDIZATION SUB-COMMITTEE NO. 7, ASPHÅLTIC BITUMEN.

THE present report sets out the work accomplished by the Soil Stabilization Panel of the Institute of Petroleum Standardization Committee and the more important conclusions arising from its deliberations since the completion of the First Report.*

CONSTITUTION OF THE SOIL STABILIZATION PANEL.

During the period to which this report relates, the membership of the Panel has been as follows :

> Mr L. G. Gabriel (*Chairman*).
> Mr J. F. T. Blott.
> Mr J. S. Jackson.
> Mr H. S. Keep.
> Mr A. E. Lawrence.
> Mr A. H. D. Markwick.
> Mr F. J. Patman.
> Dr R. K. Schofield.
> Dr H. G. Williams.
> Mr C. M. Gough.

Mr C. F. Armstrong has deputized on occasions for Mr H. S. Keep, and Mr K. E. Clare and Dr L. Maddison have assisted and deputized for Mr A. H. D. Markwick from time to time. Dr E. W. Russell, Dr H. L. Penman, Mr J. Parkin, and Mr D. R. Lamb have also assisted the Panel in its work on various occasions.

Subsequently the Panel has had to record with great regret the untimely death of Mr A. H. D. Markwick, whose energetic participation in all discussions so greatly contributed to the positive results obtained. The Panel wishes to place on record its indebtedness to Mr Markwick in all stages of its work, and its sense of loss in the absence of one of its most distinguished members.

Since the issue of the First Report of the Panel the British Standards Institution has formed Committee Rd/9 to deal with Soil Stabilization generally. This Committee is also under the Chairmanship of Mr L. G. Gabriel, and has set up panels to consider various aspects of its work. One of these panels is to deal with Bituminous Stabilization, and at the proposal of the Chairman the membership of the Institute of Petroleum Panel was appointed en bloc as the Bituminous Panel of the B.S.I. Committee.

This arrangement obviously provides for complete co-operation with the work of the new Committee.

PLAN OF WORK.

At the time of compiling the First Report, the Panel had laid down the following programme for discussion :

    1. Determination of frost resistance of compacted mixes ;
    2. Determination of stabilizer content of mixes ;
    3. Sampling and treatment of samples in field testing ;
    4. Standardization of methods of compaction, applicable to all tests.

The developments under each of these headings are given below, and further proposed tests are given in the appendixes.

DETERMINATION OF FROST RESISTANCE OF COMPACTED MIXES.

As was forecast in the First Report, this topic has proved to be one of considerable difficulty.   Contact has been made with Meteorological Stations, and information supplied by the Building Research Station has been considered.

A further series of tests is being carried out, using facilities offered by the Rothamsted Experimental Station.   These tests make use of large cylinders sunk in the ground, and containing soil that has been allowed to compact naturally under its own weight for many years.   The upper flat surface of the soil in the cylinders is flush with the surface of the surrounding ground. Bituminous coverings similar .in composition to the surfacings laid on stabilized soil roads have been placed on the exposed surface of the soil in two of the cylinders.

Free water can be introduced or withdrawn from the cylinders in such a way as to maintain the water-table in the soil specimens at a pre-determined depth below the upper surfaces.   Observations of any vertical movement of the surfacings and of the amounts of water drawn into the cylinders, together with temperature measurements, are being made during periods when the air temperature suggests that frost action may take place.   It is thought that the results of these experiments may indicate the conditions under which damage may occur to soil road bases.

DETERMINATION OF STABILIZER CONTENT OF MIXES.

The analytical control of stabilizing projects carried out with bituminous stabilizers is obviously a first necessity in all field work.   It was realized from the first that difficulties might be encountered due to adsorption of the bituminous stabilizer on the fine portions of certain aggregates.   Attempts to apply methods of analysis usual for testing bituminous mixtures in the road industry showed that these expectations were fully justified.   The initial experiments were carried out using carbon disulphide and trichlorethylene as solvents ; with trichlorethylene, stabilizer contents obtained fell short of the actual amounts incorporated in the test samples to an extent depending on the fineness of the soil used.   Better results were obtained with carbon disulphide, but the search was continued for a less objectionable solvent.

Previous work at the Road Research Laboratory on road asphalts had shown that where adsorption of binder occurred the extraction was assisted by the addition of a small proportion of an alcohol to the normal solvent. This method was accordingly applied to stabilized soils, and after several series of tests the most suitable solvent was found to be trichlorethylene containing 5 per cent by volume of methyl alcohol. A large number of tests were carried out, and in many cases very promising results were obtained.

In the meantime, however, a new method for the determination of the binder content of normal bituminous road surfacing mixtures was developed at the Road Research Laboratory, using agitation with methylene chloride, and it was decided to investigate its merits when applied to stabilized soil mixes. The results of analysis of samples containing different types of soils treated with bitumen emulsion or stabilizing oil were found to be very close to the actual quantities present. Portions of the same samples were then analyzed by several members of the Panel, employing this method, and close agreement was obtained, results lying in all cases within 10 per cent of the actual value. In addition to the greater accuracy, the time taken for the determination was considerably reduced.

Following these results it has been decided that the method should be put forward for publication in the form of a Tentative Test, and this will be found in Appendix A as Test Method No. T.2.

The Panel will be glad to receive any further suggestions for improvement of the method, particularly where the proportion of clay in the soil is high.

In view of the wide range of utility possessed by the methods involving mixed solvents referred to above, particularly in the cases of mixes stabilized with bituminous emulsion, and also in all cases where the amount of fines present is small, it has been decided to publish the mixed solvent method for reference purposes. This will be found in Appendix B. It is not suggested that it be considered at this stage as a method for standardization.

Sampling and Treatment of Samples in Field Testing.

Discussions under this heading have been carried out on a broad basis. Throughout the Panel has realized that its function is solely directed to advising and specifying methods of test likely to be useful in the practice of bituminous soil stabilization. Nevertheless, it was felt that general discussion of all matters connected with field sampling was necessary in the first place, as such apparently irrelevant questions as the frequency of sampling, the reinstatement of damage caused by sampling, and the coherence of large portions of stabilized material all have a practical bearing on the ultimate specification for the methods of sampling to be used.

A great many points raised in the general discussion would ultimately be best gathered together in a Code of Practice. Possibly the associated B.S.I. Committee RD/9 might ultimately consider this matter, and it would, of course, be advantageous for technicians concerned with other systems of stabilization to participate in these discussions. The frequency with which samples should be taken on a soil-stabilization project is a matter of some importance because there is a considerable reinstatement problem to deal

with the holes left where samples are taken, and if these occur too frequently the running surface may be impaired. The suggestion has been made that a suitable frequency of sampling would be one sample per 1000 sq yds.

(a) *Field Samples for Water-Absorption Tests.*

The principal purpose for which the frequent taking of samples from soil stabilization projects will be necessary is the determination of the water-absorption characteristics of the material laid. In considering the cutting out of samples for this purpose, core-cutting was first discussed and, provided no large stone is present, cores can be cut, and would prove suitable for test purposes. It is probable that with a considerable range of aggregates used for stabilization, large stone may not be present in any quantity, and it will be easy to cut cores without touching stone in the process of cutting. Furthermore, various improved designs of core-cutting appliances are under test, and it is hoped that ultimately they may render sampling by this method much easier than at present. For the moment, however, it has been thought wise to adopt a simple excavation process as a normal method of obtaining samples for investigation, and although this technique is laborious, a trial has shown that the method is perfectly practicable. Samples obtained in this way have been examined from the point of view of their use in testing for water absorption. A specification put forward by the Panel for sampling and testing in this connexion is included in Appendix C as Test Method No. A.6.

(b) *Determination of Density of Samples of Finished Work.*

The second important purpose for which samples of this type will be required is in connexion with density measurements. The Panel has considered several alternative methods for measuring the density of samples taken from finished work, of which two have been discussed in detail. These two are the Sand Replacement (Bottle) Method and a method due to Dr Russell of Rothamsted Experimental Station, who has elaborated it principally for use in determining the density of clods of soil for agricultural purposes. A third method—that using the well-known Core Cutting technique—has also been mentioned, and will be considered further by the Panel in the near future.

(i) *Sand Replacement (Bottle) Method.*—This method consists in excavating a hole in the surface of the work and superposing over the hole an apparatus suitable for determining the volume of sand necessary to fill the hole. Much experimental work has been done with this method, and the conclusion reached is that it is satisfactory and reproducible. The limitations of the type of sand, and the experimental procedure, have been checked, and the method of operation appears in Appendix D as Test Method No. A.7.

It was originally decided to investigate the practicability of a variant of the method as now given, in which the volume of sand filled into the hole is measured in the apparatus by the fall of a piston instead of by the actual weighing of the sand. After due consideration, however, it was agreed that this method presents no special advantages. The setting up of a balance on or near the site of work is recognized as

presenting some difficulties in many cases, but it is felt that this is an absolute necessity which cannot be avoided by the substitution of a volumetric procedure.

(ii) *Determination of the Density of Clods by Oil Immersion.*—In this method a coherent sample, after being weighed in air, is immersed in oil, some of which enters the sample, thus displacing air. The sample is then weighed in the oil, and once again in air after removal from the oil. The total volume is found from the second and third weighings, using Archimedes' principle. From the first and third weighings a measure is obtained of the air displaced. The Panel has not yet formed an opinion about the usefulness of this method when applied to artificially compacted soils.

(iii) *Core-Cutting Technique.*—The method of obtaining a sample of regular shape by means of a core-cutter driven into the surface of the work is well known. The use of such samples for density measurement is liable to error from various sources, as for instance that involved where a percentage of stone is present; also to the possibility of further compaction of the sample by the operation of driving the core-cutter. It is proposed to investigate the magnitude of the errors so produced and to see whether the degree of accuracy of this method of density measurement is sufficient for the purpose in mind.

Standardization of Procedures to be Adopted in Order to Obtain a Standard Degree of Compaction.

This subject has proved an extremely difficult one, and the Panel has been careful not to accept a standard of compaction which might ultimately prove to be unnecessarily low. On the one hand, it has to be realized that the arbitrary adoption of a high degree of compaction, which could be reached only occasionally in practice under specially favourable conditions, would probably cause a great deal of harm to development of soil stabilization as a useful method of construction. Results obtained in the laboratory under high compaction would, in these circumstances, result in much work being undertaken which would not come up to expectations founded upon laboratory tests. On the other hand, the adoption of a lower degree of compaction as standard would mean that a good deal of work which could perfectly well be undertaken with care and good practical technique would in fact not be so undertaken because of hesitancy due to doubtful results obtained under laboratory tests carried out at a degree of compaction which could readily be exceeded in practice.

Consequently, the Panel has decided for the time being to adopt that degree of compaction which has been specified in America and is generally known as the A.A.S.H.O. Method. In this method the soil is compacted in three layers in a mould having a diameter of 4 in, each layer being tamped with twenty-five blows of a rammer, 2 in dia and weighing $5\frac{1}{2}$ lb, falling freely through 12 in. The blows should be evenly distributed over the surface of the specimen. The Panel has endeavoured to arrive at a conclusion as to whether this degree of compaction bears any relation to actual values achieved in the course of field operations. Obviously the various criteria of excellence of the finished work, such as water resistance, bearing capacity,

etc, will depend directly on the degree of compaction of the material, and it is important that the results obtained should approach those likely to be reached in practice. The work of the Road Research Laboratory in Great Britain tends to show that the compaction obtained by the A.A.S.H.O. method can be approached in practice provided the construction technique is suitable. Although recently in America there has been a tendency to specify an even higher degree of compaction, these new standards are tentative, and there is no evidence that work in Great Britain would at present reach the higher degree of compaction.

It will be observed, too, that in the tests issued in the Appendix to the First Report two methods are specified for obtaining the consolidation required. In Test A.4, for instance, 3500 lb, is specified as a steady load, and results obtained indicate quite clearly that the density so obtained is rather higher than that produced by the A.A.S.H.O. method. The Panel hopes, therefore, to be able ultimately to amend the former method so that the degree of compaction obtained will be the same as in the A.A.S.H.O. method.

The suggestion therefore put forward by the Panel at this time is that the aim should be to adopt a degree of compaction for all tests on stabilized soil which gives results equivalent to those obtained by the A.A.S.H.O. procedure, but to advocate that consideration should be given to the possibility of working at a higher degree of compaction so that a wider range of aggregate may be handled with success. To this end the Panel recommends that constant contact should be maintained with methods of work in the field so that a higher degree of compaction may be specified as soon as this can be achieved in practice.

FUTURE PROGRAMME.

From the foregoing it will be seen that progress has been made with the programme outlined in the First Report. At present a good deal more work remains to be done under the four headings, and in particular it is hoped that the work planned to deal with the effect of frost and to be carried out with the valued co-operation of Rothamsted Experimental Station will lead to the possibility of greater progress in relation to the determination of frost resistance of compacted mixes. It is hoped at an early date to be able satisfactorily to terminate the work on the determination of stabilizer content of mixes. Sampling and treatment of samples in field testing awaits further experience with the core-cutting method for its final elucidation, and it is hoped in this connexion that the Panel may render assistance, possibly in conjunction with B.S.I. Committee RD/9, with the compilation of a Code of Practice for Soil Stabilization which will lay down suitable procedure for the sampling of work in the field. The frequency of samples and their location with respect to the work as a whole is obviously a matter of great importance, but in view of the fact that the same system of sampling should be adopted, if at all possible, for all methods of stabilization, this work should obviously be undertaken in conjunction with other stabilization interests.

Standardization of methods of compaction applicable to all tests now requires further work on the equivalence of static load and rammer technique, and this will be undertaken in due course. It is expected also that
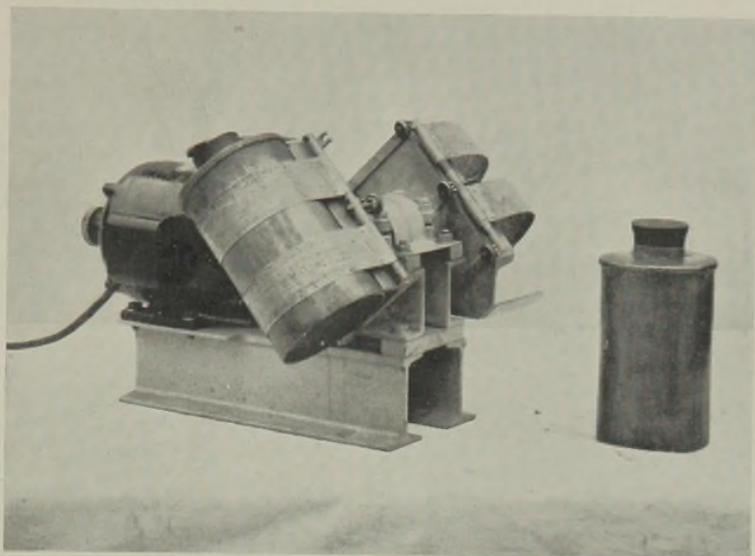
FIG. 1.
ROTARY SHAKER WITH 90-OZ. BOTTLES.

the co-operation with the B.S.I. Committee RD/9 will in the near future result in the addition of certain other items for consideration.

APPENDIX A.

STABILIZER CONTENT OF SOILS CONTAINING BITUMINOUS STABILIZERS BY THE COLD EXTRACTION METHOD.

Test Method T.2.

INTRODUCTION.

1. This test determines the stabilizer content of soils containing bituminous stabilizer. It necessitates use of Method I.P.–74 for determination of water content.

OUTLINE OF METHOD.

2. (*a*) After extraction from the soil with methylene chloride, the stabilizer is recovered from an aliquot portion of the solution by distilling off the solvent under vacuum.

(*b*) The water content of the sample is determined on a separate portion of the stabilized soil.

APPARATUS.

3. (*a*) *Metal Bottle.*—Capacity 500–600 ml, with a tight-fitting rubber stopper.

(*b*) *Steel Balls.*—Three, of 1 in diameter.

(*c*) *Bottle Shaker.*—Mechanical, giving an end-over-end shaking motion at 60 r.p.m., a suitable type of which is illustrated in Fig. 1.

(*d*) *Porous Alumina Filter.*—Type recommended and supplied by Thermal Syndicate, Ltd., No. 502 porosity—Ref. A/P3/8, size 43 mm by 41 mm, or Ref. A/P3/9, size 80 mm by 30 mm. This is converted into an enclosed filter by sealing in a length of glass or metal tubing through a cork or metal ring placed in the open end, to act as a support. On this is applied a cement paste composed of copper oxide powder (prepared by direct oxidation of metallic copper) and phosphoric acid, which is then left for a few hours to dry. (Fig. 2.)

(*e*) *Burette.*—50-ml capacity with a 2-way tap.

(*f*) *Water Bath.*—Diameter 6 in.

(*g*) CO_2 *Flask.*—200-ml Capacity.

(*h*) *Manometer.*

(*i*) *Vacuum Reservoir.*

(*j*) *Vacuum Pump or Source of Vacuum.*

REAGENTS.

4. (*a*) *Silica Gel Powder.*—Passing a No. 100 B.S. sieve.

(*b*) *Methylene Chloride.*—Boiling range 40–42° C.

PROCEDURE.

5. (*a*) Weigh 200 g to the nearest 0·1 g of the stabilized soil and introduce into the metal bottle. Add powdered silica gel to absorb the water

K

present, the quantity being equal to half the weight of water assumed to be present.   Measure to the nearest 0·5 ml sufficient methylene chloride to give a solution of 2–3 per cent of stabilizer, and add to the soil in the bottle.   Add the three steel balls, to assist in the breaking down of the mix.   Tightly stopper the bottle and shake for 30 minutes on the mechanical shaker.

(*b*) Filter the solution through the alumina filter into the burette by means of air pressure.   In the absence of compressed air this is best done by means of a laboratory bellows or a foot-pump.
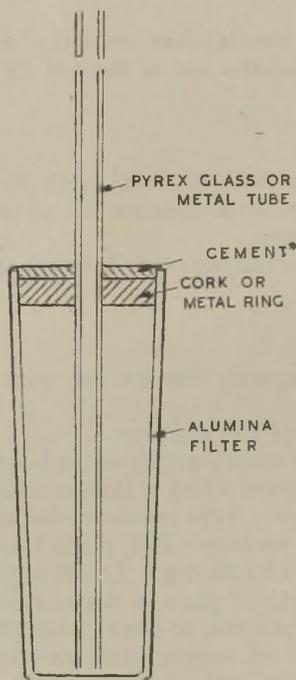

FIG. 2.
CONSTRUCTION OF FILTER.

(*c*) Run from the burette into a weighed CO_2 flask sufficient solution to give 0·75 to 1·25 g of stabilizer.   (Should the first amount recovered lie outside these limits take another suitably adjusted portion of the solution.)

(*d*) Connect the flask to a vacuum line with a manometer and a reservoir and shake the flask with rotary motion in a water-bath at 100° C, whilst the solvent is removed at a pressure of 55 to 65 cm of mercury.

Note 1.—Where water pressure is insufficient for a filter pump, the reduction in pressure may be obtained by a suitable mechanical vacuum pump, which must be

* *Cement :* Copper oxide powder is mixed to a thick paste by the addition of phosphoric acid ; it should be applied immediately and allowed to dry for a few hours in air.   The cement should not be hardened by baking, although oven heat has no detrimental effect after this period.   The copper oxide should be prepared by the direct oxidation of metallic copper.

connected to the CO_2 flask through a reservoir containing medium viscosity lubricating oil, followed by a tower containing activated carbon of 12–20 mesh, to ensure that the methylene chloride vapour does not reach the pump. When using this method most of the methylene chloride should be distilled off before connecting the flask to the vacuum.

Proceed using (i) or (ii), whichever is appropriate.

(i) *For Bituminous Emulsion Stabilizers.*—In the last stages of evaporation, when frothing of the bitumen occurs, reduce the pressure to 16 cm of mercury in $1\frac{1}{2}$ minutes, and maintain at this for a further $3\frac{1}{2}$ minutes.

(ii) *For Petroleum Oil or Cut-Back Bitumen Stabilizers.*—In the last stages of evaporation, when frothing of the stabilizer occurs, allow the pressure in the apparatus to increase to approximately atmospheric pressure, and then lower at a rate of 20 cm of mercury per minute to 46 cm of mercury. Maintain at this pressure for $3\frac{1}{2}$ minutes.

(e) Remove the flask from the bath and admit air to the apparatus. Quickly wipe the flask, remove the last traces of methylene chloride by a gentle current of air, and re-weigh the flask after cooling in a desiccator.

(f) When a sample of the untreated soil is available, test in the same manner and deduct the figure for soluble material from that obtained on the stabilized soil. The solubility of the untreated soil is usually less than 0·1 per cent.

(g) *Water Content of Sample.*—Determine the water content of the stabilized soil by method I.P.–74, using a 100-g portion of the same sample. Alternatively, in the case of soil stabilized with bitumen emulsion, determine the water content by oven drying at 110° C.

CALCULATION.

6. (a) Calculate the percentage of stabilizer in the soil by substitution in the formula :

$$\text{Per cent stabilizer} = \frac{100wV}{Wv}\left(1 + \frac{w}{pv}\right)$$

where W = weight of sample taken, in g,
$\quad\quad V$ = total volume of methylene chloride added, in ml,
$\quad\quad w$ = weight of stabilizer recovered from aliquot, in g,
$\quad\quad v$ = volume of aliquot taken, in ml,
$\quad\quad p$ = density of recovered stabilizer (which can normally be taken as 1·00 for bitumen).

The factor $\dfrac{w}{pv}$ makes allowance for the volume of stabilizer in the aliquot.

(b) Calculate the parts of stabilizer per 100 parts of stabilizer- and water-free soil, as follows :

$$P = \left[\frac{100S}{100 - (S + A)}\right] - B$$

where P = parts of stabilizer per 100 parts of stabilizer- and water-free soil.
$\quad\quad S$ = percentage of stabilizer in stabilized soil.
$\quad\quad B$ = parts of soluble material per 100 parts of stabilizer- and water-free soil.
$\quad\quad A$ = percentage of water in stabilized soil.

B is obtained from the blank test carried out on the stabilizer-free soil (Section 5 (f)).

REPORTING.

7. Report the parts of stabilizer per 100 parts of stabilizer- and water-free soil.

PRECISION.

8. No specific permissible variations can be given.

APPENDIX B.

BITUMINOUS STABILIZER CONTENT OF STABILIZED SOILS BY THE HOT
EXTRACTION METHOD.

INTRODUCTION.

1. These methods are intended for the determination of the bituminous stabilizer content of stabilized soils. The first method necessitates use of Method I.P.–74 for determination of water content, whilst the second method enables the stabilizer and water content to be determined simultaneously on the same sample.

OUTLINE OF METHOD.

2. The stabilizer is extracted from the soil by refluxing with a reagent containing trichlorethylene and methyl alcohol and the soil re-weighed. Procedure A involves a separate determination of water content. Procedure B estimates stabilizer and water contents on the same sample.

APPARATUS.

3. (a) *Extraction Apparatus*.—A 600-ml conical flask, with a small wire-gauze basket suspended from the stopper, through which is fitted a reflux condenser.

(b) *Water Content Apparatus*.—As in Method I.P.–74.

REAGENTS.

(a) *Xylene*.—Reagent chemical quality.

(b) *Trichlorethylene Reagent*.—95 per cent by volume of trichlorethylene in methyl alcohol.

PROCEDURE " A "—STABILIZER AND WATER CONTENTS DETERMINED
INDEPENDENTLY.

5. (a) Weigh out about 50 g to the nearest 0·01 g of the sample and place in a 12·5-cm No. 41 Whatman filter paper contained in the small wire-mesh basket. Suspend the latter from the stopper in the 600-ml conical flask and fit the reflux condenser. Add to the flask 100 ml of the trichlorethylene reagent and heat. Reflux until all the stabilizer is in solution; this will require approximately 6 hours for soils containing stabilizing oil and 3 hours for soils containing bitumen emulsion. (The extraction can be speeded up if the liquid is decanted off and fresh solvent added after about 3 hours.)

(b) Allow the basket containing the soil to drain and dry to constant weight in an oven at 135° to 140° C. If a small quantity of fine material passes over into the stabilizer solution, estimate it either by filtration or, more rapidly, by centrifuging from the liquid, washing, drying, and weighing. Add this weight to the weight of soil in the basket.

(c) Repeat the test on the untreated soil and determine the weight of soluble material present.

(d) Determine the water content of the stabilized soil by Method I.P.–74, using a sample of 50 to 100 g. When the soil contains bitumen emulsion stabilizer, determine the water content by drying a sample in an oven at 110° C.

PROCEDURE " B "—SIMULTANEOUS ESTIMATION OF STABILIZER AND WATER CONTENT.

6. (a) Weigh out about 50 g to the nearest 0·01 g of the sample into a No. 41 Whatman filter paper and place in the small wire-mesh basket. Through the hole in the stopper of the 600-ml flask fit a 25-ml water-estimation tube provided with reflux condenser. Pour 100 ml of xylene into the flask, heat, and reflux for 1 to $1\frac{1}{2}$ hours to ensure that all water is driven off and collected in the tube.

(b) Decant off as much of the xylene as possible, and immediately add to the flask 100 ml of trichlorethylene reagent. Delay in introducing the fresh solvent results in incomplete extraction of the remainder of the stabilizer, even if refluxing is carried on for long periods.

(c) Continue refluxing until all the stabilizer is removed from the sample; this will require $1\frac{1}{2}$ to 4 hours. Complete removal of the stabilizer will be shown by the absence of colour in the solvent draining from the basket.

(d) Repeat the test on a sample of the untreated soil, using the same conditions, and determine the weight of soluble material present.

CALCULATION.

7. (a) Calculate the stabilizer as a percentage of the stabilized soil as follows :

$$S = \left[100 \left(\frac{W_1 - W_2}{W_1} \right) \right] - (A + B)$$

where S = percentage stabilizer in stabilized soil,
W_1 = weight of soil sample taken, in g,
W_2 = weight of soil after extraction of stabilizer, in g,
B = percentage of untreated soil soluble in solvent,
A = percentage of water in stabilized soil.

(b) Calculate the parts of stabilizer per 100 parts of stabilizer- and water-free soil as follows :

$$P = \left[\frac{100S}{100 - (S + W)} \right]$$

where P = parts of stabilizer per 100 parts of stabilizer- and water-free soil,
S = percentage of stabilizer in stabilized soil.
W = percentage of water in stabilized soil.

REPORTING.

8. Report (*a*) the stabilizer content as parts by weight in 100 parts of stabilizer- and water-free soil.

(*b*) The water content as parts by weight in 100 parts of stabilizer- and water-free soil.

PRECISION.

9. No specific permissible variations can be given.

APPENDIX C.

WATER RESISTANCE OF STABILIZED SOIL BASE.

Test Method No. A.6.

INTRODUCTION.

1. This method is intended for testing samples of a stabilized soil base, to ensure that control in construction has produced adequate water resistivity.

OUTLINE OF METHOD.

2. The lower surface of a prepared test specimen of soil is immersed in water for a period of one week, and the weight of water absorbed is determined.

APPARATUS.

3. (*a*) *Stone Screen.*—$\frac{1}{4}$-in mesh B.S. sieve.

(*b*) *Water Bath.*—To accommodate the stone screen.

(*c*) *Balance.*—Capable of weighing up to 7 kg with an accuracy of ± 1 g.

SAMPLING.

4. (*a*) Mark out an area 12 in square at the spot selected for sampling.

(*b*) Cut a trench round the marked area to the full depth of the stabilized layer and of sufficient width that the block of stabilized material can readily be lifted out in one piece.

(*c*) Place the block in a box and close with a tight-fitting lid.

Note 1.—In most cases the soil being stabilized will contain an appreciable quantity of stone, making the cutting of a core an unsatisfactory method of sampling. The method proposed will, in general, be satisfactory, and at the same time will give the smallest size of sample considered necessary to produce a representative result in the test.

PREPARATION OF TEST SPECIMEN.

5. (*a*) Place the 12-in square sample with its '' top '' surface downwards in contact with a plane surface.

(*b*) Draw a circle of 9-in diameter on the '' bottom '' surface, and cut the sample back to this circle to give a cylindrical specimen with the walls as smooth and as vertical as possible. Do not disturb the '' bottom '' surface of the sample.

Note 2.—The face of the sample which was originally uppermost is referred to as the " top " surface, and that which was originally in contact with the subgrade as the " bottom " surface.

PROCEDURE.

6. (*a*) Place the test specimen in the stone screen with the " bottom " of the sample resting on the mesh.

(*b*) Place the screen and sample in the water-bath and adjust the water level to be 5 mm above the mesh of the screen. Allow the sample to soak for 10 minutes, then remove the screen from the water-bath.

(*c*) Dry the outside of the screen with a cloth and weigh the assembly to the nearest gram.

(*d*) Return the screen and sample to the water-bath, allow to soak for 1 week and re-weigh as before.

CALCULATION.

7. Calculate the water absorbed by the specimen through 1 sq cm of the " bottom " surface in 1 week thus :

$$\text{Water absorbed (g/sq cm/week)} = \frac{W_2 - W_1}{409}$$

where W_1 = original weight of immersed specimen, in g,
W_2 = final weight of immersed specimen, in g.

REPORTING.

8. Report the weight in grams of water absorbed per square centimetre of the " bottom " surface per week.

PRECISION.

9. No specific permissible variations may be given.

APPENDIX D.

SOIL DENSITY BY SAND REPLACEMENT (BOTTLE) METHOD.

Test Method A.7.

INTRODUCTION.

1. This method is intended for the determination of the dry density of natural or compacted soil. Dry density is defined as weight, in pounds, of dry soil per cubic foot.

OUTLINE OF TEST.

2. The wet density of the soil is determined by comparing the weight of a volume of the soil with that of the same volume of sand of known density. Using Method I.P.–74, the moisture content of the sample is obtained and the dry density calculated.

APPARATUS.

3. (*a*) *Sand-pouring Cylinder.*—With conical funnel and tap as illustrated in Fig. 3.

(b) *Calibrating Container.*—A cylindrical, metal container.   (Fig. 4.)

(c) *Metal Tray.*—12 in square with 4-in dia hole in centre.

(d) *Excavating Tools.*—Spatula spoon, trowel, and chisel suitable for excavating holes in soil.

(e) *Balance.*—Capable of weighing 7 kg and accurate to $\pm$ 1 g.

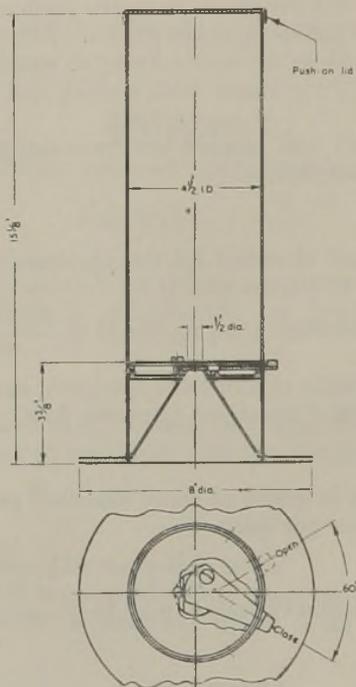(f) *Water Content Apparatus.*—As in I.P.–74.

FIG. 3.
SAND POURING CYLINDER.

REAGENTS.

4. *Sand.*—Dry, clean, closely graded natural sand, free of organic matter, passing a No. 25 B.S. sieve and retained on a No. 52 B.S. sieve.

PROCEDURE.

5. *Calibration of Apparatus.*—(a) Fill the sand-pouring cylinder with the prepared sand and remove approximately that amount of sand which will fill the calibrating container.   Close the tap and place the cylinder so that the base of the funnel rests on a plane surface.   Open the tap, allow the sand to run out until no further movement is observed in the cylinder, and close the tap.   Remove the cylinder, collect and weigh to the nearest gram the sand which has filled the funnel (W_1).

(b) Determine the internal volume in ml of the calibrating container (V ml).

6. *Determination of Bulk Density of Sand.*—(a) Fill the sand-pouring cylinder with sand and weigh to the nearest gram (W_2).

(*b*) Place the sand-pouring cylinder on top of the calibrating container, open the tap, and allow the sand to run out until no further movement of the sand in the cylinder takes place. Close the tap, remove the pouring cylinder, and weigh to the nearest gram (W_3).

7. *Measurement of Soil Density.*—(*a*) Expose and trim down to a level surface an area 18 in square of the soil to be tested.
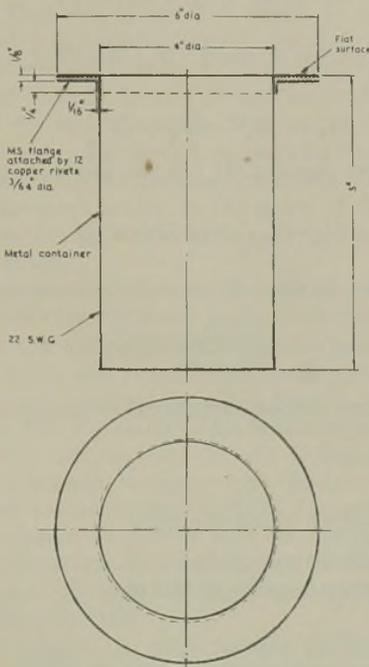

FIG. 4.
CALIBRATING CONTAINER.

(*b*) Excavate a round hole 4 in in diameter and 5 in deep in the soil, using the metal tray laid on the prepared surface as a guide (Note 1). Collect the soil carefully and weigh to the nearest gram (W_w).

Note 1.—If it is necessary to excavate the holes to depths other than 5 in, the calibrating cylinder should be replaced by one whose depth is the same as the hole excavated.

(*c*) Fill the sand-pouring cylinder and weigh to the nearest gram (W_5). Place the cylinder over the hole in the soil so that the base covers the hole concentrically. Open the tap, allow the sand to run out until no further movement takes place, close the tap, and re-weigh to the nearest gram (W_6).

(*d*) Place a representative sample of the soil in an air-tight tin and subsequently determine its moisture content, using method I.P.–74.

CALCULATION.

8. (a) Calculate the weight of sand (Wa) required to fill the container from the formula :

$$W_a = W_2 - W_3 - W_1.$$

(b) Calculate the bulk density of the sand (S) from the formula :

$$S = \frac{W_a}{V} \times 62{\cdot}4 \text{ (lb/cu ft)}$$

(c) Calculate the weight of sand (W_b) required to fill the excavated hole from the formula :

$$W_b = W_5 - W_6 - W_1$$

(d) Calculate the wet density (D_w) of the soil from the formula :

$$D_w = \frac{W_w}{W_b} \times S \text{ (lb/cu ft)}$$

(e) Calculate the dry density of the soil (D_s) from the formula :

$$D_s = \frac{100D_w}{100 + m} \text{ (lb/cu ft)}$$

where m is the moisture content, expressed as parts of water per 100 parts of dry soil.

REPORTING.

8. Report to the nearest whole number :

    (a) the dry density of the soil.
    (b) the moisture content of the soil.

PRECISION.

10. No specific permissible variations can be given.

OBITUARY.

ASHLEY CARTER.

It is with regret that we record the death of Ashley Carter, which occurred at his home at Sutton, Surrey, on January 9. An Original Member of the Institution of Petroleum Technologists he was a keen and energetic supporter of that body and of the Institute of Petroleum until his death. In 1923 he was elected a Member of Council and in 1933 became a Vice-President. He served on various Committees of Council as chairman or member and, on the occasion of the First World Petroleum Congress in 1933, was most active in the work of the General Purposes Committee responsible for the organization of the Congress and the functions connected therewith.

One of his main interests in the Institute was the encouragement of the work of the Students Section, to which he devoted much time and thought. In 1942 he accepted the Council's invitation to undertake the duties of Joint Honorary Secretary, and it was to his deep regret that failing health caused him to resign from that position last year.

Born in 1873, Ashley Carter received his technical education at Birkbeck College, Battersea Polytechnic, and King's College, London, and subsequently trained as a locomotive engineer on the London & South Western Railway. In 1899 he was appointed District Locomotive Superintendent of the Ceylon Government Railways, and on his return to England in 1913 became London Representative of the Oil Well Supply Co. He was later appointed London Manager of the Company, a position which he held until his retirement in 1945.

His interests were many. In 1916 he was elected a Freeman of the City of London and a Liveryman of the Worshipful Company of Needle-makers and, in 1934, was elected to the Court of this Company. In Masonry he also held high distinctions, being Past Master of two lodges, appointed to London Grand Rank in 1932, and was given Grand Lodge of England Honour in 1946.

Well-known in petroleum circles in Great Britain, his charming personality won him many friends who will long cherish the memory of Ashley Carter's devotion to the service of the industry. He is survived by his widow and two sons, to whom we extend our condolence in their loss.

CAMPBELL MURRAY HUNTER, O.B.E.

Campbell M. Hunter, who died on December 23, 1946, was born in Edinburgh in 1877, the son of Sir William Wilson Hunter, K.C.S.I., C.I.E., LL.D. Educated at Eton and Trinity College, Cambridge, he started his career as a consulting engineer and petroleum technologist in London in 1904, and subsequently carried out geological and technical

investigations and conducted drilling operations in oilfields in various parts of the world.   He was also a director of Hunter Valley Oil Co., Ltd., Northern Oil Royalties & Development Co., Dallas Dome Wyoming Oil-fields Co., Dallas Syndicate, Ltd., and Nimrod, Ltd.

During World War I he was attached to the Royal Engineers as water expert to the Allied forces in Salonika and was later Director of Railway Materials Production in the Ministry of Munitions.   In World War II he held an important post in the Ministry of Works and Planning.

A Member of the Institute since 1919 and a Fellow since 1939, Campbell M. Hunter was the author of several papers published in the *Journal*, his last contribution being on " The Oilfields of Western Canada " in 1943.   He was also a member of a number of learned societies in Great Britain, Canada, and the United States, and a certified professional engineer in the Province of Alberta, Canada.