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AUGERING AND CORE-DRILLING FOR GEOLOGICAL PURPOSES IN TRINIDAD.*

By E. C. Scott, M.Inst.Pet.

Introduction.

Augering and core-drilling are undertaken to supply information which cannot be obtained from surface exposures and hand-dug pits.

Hand-dug pits have a general depth limit of from 10 to 12 ft., but in the past they have been carried to 15 and 30 ft., in order to get through alluvium and below the weathered zone, which is sometimes very deep in clays and marly clays.

They have the advantage over augering and drilling that each one gives a dip, strike, and a full view of the strata *in situ*, but it should be noted that, where marker beds exist, dip and strike can be obtained by three-point auger work.

Where alluvium or weathered zone is thick, they are of little use and, in addition, weathering of the forams often necessitates going deeper than ordinary pitting permits, even when the clays and shales look comparatively unweathered.

Natural recourse to augering is made when it is required to make examinations below practicable pit depth for foram determinations, position of contacts, etc.

Twenty feet is generally easily obtained with an ordinary carpenter's earth auger (50 or even 100 ft. having been obtained), but in the latter cases it is necessary to employ a tripod and snatch-block for withdrawing the tools. Photos A and B show types of augers commonly employed.

Augering is more particularly applicable to clays, shales, and sandy shale. Soft sands are prone to caving, and hard sandstone and lime cannot be penetrated with economy.

Special augers have been devised to deal with caving and sticky conditions, and have operated with varying degrees of success.

They have included elaborations of the Banka drill, used extensively for alluvial metal examinations, and certain percussion-type instruments have appeared on the market which, it is maintained, can be used to take orientated cores.

All these tools have distinct limitations, principally that most of them require more supervision than can ordinarily be devoted to them in practice.

At depths of over 50 ft. it has been found necessary to employ a light rotary or percussive drill. Percussive drills have not found much favour, and it is possible that, in certain types of country, they offer advantages. Their great objection is that they nearly always demand the use of casing and are not very flexible in application.

The rotary machine has been used almost exclusively in Trinidad, and its use and limitations form the principal part of this paper.

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* Paper presented at a Meeting of the Trinidad Branch held on 22nd March, 1939.

Rotary Machines—Types Used.

The types of rotary machines used fall into four main categories :—

(1) Completely hand-operated.
(2) Hand-rotated with motor-driven pump.
(3) Completely power-driven.
(4) Contra-flush system.

(1) Completely Hand-operated Machines.

With these, the Banka drill and auger might almost be included *sensu stricto*. The usual machine consists of a rotating head with a chuck for gripping the drill-pipe, a feeding device, and a geared assembly for transmitting rotary motion to the drill-rods by means of manual rotation. A hand-operated pump is provided for maintaining flush or circulation round the drill-head.

These machines were the outcome of shallow mining machines, one of which, " the Wombat," was used extensively for military mining purposes during the War.

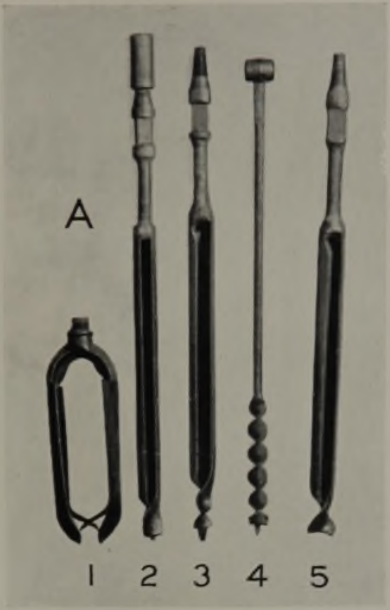
It is almost impossible to supply flush at a rate sufficient to lift cuttings by means of a hand-pump, and therefore the original machines were equipped with an auger-head or core-barrel, in order that excavated material could be removed *en bloc* by withdrawing the tool. The sole function of the flush was then to lubricate the bit and wet the material. Since full circulation could not be maintained, this meant carrying what was essentially a dry hole.

The method will perform quite satisfactorily down to 100 ft., and should show advantage over the auger between 30 and 50 ft., especially as it is possible to obtain cores with a basket-type bit in well-consolidated material.

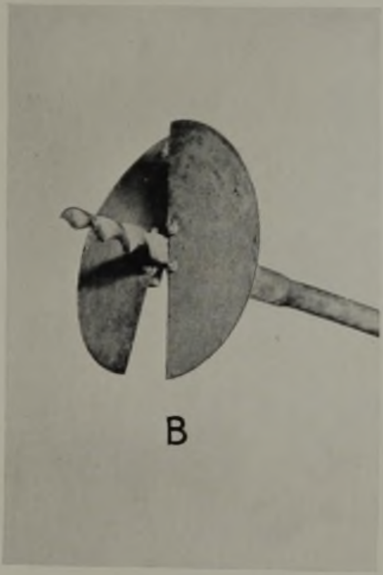
(2) Hand-rotated Machines with Motor-driven Pump.

When continuous flush is required, as it is in unconsolidated ground, a power-pump is almost essential, and it has been proved by experiments in Trinidad that the rate of drilling is almost entirely controlled by the rate of flush down to 300–400 ft. as the following data show :—

Footage drilled.	Time required.	Manometer pressure.	Amount of fluid circulated per minute.	Remarks.
		(*a*) *With Craelius Pump.*		
10 ft. (100–110 ft.)	38 min.	5 lb. = 70 lb./sq. inch.	9 gals. per minute.	While drilling bit partly got plugged.
10 ft. (110–120 ft.)	40 min.	5 lb. = 70 lb./sq. inch.	10 gals. per minute.	Belt kept slipping.
		(*b*) *With* 6 × 4 × 6 *in. Worthington Steam Pump.*		
10 ft. (120–130 ft.)	12½ min.	10 lb. = 140 lb./sq. inch.	15 gals. per minute.	Installed high-pressure hose.
10 ft. (130–140 ft.)	19 min.	10 lb. = 140 lb./sq. inch.	15 gals. per minute.	—



1. Normal 4″ post hole auger.
2, 3 and 5. " Shell " pattern auger for soft formation.
4. 1½″ Carpenter's auger (the most commonly used).



12″ AUGER FOR TAKING LARGE VOLUME SAMPLES AT SHALLOW DEPTH.

[*To face p.* 502.

VIEW OF 1000 FT. CAPACITY DRILLING MACHINE OPERATING IN TRINIDAD.

1000 FT. CAPACITY DRILLING RIG, SHOWING LOCALLY FABRICATED DERRICK DRILLING IN MONE DIABLO QUARRY TRINIDAD.

In other words, down to these depths it takes little or no power to rotate the tools and to withdraw them.

(3) COMPLETELY POWER-DRIVEN MACHINES.

Originally these were the diamond and shot drills, well known in metal-mining practice and, whilst these were perfectly satisfactory for dealing with hard and semi-hard rocks, a good deal of modification for soft, and particularly for sticky, formations was necessary.

The original diamond drill could use a single-tube core-barrel, *i.e.* the flush passed between the core and the outer single barrel, and also water could be used for circulation, the velocity of which could be maintained, since only a small-diameter hole was necessary.

In soft formations the hole must be plastered with mud and a double-tube core-barrel must be used, since the soft core will not withstand the washing action of the circulation, and sticky ones plug the required annulus.

The double-tube core-barrel must of necessity be of larger outside diameter than the single type; also it has been found that very small-diameter soft cores will not withstand torsional stress, becoming sheared and deformed.

The carrying of the larger hole required for coring and circulation of thick mud introduces another complication—namely, increase in the size of drill-pipe.

Rigs were originally equipped with " A " class rods, and these have been used fairly satisfactorily down to 500–600 ft. However, since the smallest hole that will pass a double-tube core-barrel is 3 in., which gives unsatisfactory cores, it may be accepted as a general principle that " A " class rods are unsatisfactory.

Machines now being ordered are equipped with " N " class rods which permit a 3½-in. or 4-in. hole to be drilled to depths in excess of 2000 ft.

Photos C and D show two views of a 1000 ft. capacity drilling rig, mounted on skids for dragging into locations to which no road exists.

Data concerning these rod sizes are as follows :—

Size.	*E.*	*A.*	*B.*	Old style *N.*	*N* blue.	*N* yellow stripe.	*N* seismograph.	*PK.*	*PK* (2½ in.) acme th'd.
O.D., ins.	$1\frac{5}{16}$	$1\frac{21}{32}$	$1\frac{29}{32}$	$2\frac{3}{8}$		$2\frac{3}{8}$	$2\frac{3}{8}$	$2\frac{7}{8}$	$2\frac{7}{8}$
I.D., ins.	$\frac{27}{32}$	$1\frac{11}{32}$	$1\frac{19}{32}$	2		$2\frac{1}{8}$	$2\frac{1}{8}$	$2\frac{11}{16}$	$2\frac{5}{16}$
I.D. of coupling, ins.	$\frac{7}{16}$	$\frac{9}{16}$	$\frac{5}{8}$	1		$1\frac{1}{8}$	$1\frac{1}{4}$	$1\frac{3}{16}$	$1\frac{3}{16}$
Weight per ft., lb.	2·7	3·3	4·5	4·9		4·9	4·0	8·7	9
Number of joints packed per box	10	6	6	4		4	4	2	2
Gross weight, lb./ft. (boxed) :									
For domestic shipment	3·1	3·6	5·2	5·9		5·9	5·4	11·3	11·9
For export shipment	3·2	5·4	5·4	6·2		6·2	6·0	12·3	12·9

Here it may be stated that there is often a hope expressed that these light rigs can be used for production purposes, and it should be clearly understood that drill-pipe sizes, diameter of hole, and depth are all inter-related, as they are in ordinary oil-field drilling.

Producing even a shallow well demands the setting of casing, and the entire equipment of the geological rig is not designed for this. Furthermore, setting 4-in. casing demands a 6-in. hole, and flush velocity has to be increased to limits outside the capacity of pumps if this is to be done.

These rigs will drill large diameter holes, but to smaller depths than their rated capacity for normal holes.

A warning, to those who attempt these large-diameter holes, is perhaps necessary that adequate drill-collar weight should be supplied. Most of the machines (as will be described later) have mechanism for exerting a downward pressure on the cutting tool. If this is done in large-diameter holes, the strain placed on the tool couplings is excessive and in a very short time " twist-offs " will occur.

(4) CONTRA-FLUSH SYSTEM.

As the name implies, this system utilizes a reversed flush circulation down the casing and up the drill-pipe. The same principle was adopted in the well-known Fauck system of percussive drilling.

It has three main advantages, viz. :—

(*a*) Since a stuffing-box is necessary to seal off between the drill-pipe and the casing, it is possible to maintain a pressure on the formation.

(*b*) Increased velocity up the drill-pipe assists in removing cuttings.

(*c*) Cuttings are removed directly from the bottom, and a good record is obtained when the formation is suitable.

The application of the method is, however, limited. A seal on the surface casing must be obtained, or flush will break out round it and this is liable to occur when no casing seat is available. Furthermore, when porous formations are encountered, fluid will be lost, due to the increased pressure which must be applied to them in order to obtain circulation.

A novel three-plunger slush-pump is used, and is driven off the drilling engine through a gear-box.

It is claimed that over 2000 ft. can be drilled with a machine of this type, weighing 5100 lb.

The system is obviously mainly applicable to dense well-consolidated rocks.

DESCRIPTION OF MACHINES.

(1) *Mountings.*

In designing, the prospecting drill manufacturers have to fulfil exacting requirements of portability, and have, to date, concentrated on two main mountings :—

(*a*) Truck or tractor.
(*b*) Skid.

Whilst the original diamond drill was almost always skid-mounted, as it had to operate on locations over dams, down mines, etc., the modern oil country equivalent has been preponderantly truck- or tractor-mounted.

Whilst truck-mounting is eminently satisfactory for open flat country with moderate rainfall, it is useless in Trinidad, with its maturely eroded peneplanation, forests, and high rainfall.

Tractor-mountings have some advantages, but they have not been employed as yet, due to :—

(*a*) The difficulty of getting them over public roads. (This disadvantage has now been modified by the invention of the rubber track.)

(*b*) Costly bridges and fillings would be required in hilly country.

(*c*) The cost of clearing forest for a tractor and the royalty to be paid are both excessive.

(*d*) The initial cost of the machine is much greater.

Skid-mountings are normally used in Trinidad, and the smaller machines are towed to the location by bulls. Some attempts have been made to drag machines by their own winch-power, but gear ratios are not at present designed for this, and the skid-beds are not given a sufficient upward curve to permit of easy riding over uneven ground. Altogether, this subject has not been closely studied by manufacturers, probably because the wider demands for truck-mounted units, due to seismology requirements as well as those of geology, in flat countries heavily covered by alluvium have kept them fully employed.

In transporting the present skid-mounted units by means of their own power, it has been found essential to make use of a cat-head, and not of the clutch and wire line used for rod-hoisting, since, if the latter is used, clutch linings burn out very rapidly.

A recent design which equips the pump-engine with a pulling-winch has much to recommend it.

(2) *Drive.*

As has already been stated, the machines are usually of the type which permits a downward pressure to be exerted. Thus, a Kelly or drill-stem is generally dispensed with, and the drill-pipe is gripped in a chuck, the down pressure being supplied either by a ratchet and spur-wheel or by hydraulic cylinders. One medium-depth machine uses a Kelly, and the downward motion is obtained from tandem wire-lines operated from the hoisting-drum and attached at the other end to eyes in the swivel.

The immediate reaction is towards the Kelly type of machine, because of its similarity to the normal oil-field rotary and because it provides a spudding device, but there is no doubt that the facility of the hydraulic rams has much to recommend it, as it provides, besides emphatic down pressure, upward lift, which can be used to free jammed piping and to alleviate the load which must otherwise be thrown on an admittedly light derrick.

(3) *Engines.*

Engine-power for the light rigs is produced from gasoline motors.

With cheap fuel available, it has been the principle to sacrifice engine size and efficiency for uniformity. Thus, on the 1000-ft. machine, 20-h.p. motors have been used on both the pump and draw-works engines, although considerably less than 20 h.p. would be satisfactory for the draw-works.

In line with this desire for uniformity is the practice of some manufacturers to use standard mass-produced car engines, since a local supply of spare parts for these is generally available.

The weight of the power units can be somewhat cut if they are interconnected with clutches and chain or Tex-rope drives, and, furthermore, this principle permits of a rig being increased in power in order to add to its depth capacity, although there is obviously a limit to the practicability of the scheme.

(4) *Cutting-tools.*

The normal cutting-tools used in soft formations are the fishtail bit and soft-formation core-barrel.

For hard formations the diamond-set single-tube core-barrel is used almost exclusively in Trinidad, but medium-hard formations, such as limestone, can be successfully drilled with borum-tipped saw-toothed crowns.

Diamond bits are a very expensive item, and in other countries are being replaced by the rock-bit, Calyx shot, and weld-set diamond-head in medium-hard ground.

At present the rock-bit is not made in sizes below 4 in., and in any case it does not provide a core in this small size.

Calyx shot are satisfactory only in ground which is continuously hard. If there are any appreciable soft layers, the shot are side-tracked into the formation and lost.

The weld-set diamond bit is a new innovation; it is much cheaper than the normal hand-set article, since it is more quickly made and smaller stones may be used.

It would be surprising if this article did not eventually provide a solution for some hard-rock drilling encountered with big oil-field rigs.

Methods and Scope of Work.

Apart from its almost universal application to seismic work, the geological rig is being used with increasing frequency to aid surface examinations. Not only are normal contacts checked by sections and groups of holes, but also the hade and throw of faults are ascertained.

During the last few years, co-operation with Messrs. Schlumberger has provided a service whereby coring can be cut out when examining contacts of porous with non-porous rocks. In Trinidad this has been particularly useful, since faults play a major part in oil accumulation.

Another most important rôle of the geological drill is to check and elaborate stratigraphical sequences at type localities. So many type-sections in Trinidad are confused by epidiapiric influences, mud-flows, and other complex conditions, that this service is of great value.

It has been found economical to operate two or more small machines together, information being thereby more rapidly to hand and supervision and distribution of labour easier. The method at present adopted is to use three crews for two rigs. Thus, all three can be employed on one rig for continuous work if conditions demand it.

As a general principle, it is accepted that a number of shallow holes are preferable to one or two deep holes for dealing with specific problems.

As regards scope, these machines are obviously designed to fill the gap between normal surface surveys and exploration drilling proper.

The limit of a light portable outfit is about 1200 ft., although a tendency is now manifest to copy the multiple-engined diesel rigs, and so make them light rigs capable of additional depth without increasing the weight of components.

Some truck- and tractor-mounted units are capable of between 2000 and 3500 ft., but the latter depth is obviously encroaching on the duties of a normal oil-field rig.

The normal sequence of exploration is suggested as being :—

(1) Surface and/or geophysical surveys.
(2) Confirmation drilling with geological outfits.
(3) Testing to depth with normal rigs.
(4) Full testing for production.

This paper would not be complete without some mention of recent developments under (3), known as slim-hole drilling.

There is obviously a gap between the 1000–2000 ft. potential of the prospecting drill and the heavy 5000–10,000 ft. rigs used for normal oil exploitation, and experiments have produced the small-hole practices now reported from the United States of America.

These latter practices call for a rig as heavy as that used for exploitation, but it is maintained that very appreciable savings can be made in casing, speed, and wear of equipment, but that weight cannot be much reduced is due to the fact that pump pressures increase in small holes. Heavily powered big pumps are therefore still required, and these largely control the weight of the rig.

Most of these slim-hole outfits are capable of from 6000 to 8000 ft. with 3- to 4-in. drill pipe. The gap therefore still exists, and in all probability the companies involved in considerable exploration programmes would be well advised to equip themselves with a rig which would operate economically with 4½-in. drill-pipe down to 3500 ft., and might be used to 5000 ft. with smaller sizes. Much will be possible along these lines when operators cease their demands for a pump which will provide big volume but which can be converted by the use of liners to provide high pressure and small volume.

The technique of slim-hole drilling to considerable depths must obviously be dependant on local conditions, but already sufficient experiment has been made in Trinidad to warrant the assertion that worth-while savings are possible by reducing the diameter of exploration holes where the terrain does not demand the setting of an abnormal number of strings of casing.

The author wishes to express his thanks to Mr. Trafford and Mr. Laidlaw for information given, and to Trinidad Leaseholds, Ltd., for permission to read the paper.

DISCUSSION.

In opening the discussion the author said that since the paper was a rather bare recital of facts, he would ask the Chairman's permission to digress from normal procedure and to initiate an informal debate on two subjects which were connected with exploration drilling in Trinidad, namely,

1. The abnormal pressure gradients encountered in Trinidad oilsands which were such that very heavy mud had to be used in drilling.

In normal oilfield practice it could be assumed that if a certain weight mud would deal with the pressure in an upper oilsand, it would also be satisfactory for one lower down.

In Trinidad, however, abnormal pressure sands are frequently encountered and geologists were invited to comment and suggest explanations.

2. There had been suggestions in current literature to the effect that—" since the probability of finding oil in an exploration well was in excess of 1 in 10; in general it would be economic to drill such wells with the object of obtaining information only, and to forgo any possibility of producing them if oil were encountered."

Discussion on the value locally of such practices was suggested, and in addition members were asked to consider whether it would not be possible to design a rig to drill a small hole to a considerable depth (4000 ft.) using light equipment which would not call for the building of a heavy duty road.

An absorbing discussion took place on the lines suggested by the author, in which Messrs. Harris, White, Bushe, Porter, Kugler, Halse, Fletcher, and Suter took part.

It was agreed that the reason for formation-pressure anomalies in Trinidad oil-sands was not clearly understood. Compression of competent members in the cores of anticlines and similar phenomena related to epidiapiric folding have probably played their parts, as may also wholesale *décollement* of blocks of soft strata from the continental shelves. It was noted, however, that, oil concentration being undoubtedly connected with faulting, it was difficult to reconcile a theory of upward migration with many of the observed pressure anomalies.

Other suggestions mentioned as possible solutions were periods of erosion after compaction of successive zones and varying polymerization changes of the oil within different sands.

Regarding the scope of so-called slim-hole drilling, it was admitted that abnormal formation pressures and the incidence of caving formations, as common occurrences in Trinidad, curtail to some degree the extent to which this can be practised. Some interesting figures, however, were given which indicated a growing tendency to drill smaller holes for production purposes as well as for exploration wells.

It was generally agreed that an appreciable saving could be made in the total cost of exploration drilling on a large scale by adopting slim-hole methods. It was assumed that slim-hole would prevent, or at any rate restrict, the possibilities of producing a well drilled on these principles, and they could not therefore be deemed to apply to outstepping or " semi-exploration " wells on producing fields.

The suggestion that it should be possible materially to reduce the weight of machinery necessary to drill small-diameter holes to a given depth was fully discussed, and the general consensus of opinion was that a machine had not yet been designed which could be transported into the forest and serviced there without the facility of a road.

It was felt that, once a road was admitted as being necessary, the small curtailments in machinery weight which were possible would not be justified, as they would sacrifice the efficiency.

Thus, it appears that, whilst very appreciable saving in casing, bits, time, fuel, etc., may be visualized by the proper employment of slim-hole drilling, at present machinery weight and roads must remain essentially as required for a normal rig to depths over 6000 ft.

A further discussion developed on the possibility of adapting steam power to furnish more mobile rigs, and it was pointed out that water-tube boilers of increased pressure, poppet valve-engines, and single-acting three-throw pumps were all possible solutions to the weight problems where adequate fuel and water were available.

THE MEASUREMENT OF THE FLOW PROPERTIES OF BITUMENS.*

By D. C. Broome, F.C.S., M.Am.Chem.Soc., F.Inst.Pet.

Introduction.

The flow properties of bitumens have always been regarded as of considerable importance and, ever since laboratory testing of such substances has been employed, the tests carried out have included various forms of flow measurement. Originally, these tests were confined to direct measurement of flow by such instruments as the Redwood or Engler viscometers and measurement of the " hardness " or " consistency " by means of the penetrometer. The latter test in particular was found to be very useful as a factory control test, but with the development of the asphalt and bitumen industry other methods were evolved to give a wider and truer picture of the flow properties of the materials employed. Thus the following tests, amongst others, are now extensively employed for routine purposes in this country, in addition to those already mentioned :—

(1) Softening-point tests by Ring and Ball [1] or by Kramer–Sarnow method.[2]
(2) Twisting-point test.[3]
(3) Float test.[4]
(4) Fraass brittle point.[5]
(5) Ductility.[6]

All these, however, suffer from certain disadvantages, and in particular they are inadequate for providing the information required for a full understanding of the properties of the materials employed, in that the majority of the tests give no information as to the properties of the materials *at the temperature at which they will exist on the road.* The principal exceptions to this are the penetration and ductility tests, but even here the information obtained is very inadequate, as the tests are normally carried out at one temperature only. With the majority of bitumens, the ductility test at 25° C.—as normally specified—gives results of " plus 100." The actual ductility may be 200, and it may be 500, but with the limited scope of the standard machine there is no means of telling. The situation, with all the above-mentioned routine tests, is still further complicated by the fact that very few bitumens employed in this country are true fluids. This means that :—

(*a*) it is difficult to compare results obtained by one method with those obtained by another;

(*b*) it is difficult to express the results of any tests in terms of absolute units;

(*c*) it is generally not possible to extrapolate consistency/temperature curves—*e.g.*, to give data for lower temperatures.

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* Paper presented to a Meeting of the Asphaltic Bitumen Group of the Institute of Petroleum on 28th March, 1939.

In addition, it is important to determine the extent to which a bitumen deviates from the laws of true fluids, as if, for example, a road is made with a bitumen which is a true fluid, this will tend to displace even under the slightest stress. On the other hand, if the bitumen is at all plastic, it offers a definite resistance to displacement, and the greater the degree of plasticity the greater will be the force necessary to displace the bitumen. In other words, the higher the " degree of plasticity," the less tendency there will be for a road constructed with that bitumen to suffer from deformation. For the sake of simplicity at this stage, the term " plasticity " is used here to express that property which enables a material to be moulded; and the term " degree of plasticity " to indicate the extent to which a material deviates from being a true fluid. As this property will be referred to again later in this paper, it may perhaps be wise to bear in mind the more scientific definition proposed by Bingham : [7] " If, in non-turbulent flow, the ratio of flow to force is constant, the material is said to be fluid; otherwise it is plastic."

A considerable amount can be done by making fuller use of the routine apparatus. For example, all the tests can, and should be carried out over the widest possible temperature range. This gives most useful data, particularly with the ductility test, as, when ductility/temperature curves are plotted, these are usually found to be of the general form shown in Fig. 1. For example, test at 25° C. only tends to indicate that Sample C is much better than Sample B, whereas if the temperature is increased somewhat, the situation is reversed. In fact, Sample B would be much better in practice than Sample C. In the same way, tests should be carried out over a range of temperature with other apparatus.

It has been suggested by Thelen [8] that the flow properties of bitumens can be evaluated in terms of absolute viscosity by obtaining a series of successive penetrations without touching either the sample or the needle. This method was modified by Rhodes and Volkman [9] and further studied by Traxler and Moffatt.[10] The viscosity may be calculated according to this method in accordance with the equation :—

$$V = \frac{M \times D^t \times 1{\cdot}25 \times 10^7}{(P_f + P_i - 46)(P_f - P_i)}$$

where V = viscosity in poises,
P_f = final penetration in decimillimetres,
P_i = initial penetration in decimillimetres,
D_t = time interval in seconds,
M = mass in grams of load on the needle.

The average shearing stress at the surface of the needle and the corresponding rate of shear may be evaluated as follows :—

$$\text{Shearing Stress, } F = \frac{0{\cdot}6243M \times 10^6}{(P_f + P_i - 46)}$$

$$\text{Rate of Shear } \frac{dv}{dr} = \frac{0{\cdot}4999(P_f - P_i)}{D_t}$$

This is interesting, but, as shown by Traxler and Moffatt, the most essentially viscous asphalts give rheological diagrams by this method indicating negative yield stresses. This shows that the test as now used is not on a sound theoretical basis. It is, however, of some help in the study of certain problems, such as the age-hardening of bitumens, since a number of tests may be performed on a single sample of hard bitumen without appreciably disturbing it.

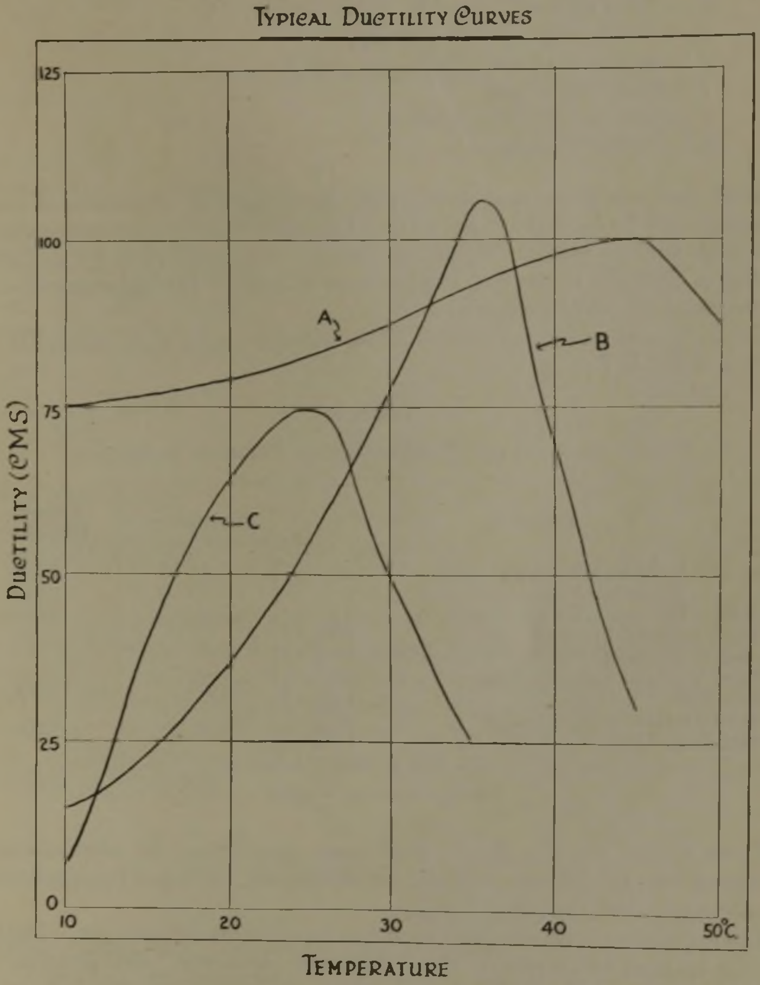

FIG. 1.

MODIFICATION OF ROUTINE APPARATUS.

Still more information can be obtained by simple modifications of existing routine apparatus. One of the best examples of this is the adaptation of the original Frankland Taylor twisting-point apparatus [3] as an absolute viscometer [11] by the use of a cylindrical specimen with square ends to fit into the cups of the standard apparatus. If the temperature is kept constant throughout the test, the viscosity may readily be calculated by means of the equation :—

$$V = \frac{mgrlt}{1000\pi^2 R^4}$$

where V = viscosity in kilopoises,
m = mass of weight used to apply torque,
g = acceleration due to gravity,
r = radius of torque drum plus card,
l = length of sample,
t = time per revolution (secs.),
R = radius of sample.

With this modification a detailed study of the flow properties of many bitumens can be carried out by performing the test at various temperatures, and with various loads. Normally, this test is suitable only for materials having a viscosity at the test temperature of 1–40 × 10^3 kilopoises—*i.e.*, of approximately 15–75 penetration.

Some typical examples of viscosities obtained with this apparatus are shown in Table I :—

TABLE I.

Typical Viscosities with Twisting-Cylinder Viscometer at 25° C.

Bitumen.		Penetration.	Viscosity kilopoises.
Asphaltic Bitumen—Mexican Crude		61	5,499
Asphaltic Bitumen—Venezuelan Crude		59	1,310
Asphaltic Bitumen—Panuco Crude		68	3,582
Refined Trinidad Lake Asphalt Asphaltic Bitumen 200 Pen. (Panuco Crude)	50% * 50%	44	17,512
Refined Trinidad Lake Asphalt Liquid Flux " A "	85% 15%	33	14,328
Refined Trinidad Lake Asphalt Liquid Flux " B "	83% 17%	36	7,959

* Proportions by weight.

These figures indicate clearly that, quite apart from the more scientific nature of such an absolute viscosity determination, the latter is a much more sensitive test than the penetration.

The apparatus in its modified form has two further advantages. Firstly, it may be used to determine the " degree of plasticity," and secondly for elastic recovery measurements. For the former, reference should be made to some work by Saal and Koens,[12] who found that the viscosity of a bitumen may be calculated from the penetration, thus :—

$$V = \frac{5{\cdot}13 \times 10^6}{(\text{penetration})\ 1{\cdot}93}$$

This is applicable only to those bitumens which are true fluids, but if the penetration and absolute viscosity are determined experimentally, the percentage difference between the observed and calculated viscosity will be a measure of the degree of plasticity of the material, thus :—

$$\text{Degree of Plasticity} = \frac{(V \text{ obs.} - V \text{ calc.}) \times 100}{V \text{ obs.}}$$

A few typical figures are given in Table II :—

TABLE II.

Typical Plasticity Figures at 25° C.

Bitumen.		Penetration.	Plasticity.
Asphaltic Bitumen—S. Mexican Crude		61	33·8%
Asphaltic Bitumen—Panuco Crude		68	58·9%
Asphaltic Bitumen—Venezuelan Crude		59	8·4%
Asphaltic Bitumen—Texas Crude		59	12·3%
Trinidad Lake Asphalt 200 Pen. Bitumen (Panuco)	50% 50%	44	79·8%
Trinidad Lake Asphalt 200 Pen. Bitumen (Venezuelan)	50% 50%	39	18·8%
Trinidad Lake Asphalt 300 Pen. Bitumen (Panuco)	50% 50%	49	81·8%
Trinidad Lake Asphalt 500 Pen. Bitumen (Panuco)	50% 50%	65	81·2%
Trinidad Lake Asphalt Trinidad Flux	85·5% 14·5%	44	72·8%
Trinidad Lake Asphalt Trinflux	83% 17%	43	53·5%
Trinidad Lake Asphalt Texaco Flux	80% 20%	26	80·5%
Asphaltic Bitumen (Lobitos Crude) Trinidad Lake Asphalt	60% 40%	31	67·4%

Another useful modification of existing apparatus consists in carrying out ductility tests at varying speeds. By this means the very high ductility materials may be made to give figures well within the range of the apparatus. Similarly, the very hard materials will give more " reasonable " results if pulled apart very slowly. Convenient speeds are 1, 5 and 25 cms. per minute. Some indication of the value of this technique may be gained from the figures in Table III :—

TABLE III.

Typical Ductilities at Various Speeds.

Bitumen.	25° C.			35° C.			45° C.		
	1 cm. min.	5 cm. min.	25 cm. min.	1 cm. min.	5 cm. min.	25 cm. min.	1 cm. min.	5 cm. min.	25 cm. min.
A	0·5	0·5	Nil	15	8	3	82	59	20
B	2·5	Nil	Nil	115	26	Nil	150	124	145
C	45·6	26·5	11·0	150	75	56	140	145	150
D	5·0	1·5	Nil	28	11·5	5	50·5	38	30

Apart from the modification of existing apparatus, it is necessary to have apparatus specially designed for absolute measurement if a complete picture of the rheological properties of a wide range of materials is to be obtained. The more important of these may be classified under the following group headings :—

(1) Falling-sphere viscometers.
(2) Rotating-cylinder viscometers.
(3) Coaxial-cylinder viscometers.
(4) Micro and other viscometers.

Falling-Sphere Viscometers.

The principle of viscosity measurement by determination of the rate of fall of a solid sphere through the material under test is probably one of the soundest scientific methods, and is based upon the following equation :—

$$\eta = td^2(\sigma - p)g/18s(1 + 2{\cdot}4d/D)(1 + 5d/3h)$$

where η = viscosity in poises,
g = 981 cm./sec.^{2},
d = diameter of sphere in cm.,
σ = density of sphere (gm. per c.c.),
p = density of liquid (gm. per c.c.),
s = distance between two marks (cm.),
t = time (secs.) for the sphere to fall distance s,
D = diameter of viscometer jar (cm.),
h = height of column of liquid (cm.).

Unfortunately the majority of bitumens are too opaque to permit of visual observation of the fall of a (steel) ball, but the fall may be detected electrically or by an X-ray method evolved by Broome and Thomas [13] and by Barr and Thorogood,[14] respectively.

A useful modification of the falling-sphere method is the inclined apparatus of Höppler.[15] For accurate work with the ordinary falling-sphere viscometer the diameter of the viscometer jar should be not less than ten times the diameter of the falling ball, but the Höppler modification is designed to employ a ball only slightly smaller than the internal diameter of the tube in which it falls. The viscosity is calculated in accordance with the equation :—

$$\eta = F \times (S_k - S_f) \times K$$

where F = time of fall of the sphere through 5 cm.,
S_k = density of the sphere,
S_f = density of the liquid under test,
K = a constant determined experimentally for each apparatus.

These falling-sphere viscometers are, however, only suitable for the measurement of relatively low viscosities, the practical limit having been found to be approximately $1{\cdot}2 \times 10^4$ poises. They can, therefore, only be used for the examination of normal types of asphaltic bitumen at relatively high temperatures, and the author feels strongly that most attention should be paid to the temperatures at which the material will exist in practice on the road, in the building and so on—*i.e.*, over the normal atmospheric temperature range. Attention is therefore directed to the alternative methods.

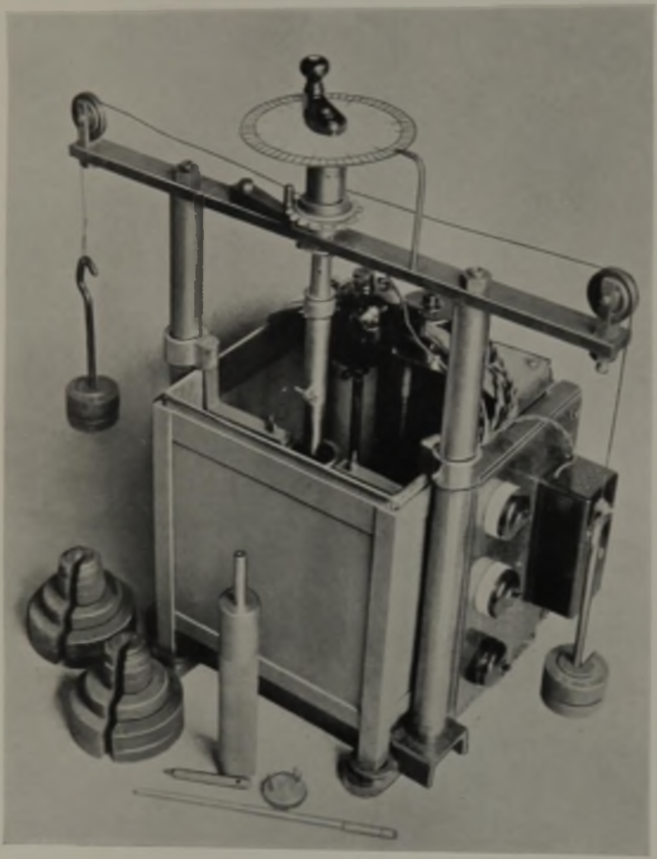

Plate I.

ROTATING-CYLINDER VISCOMETER.

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ROTATING-CYLINDER VISCOMETER.

There are two possible methods of carrying out viscosity determinations by observation of the relative movement of two cylinders of bitumen, etc., in the intervening annular space, namely :—

(*a*) Measurement of the speed of rotation of an inner cylinder actuated by a known force, the outer cylinder being kept stationary.

(*b*) Measurement of the torque acting on the inner cylinder when the outer cylinder is rotated at a constant angular velocity.

Principle (*a*) was first suggested by Couette,[16] and has since been modified by others, but, in relation to the present problems, particularly by Mooney and Ewart.[17] The general form of the apparatus as used by the author is shown in Plate I, and, as will be seen, the inner cylinder is rotated by means of falling weights, the viscosity being subsequently calculated in accordance with the equation :—

$$\eta = \frac{mgr}{8\pi^2 lw}\left(\frac{1}{r_2{}^2} - \frac{1}{r_3{}^2}\right)$$

where m = load in grams,
g = acceleration due to gravity,
r = radius of pulley plus cord (cm.),
r_2 = radius of inner cylinder (cm.),
r_3 = radius of outer cylinder (cm.),
l = length of inner cylinder immersed (cm.),
w = velocity of inner cylinder (revs. per sec.).

The mean shearing stress is given in dynes per sq. cm. by the equation :—

$$F = \frac{mgr}{(r_2 - r_3)^2 l}$$

It will be noted that in these equations there is no correction for any error resulting from " friction " between the bottom of the inner cylinder and the bitumen. This " end correction " has been deleted by the use of mercury in the bottom of the container to an amount just sufficient to cover the lower end of the inner cylinder. The remaining error by this method is much less than the general experimental error, and has been found very satisfactory in practice. Slip at the surface of the inner cylinder is prevented by fine corrugation of this cylinder. The principal advantage of this apparatus is that materials can be sheared for any desired length of time in one direction at constant shearing stress. Also the rotating cylinder viscometer permits measurements over a wider range of consistency than most other types of instruments.

The apparatus in which the outer cylinder is rotated and the torque acting through the bitumen to the inner cylinder being the factor actually measured, may be typified by that used by J. Csagoly.[18] He gives the following equation for this method :—

$$\eta = \frac{K}{cv}$$

where K = the torque acting on the inner cylinder,
c = an apparatus constant,
v = the angular speed of rotation of the outer cylinder.

This is ingenious, and doubtless useful for certain purposes, but for normal bitumen work its viscosity range is too low to permit of atmospheric temperature measurements.

COAXIAL CYLINDER VISCOMETERS.

Although the rotating-cylinder viscometers just described are in fact coaxial cylinder instruments, this term is usually used only in reference to coaxial cylinder arrangements in which the inner cylinder is moved longitudinally through the outer cylinder without rotation. The use of this principle for study of the rheological properties of bitumens was first demonstrated by Traxler and Schweyer,[19] although originally suggested for other materials by Segol [20] and Pochettino.[21] In the form of apparatus recommended by Traxler,[22] the bitumen under test is poured into the annular space between two cylinders and, after cooling, the whole is supported vertically and a load applied to the inner cylinder so as to displace this through 1 mm. From the time in seconds necessary to effect this displacement, the viscosity may be calculated. The calculations necessary for this have been studied, notably by Tolstoi [23] and by van Nieuwenburg.[24] In most cases the conditions are represented by the equation :—

$$\eta = \frac{Pg}{2\pi Vh} {}^{e}\log \frac{R_2}{R_1}$$

where V = the velocity of the inner cylinder,
P = the weight of the inner cylinder,
h = the length of the inner cylinder in contact with the bitumen,
g = acceleration due to gravity,
R_1 = the radius of the inner cylinder,
R_2 = the radius of the outer cylinder,
η = viscosity in poises.

Traxler's apparatus in its latest form [25] is so constructed that with a given weight the number of seconds required for a 1 mm. movement multiplied by 100,000 gives the viscosity. In this way a determination of viscosity can be made in this apparatus in less time than is required for a penetration test, and it has been found very suitable for a study of age-hardening over short periods of time under conditions where no differences are shown by the penetrometer.

OTHER VISCOMETERS.

Although the scope of this paper precludes a detailed study of all the viscometers suitable for the study of the flow properties of bitumen, the following additional methods may be referred to, details being available in the original literature :—

(1) A modified capillary-tube viscometer for 10–1,000,000 poises.[26]
(2) The alternating-stress method suggested by Bingham and

Stevens [27] and developed with particular regard to bitumens by Traxler and others.[26, 28, 29] This is suitable for 10^5–10^8 poises.

(3) A rod viscometer, suitable for about 10^7–10^{13} poises.[30]

(4) Sinker viscometer, used by several workers, notably by Saal.[31] Suitable for 0·1–10^5 poises.

(5) Disc viscometer, proposed by Obermayer [32] and developed by Manning [33] suitable for 10^7–10^{12} poises.

In addition to the above, reference might be made to the following instruments, particularly suitable for the examination of bitumen, etc., at viscosities of less than about 100 poises.

(1) The torsion viscometer as used by Fuidge,[34] and advocated by the Standardization of Tar Products Tests Committee.[35, 36]
(2) The trough viscometer.
(3) The metro plastimeter, both developed by Evans and Pickard.[37]
(4) The ball-and-bucket viscometer of Beale and Docksey.[38]
(5) The British road-tar viscometer.[39]
(6) The modified Ostwald viscometer proposed by Lee.[40]

If the quantity of material available for test is very small, the methods of Levin [41] and of Bondi [42] may frequently be employed.

PLASTICITY.

It has already been noted that the majority of bitumens are not true fluids at normal atmospheric temperatures, and this deviation has been studied particularly by means of the Couette type viscometer. It was originally suggested by Bingham [43] that, whereas true fluids give straight-line curves passing through the origin if rate of shear is plotted against shearing stress, other materials give curves such as *B* in Fig. 2, in which for shearing stress below a certain value no appreciable shearing motion appears. Bingham's idea is to extrapolate the experimental curve to the stress axis, and to take two constants, the intercept and the slope. The intercept was originally called " yield-value " or " critical shearing stress," but is better named " shearing strength." The slope has been called " pseudo-viscosity " or " stiffness." It was at one time erroneously called " plasticity." Its reciprocal is " mobility " or " liquidity." Saal [30] pointed out that bitumens can give curves of an intermediate type such as *C* in Fig. 2, where the ratio shear/stress increases with rate of shear up to a relatively high stress. This does, in fact, seem to represent the behaviour of many asphaltic bitumens, although under certain conditions curves of type *D* have been obtained with shear/stress ratios *decreasing* with rise of shearing stress over the lower part of the curve. This phenomenon remains largely unexplained, but it is interesting to note that it is particularly apparent in the case of highly elastic materials such as rubber–bitumen mixtures.

The identification of the presence of a " yield value " or " shearing strength " is difficult, and apparently depends largely on test conditions, it being very doubtful whether any of the asphaltic bitumens normally employed in this country have definite yield points. Study at low rates of shear (less than 0·01 cm. per sec.) has, however, given some indication of the " apparent shearing strength," although the methods of examination are not as accurate as might be desired at rates of shear lower than about 5×10^{-3} cm. per sec. Some typical curves are shown in Fig. 3, which would indicate shearing strengths of the order shown in Table IV :—

TABLE IV.

Typical Shearing Strength Figures at 30° C.

Bitumen A	$0{\cdot}7 \times 10^3$
Bitumen B	1·2
Bitumen C	5·2

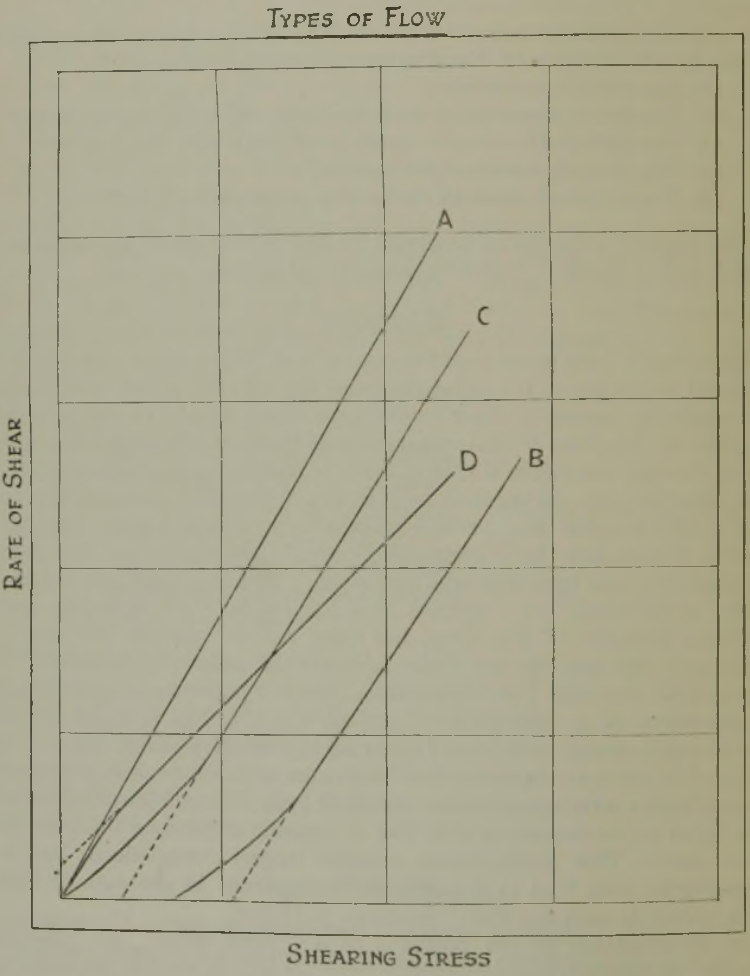

FIG. 2.

An interesting treatment of results obtained with viscometers such as the rotating concentric cylinder instrument consists in plotting log rate of shear against log shearing stress. This gives approximately straight lines, which may be represented by the equation :—

$$v = kF^p$$

wheer v = rate of shear,
k = a constant,
F = shearing stress,
p = the slope of the curve.

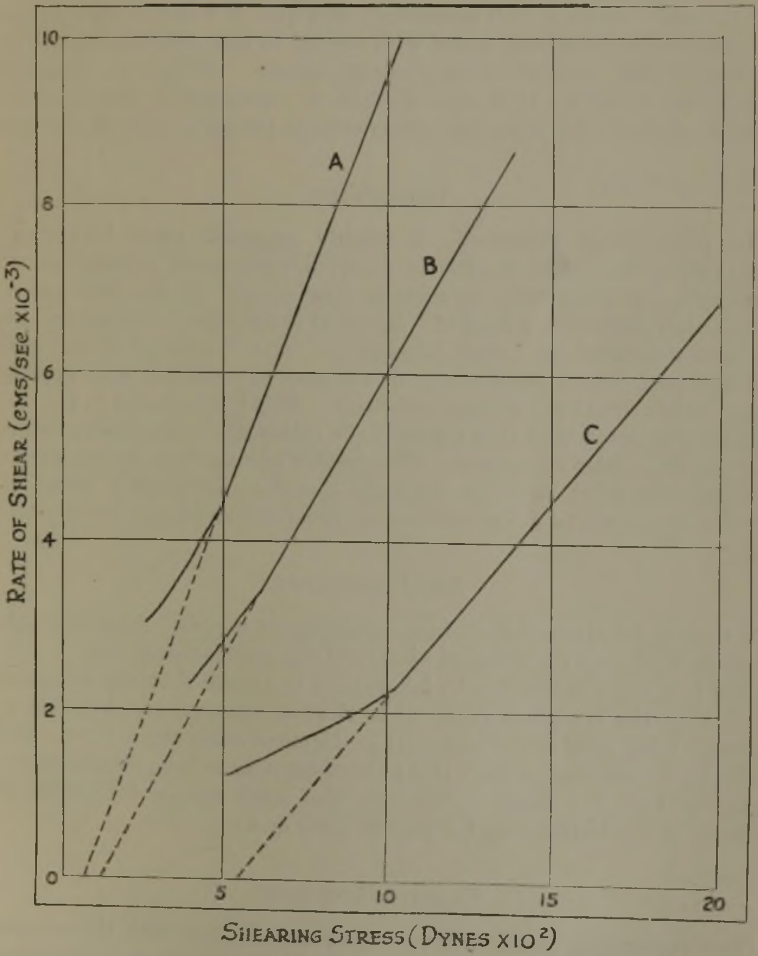
BEHAVIOUR OF BITUMENS AT LOW RATES OF SHEAR

FIG. 3.

The value of p may also be regarded as a measure of the plasticity of the material, the higher the value the greater being the deviation from being a true fluid. Some typical values of p are given in Table V.

TABLE V.

	Value of p.	
	25° C.	60° C.
65 Pen. Bitumen A . .	1·07	1·03
200 Pen. Bitumen A . .	1·04	1·0
200 Pen. Bitumen B . .	1·42	1·21
200 Pen. Bitumen C . .	1·78	1·33

It has been found that, as illustrated by the figures in Table V, the value of p generally tends to fall somewhat with rise of temperature, although some anomalies have been noted with regard to this, presumably owing to thixotropic and work-hardening complications. Moreover, comparison with Table II shows that this method is considerably less sensitive a measure of plasticity than that referred to in the early part of this paper.

THIXOTROPY.

The presence of thixotropy is readily apparent when bitumens are examined by the methods already described, the speed of rotation of the inner cylinder frequently increasing appreciably as the test proceeds. Occasionally, however, a kind of " inverted thixotropy " is observed, which has been described as " work hardening " or a " winding spring effect." This has been found particularly in the case of materials that are highly elastic, such as rubber–bitumen mixtures. This is illustrated in Fig. 4. It has been suggested that this is due to the molecular arrangement becoming more regular under the strain. This greater regularity is, thermodynamically, less probable, and the material therefore develops a stress in an attempt to revert to a less ordered or thermodynamically more probable state.

AGE-HARDENING.

In the examination of thixotropic phenomena it is very necessary to have a full knowledge of the thermal history of the sample under test.

Care is always taken in the laboratory to ensure that the temperature throughout the sample is adjusted to the test temperature, but this is not sufficient when studying rheological problems of bitumens. Even standing overnight is sufficient to show this phenomenon, as may be illustrated by the curves of Fig. 5. Tests *repeated* on this same sample frequently show evidence of age-hardening and thixotropy (Fig. 6).

ELASTIC RECOVERY.

Data concerning elastic recovery may be obtained with the concentric cylinder viscometer in the same way as with the twisting-sample method—*i.e.*, by permitting rotation through a convenient angle, and then removing the shearing stress and measuring the angular recovery after the material has come to rest. The figures recorded must only be compared with other elasticity data with caution, as they are found to vary according to :—

(*a*) The rate of shear prior to release of the load.
(*b*) The angle through which the sample has been displaced.
(*c*) The dimensions of the test specimen.
(*d*) The temperature of test.

Care must also be taken to ensure that ample time is allowed for the sample to come to rest. This takes very much longer than is sometimes realized, and may be illustrated by Fig. 7. A few typical recovery figures are given in Table VI.

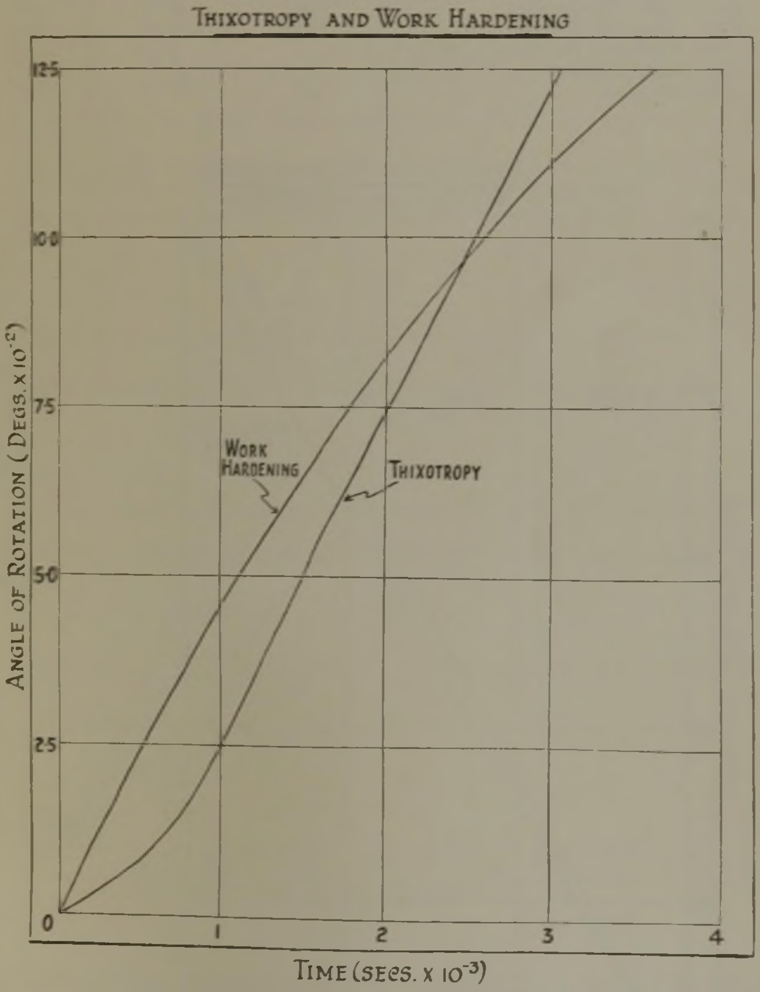

FIG. 4.

TABLE VI.

Bitumen.	Penetration at 25° C.	Temperature.	Elastic Recovery.
Steam Refined Bitumen	200	0° C.	30°
Steam Refined Bitumen	200	15° C.	10°
Do. plus 1% Rubber	150	0° C.	62°
Do. plus 1% Rubber	150	15° C.	40°
Fluxed Lake Asphalt	203	0° C.	37°
Fluxed Lake Asphalt	203	15° C.	15°
Do. plus 1% Rubber	170	0° C.	67°
Do. plus 1% Rubber	170	15° C.	35°
200 Pen. Asphaltic Bitumen 80% Trinidad Lake Asphalt 20%	—	0° C.	60°
Oxidized Bitumen	40	15° C.	130°

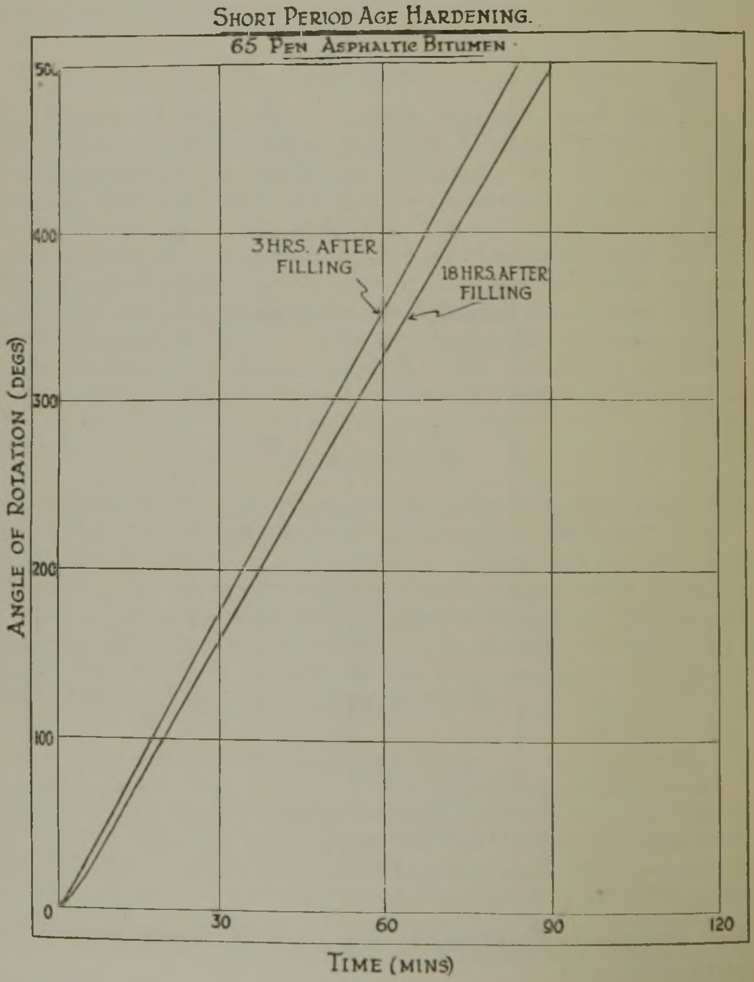

FIG. 5.

VISCOSITY–TEMPERATURE RELATIONSHIP.

It is obviously of very considerable importance to have a knowledge of the "temperature susceptibility" of any bitumen to be used for such work as the manufacture of asphalt for road or building construction, and it may be of value to review briefly some of the methods that have been proposed for this purpose.

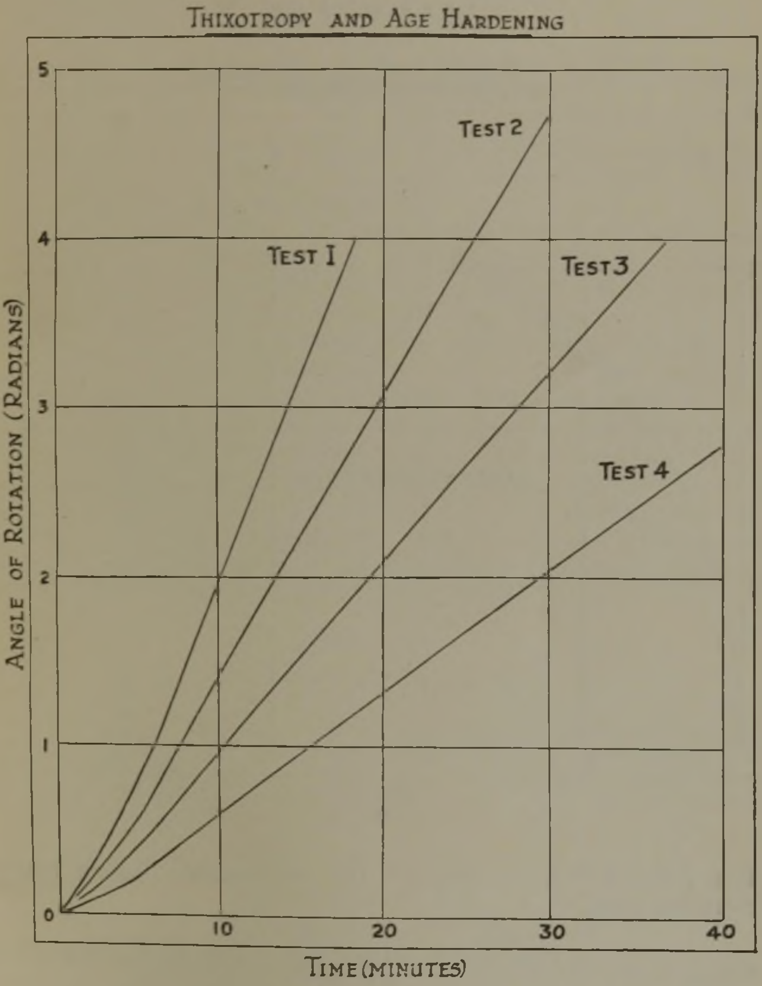

FIG. 6.

An early method consisted merely in recording the extent of the plastic range—*i.e.*, the temperature difference between the softening point (*e.g.*, by Ring and Ball) and the brittle point (*e.g.*, by Fraass). Later methods suggested graphical methods based on rather complex equations. For example, Saal [44] obtains a straight line relationship by plotting :

$$\log \log (V_t + 1) = m \log T + c$$

where V_k = kinematic viscosity (centistokes),
T = absolute temperature,
$m + c$ = constants.

Umstatter [45] suggests plotting log viscosity against the reciprocal of the square of the absolute temperature, thus :—

$$\log \eta = mT^{-2} + C$$

ELASTIC RECOVERY OF BITUMENS

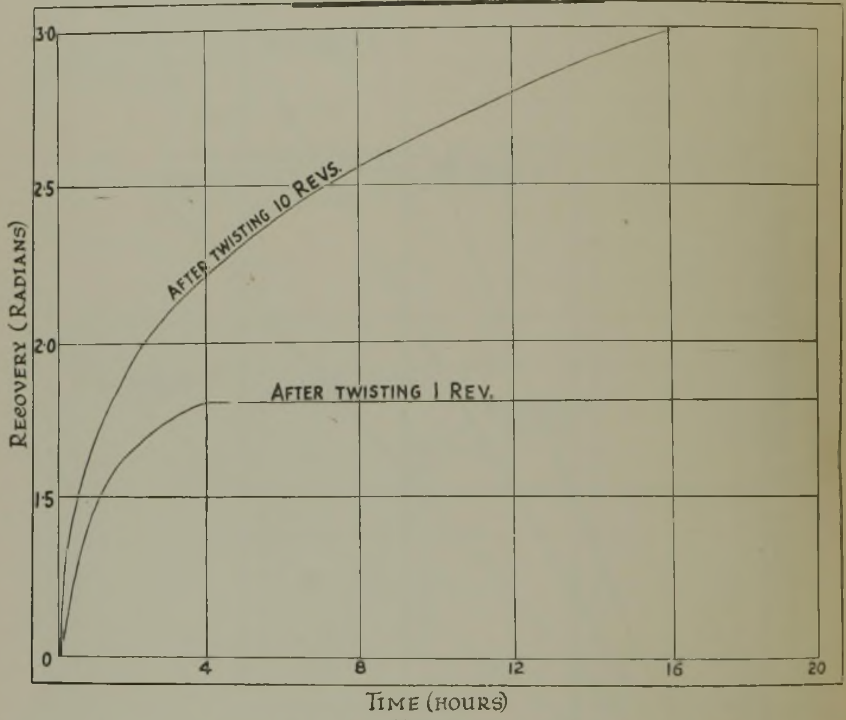

FIG. 7.

The A.S.T.M.[46] have proposed two susceptibility factors based on penetration tests :—

$$\text{Susceptibility} = \frac{\text{Pen. } 115^\circ \text{ F., } 50 \text{ g., } 5 \text{ sec.} - \text{Pen. } 32^\circ \text{ F., } 200 \text{ g., } 60 \text{ sec.}}{\text{Pen. } 77^\circ \text{ F., } 100 \text{ g., } 5 \text{ sec.}}$$

$$\text{Susceptibility} = \frac{\text{Pen. } 100^\circ \text{ F., } 100 \text{ g., } 5 \text{ sec.}}{\text{Pen. } 77^\circ \text{ F., } 100 \text{ g., } 5 \text{ sec.}}$$

Both these are unsound, as in the former the consistency is measured at three different and unknown stresses, and in the latter again in unknown stresses which change at different rates.

A fluidity factor has been proposed by Zapata [47] :—

$$\text{Fluidity} = (\text{Furol Vis. } 275^\circ \text{ F.} - \text{Pen. } 77^\circ \text{ F., } 100 \text{ g., } 5 \text{ sec.})$$
$$(\text{Pen. } 77^\circ \text{ F., } 100 \text{ g., } 5 \text{ sec.})/100.$$

Somewhat similar is Kelley's float-test index [48] :—

$$\text{Float-test Index} = (\text{Float } 176^\circ \text{ F.} \times \text{Pen. } 77^\circ \text{ F., } 100 \text{ g., } 5 \text{ sec.})^{\frac{1}{2}}$$

Also Abraham's susceptibility factor [49] :—

$$\text{Susceptibility} = \frac{\text{Hardness at } 32^\circ \text{ F.} - \text{Hardness at } 115^\circ \text{ F.}}{\text{Softening Point (K. \& S.)}} \times 100$$

All these suffer from the disadvantage of trying to reconcile figures obtained at different, varying, and frequently unknown, stresses. They are arbitrary formulæ with no scientific basis.

Pfeiffer and van Doormal [50] proposed a scheme for a " penetration index " which must be criticized somewhat in the same direction, as it is obtained by means of a nomogram establishing a relationship between the penetration and the Ring and Ball softening point. The scheme is particularly doubtful, as it assumes that the Ring and Ball point corresponds to a penetration of 800, whereas actually the softening point may correspond to penetrations ranging from about 450 to 1000 or more. This wide variation of consistency at the Ring and Ball point seems generally not to be realized, possibly because it is not possible to measure penetration at that temperature. With the aid of the Couette type viscometer, however, viscosities may readily be determined at the softening point. If this is done, it will be found that not only do bitumens have widely divergent viscosities at this temperature, but that the viscosity is still generally dependent on the stress applied. A few typical figures are shown in Table VII :—

TABLE VII.

Viscosity at the Softening Point.

Bitumens.	R. & B. Softening Point, ° C.	Viscosity at R. & B. Point.
Venezuelan Mexphalte 65° . .	52	$2{\cdot}4 \times 10^4$ poises.
Ditto plus 2% Rubber . . .	65	2·3
Venezuelan Mexphalte 200° . .	40	1·6
Ditto plus 2% Rubber . . .	47	2·1
Trinidad A.C. (200 Pen.) . . .	40·5	2·2
Ditto plus 2% Rubber . . .	65·5	1·9

A sounder temperature susceptibility scheme is that employed by Mitchell and Lee [51] :—

$$n = (\log \eta - \log \eta_2)/\log T_2{}^\circ \text{ F.} - \log T_1{}^\circ \text{ F.}$$

where n = the logarithmic temperature coefficient
η_1 = viscosity at T_1° F.
η_2 = viscosity at T_2° F.

This scheme gives figures such as those in Table VIII when applied to data obtained with the Couette type viscometer :—

TABLE VIII.

Logarithmic Temperature Coefficients.

Venezuelan Mexphalte 65°	9·4
Ditto plus 2% Rubber	10·8
Venezuelan Mexphalte 200°	8·2
Ditto plus 2% Rubber	8·3
Trinidad A.C. (200 Pen.)	10·2
Ditto plus 2% Rubber	10·0

It must, however, be pointed out that log viscosity/log temperature curves, although straight lines in many cases, are rarely parallel lines and, not only does the rate of change of viscosity with respect to temperature vary with temperature, but the slope of the curve is also dependent on the shearing stress employed. A better way of expressing temperature susceptibility is to measure the percentage decrease in viscosity (in absolute units) for 1° C. rise in temperature over the suitable temperature range. The method was proposed by Traxler and Schweyer,[52] who express the numerical value of the susceptibility by the equation :—

$$\text{Asphalt Viscosity Index (A.V.I.)} = 100\ [(\eta_c/\eta_d)^{1/(t_c-t_d)} - 1]$$

where η_c and η_d are the viscosities, in poises, of the bitumen at temperatures t_c and t_d (°C.). The values for the A.V.I. are negative, since the viscosity decreases with temperature, but the sign may be neglected without detracting from the value of the index. A few typical figures are given in Table IX :—

TABLE IX.

Asphalt Viscosity Index.

200 Pen. Venezuelan Mexphalte	19·3
Ditto plus 2% Rubber	18·3
200 Pen. Trinidad A.C.	21·5
Ditto plus 2% Rubber	20·0

With either of these methods care should be taken to employ them only over a relatively small temperature range as the variation of viscosity with temperature is very complex, probably owing to the complex structure of bitumen. It would appear probable that the structure changes very considerably as the material is heated or cooled, so that with rise of temperature a bitumen may be regarded as passing successively through the following states :—

Solid—" plastic solid "—" liquid plastic "—liquid.

The first of these changes corresponds very approximately to the brittle point, whilst the last of these changes is a gradual process taking place above the " melting point." For any given bitumen the change from one state to another will take place at different temperatures, depending on the rate of change of temperature, etc., and will certainly take place at different temperatures, according to whether the material is being heated or cooled. The situation is further complicated by the phenomena of thixotropy and work-hardening, the condition at any moment being a matter of equilibrium between the process of transformation in the direction solid–liquid and the transformation in the direction liquid–solid. Further, the test operation normally upsets the equilibrium, so that the test results obtained may vary within wide limits, according to the conditions.

The author wishes to record his thanks to Mr. T. A. Sharpley, who has given considerable assistance with the experimental work.

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DISCUSSION.

Mr. L. J. Chalk wrote: Mr. Broome has given us an extremely interesting survey of the flow properties of bitumens, and has raised a number of points of considerable practical and theoretical importance. One of these concerns methods of obtaining a numerical index for what is generally referred to as "plasticity." The normal laws of viscous flow do not apply to most bitumens, and, as a consequence, the figure obtained for viscosity varies with the shearing stress; whence it follows that the function referred to as "degree of plasticity" is not a true constant. In the case of the twisting-cylinder apparatus, the observed viscosity, and therefore the "degree of plasticity," will depend on the weight used to apply the torque, the dimensions of the test specimen, and diameter of torque drum. The "degree of plasticity" cannot therefore be accurately interpreted or the figures reproduced by other laboratories, unless the precise conditions under which the test was carried out are known. A further point is that the figures given in Table I convey rather a false impression of the accuracy of the results obtained by the twisting-cylinder method. It is rarely permissible, even with true fluids, to express viscosity to more than three significant figures, and I think Mr. Broome will agree that this would have been ample in the present instance.

An alternative method of expressing plasticity is based on the fact that the equation $V = KFP$ has been shown to hold for a number of bitumens. The equation does not itself represent a straight line (as stated on p. 519), but on taking logarithms it reduces to the form $\log. V = \log. K + p \log. F$, which experimentally is found to be a straight line. The amount by which "p" is greater than 1 is the measure of the plasticity of the bitumen. The term "p" is a true constant, and, for this reason, would appear to be more suitable as an index of plasticity than the function "degree of plasticity."

Dr. F. H. Garner wrote: The paper by Mr. Broome represents a valuable summary of all the various properties comprised under the term "flow properties of bitumen," and it is interesting to have a description of the two types of apparatus which he has used for the measurement of these properties—namely, the Frankland–Taylor twisting-point apparatus and the modified rotating-cylinder viscometer.

It would appear that the plasticity figures quoted in Table II are of limited value, since it is doubtful whether it is possible to derive the degree of plasticity from a relationship between the observed viscosity at 25° C. and a figure for viscosity calculated from the penetration; this is based on the assumption that true viscosity is dependent only on penetration, but there are other factors concerned in penetration. On the other hand, Dr. Lee stated that in the case of practically all bitumens the curve obtained when the shearing test was plotted against rate of flow was a curve passing through the origin, and hence plasticity can be measured by the P in the formula:—

$$V = kF^P.$$

This would appear to be a much sounder measure of plasticity, but here again the plasticity may vary with the rate at which the shearing stress is applied, as illustrated by the figures quoted in Mr. Broome's paper.

Mr. R. Preston wrote: Mr. Broome has performed useful work in indicating the large number of methods adopted or suggested for determining the flow properties of bitumen, and although there appears to be little exact knowledge published on the correlation between laboratory tests and practice, he has directed attention to this problem by his statement of preference for the more plastic bitumens for road work, and for those of maximum ductility.

I would venture a few observations on these two properties. Mr. Broome was perhaps among the first to adopt a method of expressing plasticity in terms of a simple control test (penetration), but the very wide range of values for the "degree of plasticity" of different bitumens obtained by his method casts doubt either on the accuracy of correlation with practice, or on the method of deriving the "plasticity." The differences given in Table II of the paper for normal bitumens (as distinct from asphalts) are far too great to be truly significant of their behaviour in practice. A more reliable indication of plasticity which could be determined almost as easily as that given by Mr. Broome could be obtained by the measurement of flow under a series of different loads. The deformation of a plastic material may be written :—

$$D = F(t)f(S)\phi(\theta)$$

where t = time,
S = stress,
θ = temperature.

Under constant time and temperature

$$D = Kf(S)$$

an equation similar to that given by Mr. Broome on p. 519. Variations in D may be related to variations in S. For example, the relation between penetration and load would provide an index of plasticity, but a test on the lines of the Pochettino viscometer would be preferable, the relation between deformation and load being determined under fixed conditions of time and temperature.

It is open to question, however, whether the quality of bitumens in relation to roads can be assessed independently of their behaviour in presence of mineral matter, and without considering the nature of traffic forces. The writer found some years ago that the deformation of a beam containing mineral matter and a " viscous " binder allowed to sag between pivots could be divided into two stages—namely, a comparatively rapid movement in the initial stage, followed by a longer and steadier movement. On removal of the load, a definite recovery effect was noticed. The initial rapid rate of sag and final " recovery " were obviously manifestations of storage and release of energy. In view of the impulsive nature of traffic forces, it would appear that the phenomena mentioned more nearly represent actual road conditions than the flow under steady load conditions (plastic or viscous flow) except perhaps in the case of heavy slow traffic.

Mr. Broome has given examples of the effect of temperature on ductility, and has deduced that the superiority in practice of bitumen B over C is due to its higher maximum ductility when tested over a range of temperatures. The writer would suggest another explanation for this superiority—namely, its greater ductility at lower temperatures. It would be of interest in this connection to know the values of bitumen A of Fig. 1 compared with bitumens B and C.

Dr. R. N. J. Saal wrote : In Fig. 2, line D is given as a special type of plasticity curve which—according to Broome—is particularly found in the case of highly elastic materials such as rubber–bitumen mixtures. It seems to us that it is the elastic properties of the materials which are responsible for the phenomenon referred to. For, high elastic deformability involves, in the case of a deformation under constant shearing stress, that at the beginning of the determination the rate of shear strongly decreases with time, and subsequently becomes constant or increases again owing to thixotropy.

Hence it will entirely depend on the moment at which the determination is carried out, what value is found for the rate of shear. In the case of the measurements plotted in Fig. 3, " Behaviours of Bitumens at Low Rates of Shear," the interval between the beginning of the deformation and the measurement was perhaps too short to reach a state of elastic deformation corresponding to that in the determinations at higher rates of shear.

One is inclined to seek the explanation of the phenomenon referred to particularly in the circumstances under which the measurement was carried out, because neither line D of Fig. 2 nor the curves of Fig. 3 should ever intersect the rate of shear axis at positive values.

A similar reasoning may be set up for determinations carried out at constant rate of shear.

Furthermore, we would comment on the last chapter, in which the Penetration Index according to Pfeiffer and van Doormaal is criticized. This penetration index is based on the, experimentally found, linear relation between log. penetration and temperature; the slope of the log. penetration–temperature curve indicates the temperature susceptibility. However, since the determination of the temperature susceptibility from two penetrations offers considerable practical drawbacks when applied to bitumens of widely divergent properties, Pfeiffer and van Doormaal preferred deriving the required slope from one penetration and the softening point R. & B. This is feasible only if the softening point R. & B. invariably corresponds to about the same penetration.

From penetration measurements at softening point R. & B. with a wide range of bitumens it appeared that the penetration at this point is indeed about 800. In some cases deviating values were found (max. 900, min. 600). The influence of these deviations on the calculated temperature susceptibility is, however, comparatively small, as we are here dealing with the log of the penetration, so that the errors in the calculated temperature susceptibility are of but minor importance in practice. The errors involved in the use of two penetrations are, partly on account of the log. penetration–temperature line not being completely straight, of the same order of magnitude.

We would further point out that the differences found for the square of the penetration at softening point R. & B. are of about the same order of magnitude as the differences in viscosity at this point.

Broome prefers to determine temperature susceptibility by measuring the percentage decrease in viscosity (in absolute units) for 1° C. rise in temperature, yet he emphasizes that with this and other methods care should be taken to employ them only over a relatively small temperature range, as the variation of viscosity with temperature is very complex. In our opinion it is the chief advantage of the system proposed by Pfeiffer and van Doormaal that the relation between log. penetration and temperature is not complex, but practically linear over a rather wide temperature range. This even applies in the case of blown bitumens, where, on account of elasticity and thixotropy, it is not possible to characterize the behaviour by means of a single absolute viscosity determination.

Mr. D. C. **Broome** in reply wrote that he fully appreciated that the degree of plasticity as determined by means of the twisting-cylinder apparatus depended on the weight used to apply the torque, the dimensions of the test specimen, and the diameter of the torque drum. This meant that the test was an arbitrary one, and possibly the equation suggested by Mr. Chalk was theoretically sounder. From a practical point of view, however, he had found that the former method was extremely useful, and did seem to magnify the differences in plasticity between various materials in a manner which lined up with practical experience.

He agreed that the data in the last column in Table I should only have been quoted to three significant figures.

He also agreed that the alternative method of expressing plasticity to which Mr. Preston referred was, of course, quite reliable, but he had found, as a result of experience, that the method referred to in the paper was extremely useful in virtue of the very fact that it did magnify the differences. The situation there was somewhat analogous to the use of a microscope for examining small particles. One did not see the true size of the particles when examined under the microscope, but their very magnification was extremely useful in assisting their evaluation.

He fully agreed that the properties of the bitumen in a road were affected very materially by the presence of mineral matter. His experience was, however, that plastic or viscous flow did frequently take place under practical road conditions, and that was therefore a contributory factor, although it was certainly not the only factor.

With regard to the ductility of bitumens B and C in Fig. 1, his view was that bitumen B was superior not merely because it had a higher maximum ductility, but also because that maximum ductility occurred at an appreciably higher temperature. It was also superior in that its ductility at very low temperatures was greater.

BITUMEN EMULSIONS—THEIR DEVELOPMENT AND PRESENT SPHERE OF UTILITY.*

By L. G. Gabriel, B.Sc., A.I.C., F.Inst.Pet.

Summary.

The historical development of the manufacture of bituminous emulsions is sketched and various problems which had to be solved in order to remedy the initial difficulties are dealt with. Data are given of the types of emulsion obtained with various pure chemical compounds. Sedimentation behaviour of emulsions is considered and experimental results are quoted, showing the evaporation behaviour of emulsions. Problems underlying the chemical interaction of bituminous emulsions and stone aggregates are dealt with and the specific nature of these chemical reactions, as between any given emulsion and any given stone aggregate, is demonstrated. The physico-chemical factors underlying the viscosity/concentration relationships of bituminous emulsions are discussed in detail and the general formula of Hatschek is shown to apply. Methods of use of emulsions on the road and in industry are described and the mechanism of the breakdown of these emulsions in various circumstances is analysed. The special types of emulsion, developed for industrial purposes, are briefly considered and the development of the industry as a whole, from its beginnings to its present scientifically controlled achievement, is summarised.

The purpose of the present paper is to present, more particularly for the non-expert reader, an account of the development of the manufacture and use of bituminous emulsions of all types, and the rôle they now fill. In the course of the survey it is proposed to deal with development in manufacture and in application, and also to indicate one or two typical examples of the growth of technical knowledge in this territory, as the result of intensive research which has been carried out in the industry. It will be seen that this research work, in some cases, has applications which come outside the immediate sphere of use of bituminous emulsions, and has more general significance.

The underlying idea of the endeavour to emulsify bitumens is, of course, a cheap method of rendering them more fluid and, therefore, easier to apply. The use of bitumen, heated to render it fluid, antedated its use in the emulsion form or as cutback, but the disadvantages which were felt led to a search for a more convenient type of material, still possessing the binding and waterproofing power of bitumen. These drawbacks were principally, of course, the inconvenience, in certain circumstances, of having to heat the bitumen and, further, the care which has to be exercised if real control is to be obtained over the rate and conditions of application, in view of the rapid increase in viscosity which takes place as the heated binder cools to air temperature. It seems probable that the use of bitumen emulsion—that is, bitumen fluidified with water as the medium—antedated, at any rate on the large scale, the use of bitumen fluidified with solvent (cutbacks), merely because the cheapness of water appealed to the imagination of early workers. At any rate, we can go back to the year 1904 for the first appearance of a patented process for the emulsification of bitumen. Actually, this had been preceded in 1903 by a patent taken out by van Westrum for

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* Paper presented to a Meeting of the Asphaltic Bitumen Group of the Institute of Petroleum held on 9th May, 1939.

the emulsification of dust-laying oils. Quite a dozen other specifications for emulsifying bitumen appeared before 1910, in which year van Westrum's well-known patent for a process of this kind was taken out.

A certain amount of application of this and similar patents occurred immediately prior to the Great War, but development on a large scale was not forthcoming, and one of the reasons for this was that bitumens, in those days, were probably not as amenable to emulsification as they were after the great improvements in refinery technique which took place immediately after the War, and, further, the quantities of emulsifying agent specified in the early processes were, in our view nowadays, excessive, although here again this may have been conditioned by the characteristics of the then available bitumens. The emulsions, in any case, once made, undoubtedly possessed, for the most part, properties similar to those which we now class as semi-stable, and, as such, it is not altogether surprising that difficulties to do with setting seemed to have resulted in a discouragement of early efforts.

After the War, however, the problem of the reconstruction and modernizing of the road system of European countries began to come to the fore, with the greatly increased development of motor traffic. A large mileage of roads in those days consisted of water-bound macadam and, under the greater demands of higher-speed motor traffic, these roads began to show signs of breaking up, and maintenance became a severe problem. It was soon found that in laying the dust by means of emulsified oils and bitumens, a film of the tar or bitumen tended to remain on the road, especially after repeated treatments, and the idea then suggested itself that this film had advantages of its own, and from that time the practice began to emerge of applying heavier dressings than those strictly necessary for dust-laying, and it was only a matter of a short time before the advantages of the bitumen-surfaced road became fully apparent, particularly for pneumatic-tyred traffic.

MANUFACTURE.

The earliest process for the manufacture of bituminous emulsion which had a successful large-scale development was that which appeared in 1922 under British Patent No. 202,021 by Mackay. The emulsion made by this process was responsible for the bulk of the pioneering development of the bituminous road emulsion industry. The process consisted in stirring into the molten bitumen a quantity of fatty acid or other suitable acidic constituent of the ultimate emulsifier, then running in a solution of alkali to saponify this fatty acid in the mixer and in the body of the bitumen to be emulsified, and diluting the rather concentrated emulsion so formed with a sufficient quantity of water. This process gave very satisfactory results with Mexican bitumen, in use at that time, and, provided no unexpected changes in the characteristics of the bitumen supervened, an emulsion of uniform and standard quality was obtained. It must be realized that in those days all who were endeavouring to work emulsification on the large scale, as a scientific process, were handicapped by almost complete ignorance of the fundamental principles involved, and by a very incomplete understanding of the properties of the finished emulsion. The whole thing was rather a miracle. All failures and inconveniences had to be accounted for by rule of thumb and without very much real understanding. However, standardized methods for the application of emulsion of this type gradually developed, and before many years had elapsed it became evident that the idea was capable of a very considerable future.

At this time various competitive processes began to appear, and, in particular, note should be taken of a series of such processes, all based on the same fundamental idea, which was first set out in British Patent No. 226,032, by Montgomerie, published in 1924. This patent covered a process in which advantage was taken of the fact that bitumen itself contains a small percentage of substances of an acidic nature, which, in combination with alkali, were capable of forming soap-like bodies, which produced emulsification of the bitumen, under conditions of adequate agitation.

In the Montgomerie process a dilute solution of caustic alkali was first placed in the mixer, and into this was allowed to flow the molten bitumen. An emulsion of greater or less stability was formed, according to the precise characteristics of the bitumen, and this was usually further stabilized by the addition, at the end of the process, of a quantity of soap or similar colloidal protective body. The Montgomerie process showed up at once in a favourable light, in view of the fact that the total concentration of soap and alkali present could be established at a figure very much below that required in the Mackay process. Furthermore, the two processes could be carried out in the same type of slow-stirring mixer, in which the blades did not need to revolve at a greater speed than 60–90 r.p.m. Nevertheless, it was found at the time that the properties of the Mackay emulsions were, in some ways, superior to those of many of the emulsions made by the Montgomerie process, and, in any case, in those days competition was not so severe, consequently the prime cost of the ingredients was not so important a factor as it is now.

It will be noted that the Mackay type of emulsion depended less on the chemical composition of any substances present in the bitumen and, in the author's experience, this, on many occasions, proved a boon, in that the Mackay emulsions were less susceptible to any changes in the bitumen than those produced by the Montgomerie process.

It should be explained that these changes in the bitumen were not such as could be detected by determination of the normal physical properties of the bitumen, and at that time the variations were not at all understood, although they are more comprehensible to-day, as will be seen later.

It is curious to note that in those early days methods of control of the viscosity of emulsions were discovered : that is to say, methods by which the viscosity of the emulsion could be raised or reduced, without altering the bitumen content. In the Mackay process the rate of addition of the alkali solution accomplished this, and a certain amount of control, in a similar way, was possible in the Montgomerie process by changing the rate of addition of the bitumen. With Mexican bitumen the changes in viscosity which could be achieved in this way, at any rate with the Mackay process, were quite considerable, and it was possible, given favourable circumstances, to prepare emulsions containing, say, 50 per cent. of bitumen, which had a consistency of thick cream. The explanation of these phenomena, in the light of developments which will be described later in the paper, affords rather an interesting sphere of speculation.

The development and use of these emulsions proceeded smoothly for a year or so, until, in or about the year 1927, a series of quite unusual difficulties in manufacture occurred, at any rate in the author's experience, which necessitated much more fundamental efforts to secure a remedy than had previously been the case. After some little investigation, it became clear that the type of bitumen had changed radically. It must be remembered that at that time such a change over was not thought to have any special significance, and a good deal of surprise was experienced by everyone that the process which had gone smoothly before now showed considerable hesitation and, furthermore, the emulsions, once obtained, were very much less viscous than those obtained previously.

The ultimate result of this setback was that other methods of emulsification came into consideration. There was a prejudice at that time against the use of the newly introduced colloid mill for the dispersion of bitumen, because it was thought it yielded emulsion of tremendous stability. Here again, though ideas on the possible causes of changes of stability were quite rudimentary, there was a general inclination to associate stability with the dispersion, and it was thought that the dispersion produced by colloid mills would be much finer than that produced in the mixer. Trial, of course, readily showed that neither the dispersion nor the stability exhibited these great differences, and it soon became apparent that there was one great advantage in the use of the colloid mill : this was that it rendered the process almost independent of the percentages of acids, resins, and other bodies, which were capable of influencing the emulsification by any process involving saponification in the presence of the bitumen.

The colloid mill, therefore, became increasingly popular for the preparation of bitumen emulsions from that date onwards, although the mixer processes, in more highly developed form, are still finding considerable use.

The use of the colloid mill imposes a very much higher power consumption to produce emulsions; but, nevertheless, this is not a decisive factor, because in any case the power cost is a very small fraction of the total cost of manufacture. As against this it is possible to arrange the mill so that it can be fed by means of a system of grouped pumps for the ingredients which go to the preparation of the final emulsion, and the process is therefore a continuous one, under very good control as regards the proportion of the ingredients.

The type of mill used may vary between almost any of those on the market, but those which have achieved most use in the industry are the Hurrell, the Premier, and the Hatt-Dussek. Figs. 1, 2 and 3, show these three types of mill.

In actual practice they all function on the same principle, which is the subjection of the bitumen and emulsifier solution to very high forces developed in spaces of small dimensions. This has the effect of splitting up the bitumen into small globules, in the presence of the emulsifier solution, which stabilizes them in that form and prevents them again coalescing to the bulk phase. It would be possible to go into great detail on the relative advantages of the different types of mill, but it is not proposed to do this in a general paper of this type. However, one observation should at any rate be made. From time to time the different types of mill on the market are advertised as possessing advantages, due to saving in power consumption,

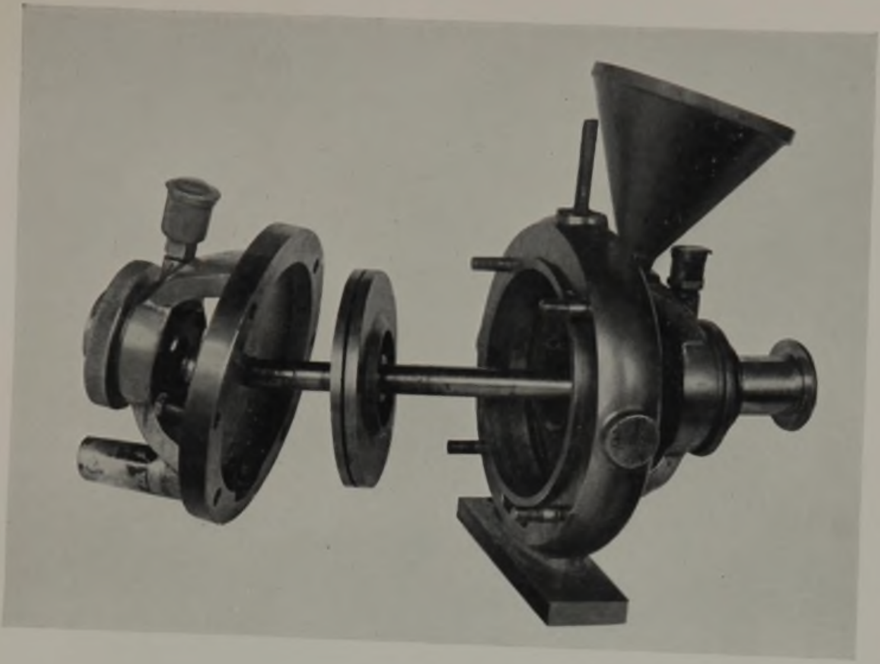

FIG. 1.
HURRELL MILL.

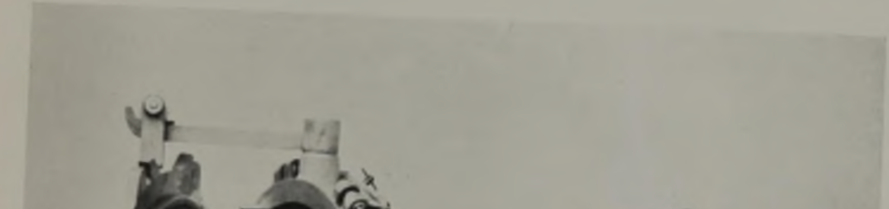

FIG. 2.
PREMIER MILL.

[To face p. 534.

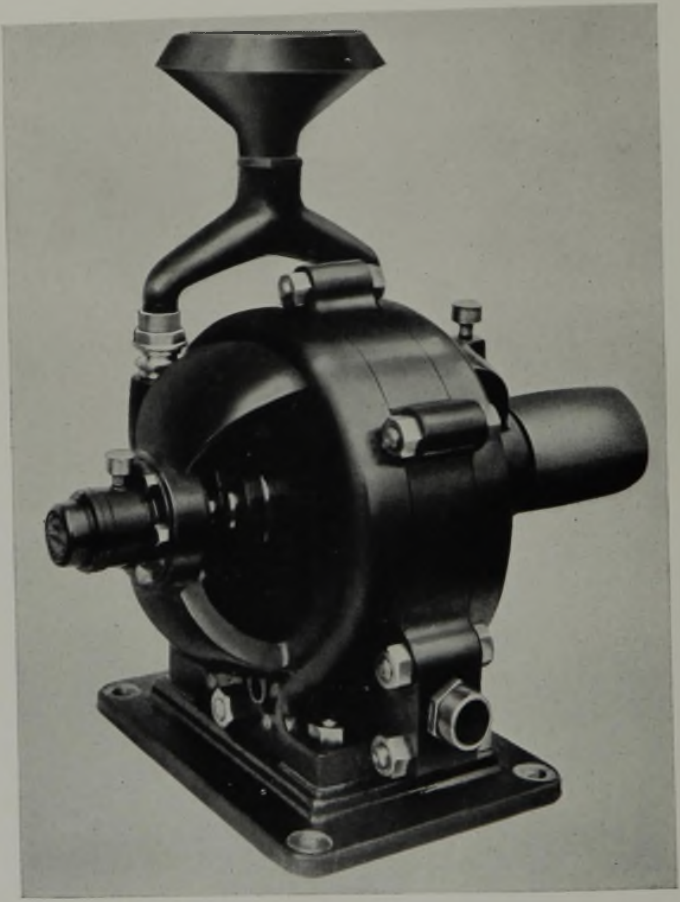

Fig. 3.

HATT-DUSSEK MILL.

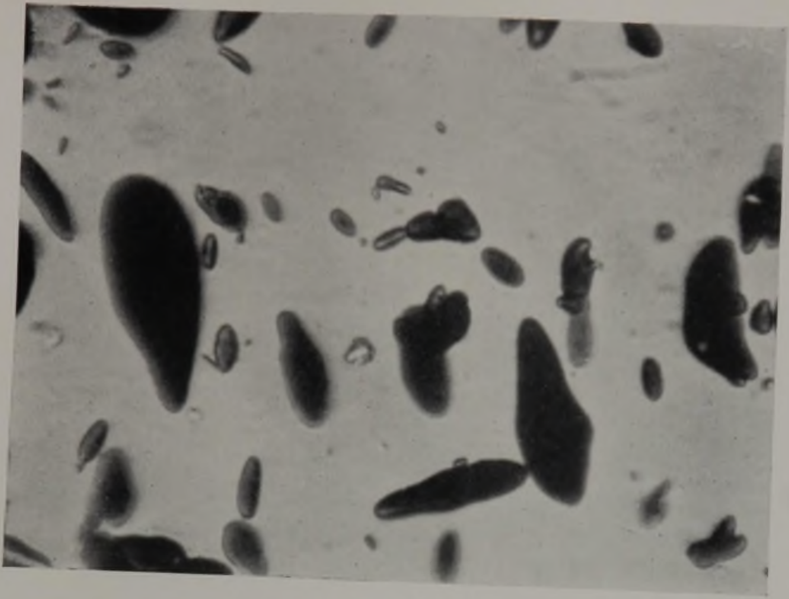

Fig. 10.

PHOTOMICROGRAPH OF TYPICAL INDUSTRIAL STABLE EMULSION, PRODUCED WITH BENTONITE EMULSIFIER. MAGNIFICATION × 900.

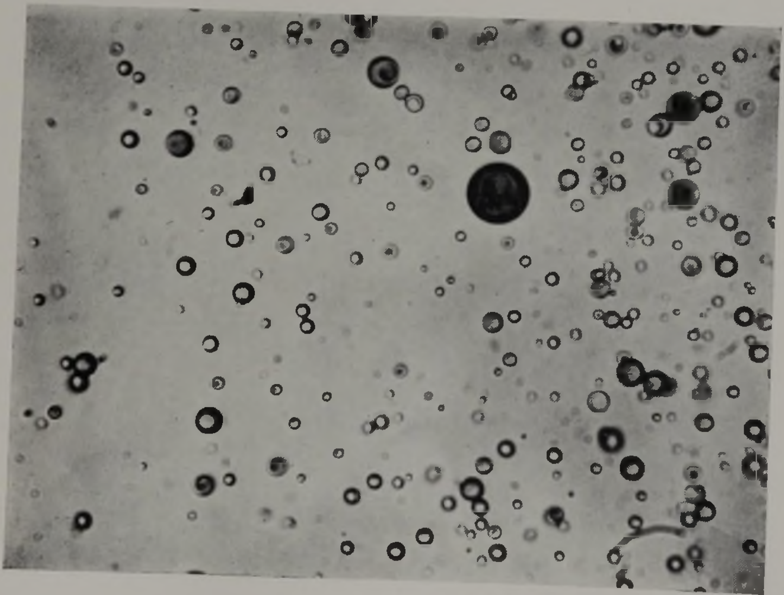

Fig. 11

PHOTOMICROGRAPH OF TYPICAL BITUMINOUS ROAD EMULSION. MAGNIFICATION × 775.

production of improved dispersions or, possibly, as possessing higher rates of throughput than their competitors. In making comparisons of this sort, it is almost always found that the results have been arrived at without adequate control of all the operating factors. It is, of course, quite possible to take a given mill—say the Hurrell—and to open up the gap setting to a figure two to three times greater than normal, and then to show a considerable reduction in power consumption. If, however, the emulsions so made are tested quantitatively for dispersion, it will often be found that, beyond a given critical setting of the gap, the dispersion falls away, so that this must be taken into account in evaluating the effect on power consumption. It will also be found generally that at slower speeds of running the dispersion falls away, so that power consumption in this direction must be considered in the light of the dispersion produced, and the same is true in measuring throughputs.

In the author's experience, the advantages and disadvantages of the various well-known mills are to be found in such points as convenience of layout and adjustment, rather than in any definite positive advantage in either the dispersion produced, the power consumption required, or the rate of throughput maintained.

As regards the influence of gap setting, the following curves are of interest :—

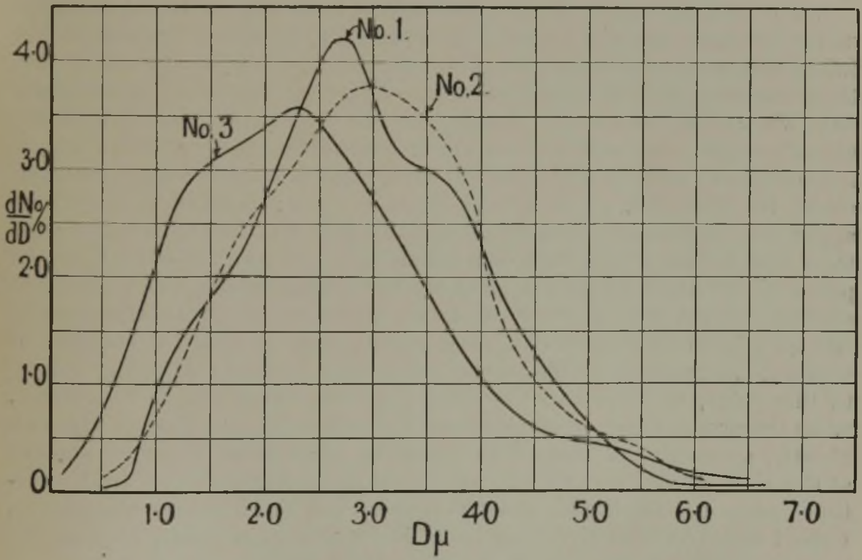

FIG. 4.

Curve No.	1.	2.	3.
Rotor size, in.	12	10	12
Speed, r.p.m.	2992	2986	2990
Gap, in.	0·020	0·014	0·015

Curves 1 and 3 are strictly comparable, being from emulsions made on mills of the same size. Curve 2 is of interest as showing the effect of using a similar mill but fitted with a smaller rotor, running at a similar speed. In other words, we have here the effect of the reduction of peripheral speed due to the smaller rotor. The gap setting is almost identical with that of Curve 3.

RESEARCH DEVELOPMENT.

We have, so far, discussed the development in methods of manufacture from the earliest commercial stages to the present day, and it has been assumed throughout that the product has remained more or less the same. This is, of course, not true, and hand in hand with advances in plant and installation technique, aimed at more convenient and economical operation, there have gone the improvement of plant from the point of view of getting a more meticulous control over the product and, in many cases, of introducing into the formulæ new ingredients and reagents for the production of the emulsion, so that it should possess a different and more definite range of properties in use than could have been contemplated at the beginning, in the absence of much theoretical knowledge of the constitution of the emulsions. It is not an exaggeration to say, in fact, that the progress achieved in the quality of emulsions from, say, 1925 to the present day represents the difference between a usable but rough-and-ready article, and a precision product which is controlled at least as accurately as any other material supplied in similar bulk on the commodity market to-day.

Let us cast our minds back to the state of knowledge of the constitution of the ultimate product in, say, the year 1925, in which the author first joined this particular industry. The first and ever-present problem at that time was as to whether emulsification would proceed normally on any given day. Variations were found, usually, as has been stated, not of a serious extent, almost every few days on which manufacture was carried on and, as a general rule, nothing but empirical explanations for the changes observed could be hazarded. The second problem was: having produced an apparently satisfactory emulsion—and by this was meant nothing more than that it had a lightish-brown colour and could be rubbed out on the palm of the hand to give a good sticky coating which was difficult to remove—would this product, of which there might be anything up to 100 tons in the storage tanks, stay as emulsion, or would it collapse, or would it change from a fluid product to a thick cream? All being well up to this point, we then had the third problem, which was as to whether, when the product arrived on the road, it would break and bind as it should. Finally, although this seemed to be rather in advance of our capabilities at this time, we did wonder why the emulsion, as originally prepared, sometimes came out thick and sometimes came out as of watery consistency. I shall endeavour to give you, in as few words as possible, some of the answers which we subsequently found to these various queries.

To begin with the question of irregular emulsification: at that time we did not know that different types of bitumen were different as regards emulsification. They gave the correct penetration and, within limits, the right melting point and ductility, and, on rare occasions when we estimated the percentage of asphaltenes, no surprises were forthcoming, although we knew that the percentage of asphaltenes varies from one crude to another. None of these tests seemed to furnish any reason for expecting differences in emulsification behaviour. At a comparatively late stage in the development we began to be aware of the importance of the acidic constituents of the bitumen, and this certainly gave us a clue to a good deal of what was happening in the mixer processes. Even to-day, however, as regards the behaviour of a given bitumen under a given emulsification process, we cannot do more than say that it is entirely specific. We may hazard a guess that with a given bitumen a preponderance of a given wax may unfavourably influence its reaction to emulsification, but we are moderately well convinced that if the action is to be traced to such a constituent as wax it is only indirectly so traceable. In the author's laboratory at that time we tried to solve the problem by investigating the emulsification behaviour of large numbers of pure chemical substances.

These were emulsified in a Hurrell mill, using 1·5 per cent. potassium oleate solution. In all cases equal volumes of 1·5 per cent. potassium oleate and the compound in question were passed through the mill and then remilled *once*. The type of emulsion was determined in each case and the dispersion examined qualitatively. The results are summarized in Table I.

The following relationships appear to hold with regard to the compounds given in Table I :—

(*a*) *Benzene* gives an oil-in-water emulsion of fine dispersion and high stability.

TABLE I.

No.	Compound.	Emulsion Type.	Dispersion and Stability.
1	Benzene	O/W	Fine, stable.
2	Toluene	Dual	,, unstable.
3	Xylene	W/O	Medium, stable.
4	Mesitylene	W/O	,, ,,
5	Ethylbenzene	Dual	Similar to toluene.
6	Butylbenzene	Dual	,, ,,
7	Nitrobenzene	O/W	Fine, stable.
8	Nitrotoluene, *o*- and *m*-	O/W	Medium, stable.
9	*p*-Nitro-*m*-xylene	O/W	Fine, stable.
10	2 : 4-Dinitro-*m*-xylene	O/W	,, coagulated on standing.
11	*m*-Nitromesitylene	O/W	,, stable.
12	Chloroform	O/W	Fine, stable.
13	Bromoform	O/W	,, ,,
14	Carbon tetrachloride	W/O	,, ,,
15	Carbon disulphide	W/O	,, ,,
16	Ethyl ether	O/W	,, ,,
17	*n*-Pentane	O/W	Fine, stable.
18	*n*-Hexane	W/O	Medium, stable.
19	*n*-Heptane	W/O	Fine, stable.
20	*cyclo*Hexane	O/W	Fine, stable.
21	*cyclo*Hexanol	O/W	,, ,,
22	*cyclo*Hexyl chloride	O/W	Coarse, unstable.
23	Naphthalene	O/W	Fine, stable.
24	Tetrahydronaphthalene	O/W	,, ,,
25	Diphenyl	O/W	,, ,,
26	Chlorbenzene	O/W	Medium, stable.

(*b*) *The progressive substitution of methyl groups* to give toluene, xylene, and mesitylene causes the emulsion type to change over to water-in-oil, passing through the intermediate stage with toluene, which forms a dual emulsion.

(*c*) *Substitution of other alkyl groups* (nos. 5 and 6) has a similar effect.

(*d*) *The strongly positive nitro-group* leads to oil-in-water emulsions (nos. 7–11), one nitro-group being sufficient to counteract the reversing influence of two or three methyl groups (nos. 9 and 11).

(*e*) *Substitution of halogens* in the benzene (chlorobenzene, etc.) does not alter the emulsion type, but leads to coarser dispersion.

(*f*) *The aliphatic compounds*, nos. 12–16, suggest that the more polar molecules tend to give oil-in-water emulsions.

(*g*) *The homologous series*, nos. 17–19, shows a progressive change in emulsion type and stability with increasing chain-length; long chains tend to give water-in-oil emulsions.

(*h*) *The cyclic compounds*, nos. 20–25, all give oil-in-water emulsions.

(*i*) *Substitution of halogens in the case of cyclic compounds* does not change the emulsion type, but leads to coarse and less stable emulsions than in the case of benzene—compare nos. 22 and 26.

These somewhat general effects of constitution on emulsification, by the process previously described, could not be correlated with surface tension or interfacial tension relationships, and the problem was complicated by the fact that many of the compounds tended to abstract a proportion of fatty acid from the emulsifier solution during emulsification, the latter then becoming alkaline.

Further interesting results were obtained with mixtures of compounds which individually gave opposite types of emulsions. These are shown in Table I*a*.

TABLE I*a*.

No.	Mixture.	Emulsion Type.	Dispersion and Stability.
27	Benzene-xylene, 75 : 25	W/O	Coarse, rather unstable.
28	,, ,, 85 : 15	W/O	,, unstable.
29	,, ,, 96 : 4	O/W	,, ,,
30	Benzene-hexane, 88 : 12	W/O	Coarse, unstable.
31	,, ,, 94 : 6	O/W	,, ,,

(*j*) *Table Ia* shows that an oil giving water-in-oil emulsions has a marked effect when added even in quite small amounts to one giving oil-in-water emulsions. Thus, as little as 4 per cent. of xylene is sufficient to prevent benzene from forming its usual fine oil-in-water emulsion and 15 per cent. of xylene is sufficient to cause reversal. Similar effects occur on adding hexane to benzene.

(*k*) *In Table I* it was seen that the longer-chain aliphatic compounds formed water-in-oil emulsions, and following the indication of (*j*) above, it was thought that aliphatic compounds such as wax might have a marked influence on the emulsifying properties of bitumens. Investi-

> gation showed that up to 10 per cent. of soft paraffin wax could be added to 300 penetration Venezuelan bitumen without appreciably affecting the dispersion obtained on emulsification in the mill with 1·5 per cent. potassium oleate. With 10 per cent. of hard wax (m.pt. 57° C.) the emulsion became definitely coarse, however, and 15 per cent. of the wax caused instability. With higher amounts of soft wax (up to 20 per cent.) rather coarse, but fairly stable emulsions were obtained. These were particularly interesting, since the emulsion particles were irregular in shape, instead of being spherical, presumably owing to crystallization of the wax. The experiments failed to show any correlation between the normal wax contents of bitumens in general use and the emulsification properties of the bitumens.

It will be seen that although these rather vague correlations may perhaps be observed, the specificity of the emulsification phenomenon remains largely where it was. Undoubtedly the substitution of mechanical means of emulsification, such as the colloid mill, does aid in producing emulsion of very regular, sound quality from a wide range of types of bitumen, but it cannot really be said that emulsification properties of a given bitumen can yet be predicted from any series of simple tests, and it should be emphasized that the properties of the given bitumen in one process of emulsification are not necessarily duplicated in any other. This is the fundamental mistake which is being made in certain countries where efforts are being directed to producing a test for emulsification as a guarantee of the suitability of supplies of bitumen for this process. The tests can have value, in the last resort, only if they are made by every process of emulsification used in the country where the bitumen is being supplied. It is not sufficient to emulsify the bitumen under test, say, by passage through a Hurrell mill, and then to imagine that when emulsified by some form of mixer process it is sure to yield equal results.

As a matter of interest on this point, reference should be made to Fig. 5, which shows the size/frequency curve of a typical emulsion of 200 penetration Mexican bitumen, with a similar curve derived from the same type of bitumen, but using a variant of the Montgomerie process, with a slow-stirring mixer.

It will be seen that although the two curves show variations of shape and uniformity, there is no striking difference in the general dispersion.

Let us now turn briefly to the second problem which engages the manufacturer of bituminous emulsions : to wit the storage stability of his product. Having got the emulsion into the storage tank, it may change its state, due to two fundamental processes : first, simple sedimentation, and secondly, some process of flocculation, which may eventually lead to complete coagulation of the disperse phase.

Taking the second alternative first, as being the less usual, it can be said that complete coagulation of an emulsion of bitumen, known to be capable of successful emulsification, must always be due to some error in the type or concentration of emulsifier used or to some mechanical fault in the process. A reservation has to be made on this observation, regarding the known susceptibility of the bitumen to emulsification, because there are certain physical and chemical characteristics of certain types of bitumen which preclude their emulsification or preclude the storage stability of their emulsions, once formed. I need only mention, in this connection, the influence of high specific gravity of the bitumen. We shall consider the normal effect of the difference in specific gravity of the bitumen, and that of the aqueous phase, when we come to sedimentation, but for the moment I would refer to a bitumen having a really high specific gravity—say 1·06 or over. It is found that with such bitumens, unless some step can be taken to raise the specific gravity of the aqueous phase, so reducing the difference in specific gravity between the two phases, ready coagulation of the disperse phase will be experienced. This seems to be due to the fact that not only is the initial sedimentation heavy, but when packing to a dense

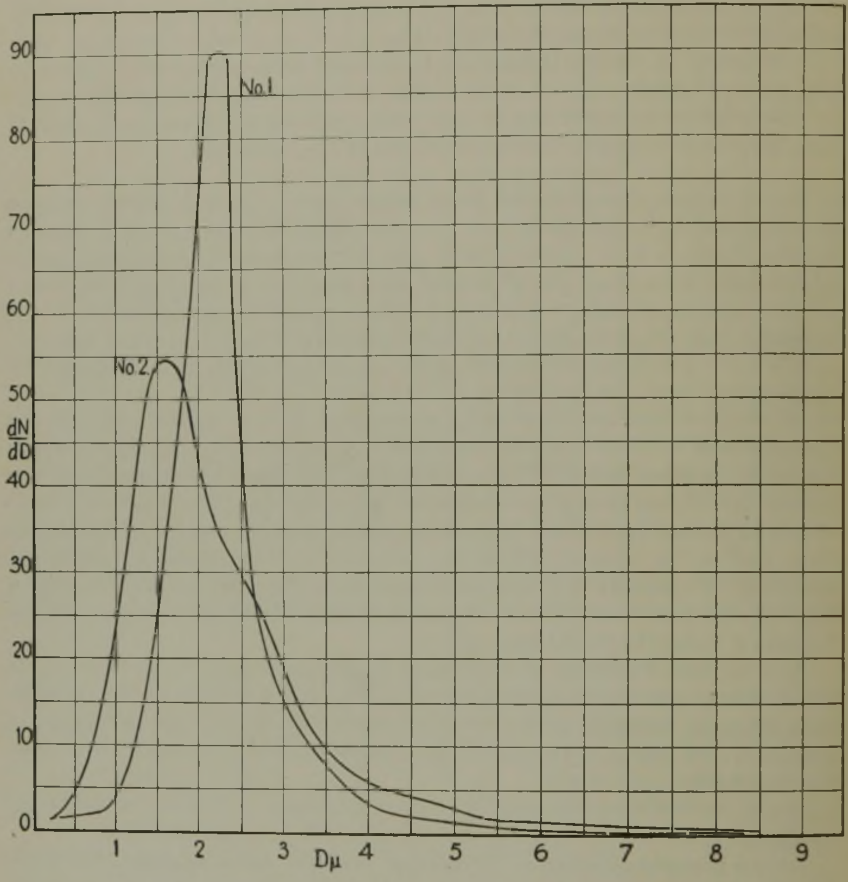

FIG. 5.

SIZE/FREQUENCY CURVES OF MONTGOMERIE AND MILL EMULSIONS OF 200 PENETRATION MEXICAN BITUMEN.

Curve No. 1. Montgomerie emulsion, laboratory mixer.
Curve No. 2. Mill emulsion (1% sodium oleate), laboratory mill.

formation of particles occurs at the bottom of the sedimenting column of liquid, there is always a very high pressure developed at the points of contact between superposed spheres of bitumen. This high pressure naturally tends to force out the adsorbed film of emulsifier, which keeps the particles from coalescing normally, so that the greater the pressure so exerted, the more likely becomes the coalescence of the particles in contact. It is, in fact, very well marked in various types of bitumen which have been investigated.

It is also possible to get this coagulation of the emulsion in the case of very concentrated emulsions—say with a bitumen content of more than 70–75 per cent., when the particles of the emulsion become so tightly packed that they commence to deform in the bulk of emulsion, merely due to the contact pressures between them. It is not infrequent to find the whole system set up to a sort of gel, which is not able to disperse again, except by re-submission to the emulsification process.

As has been said, however, these cases of coagulation are rather rare in the case of bitumens normally found satisfactory for emulsification.

The second type of phenomenon which may occur in storage is, as has been stated, simple sedimentation. The factors governing sedimentation are normally given, in the somewhat loose way common to text-books, as those entering into Stokes' Law, as follows :—

$$6\pi\eta r v = \tfrac{4}{3}\pi r^3(d_1 - d_2)g$$

where η = the viscosity of the aqueous phase.
r = radius of the falling particle.
v = velocity of the fall of the particle.
d_1 = density of the particle.
d_2 = density of the aqueous phase.
g = gravitational constant.

In fact, however, Stokes' Law cannot be directly applied to common bituminous emulsions in the ordinary sense. The reason for this is that Stokes' Law presupposes that the particles of disperse phase are free to fall through the continuous medium uninfluenced by each other or, of course, the walls of the vessel. In the case of an emulsion with a concentration of disperse phase over about 50 per cent. by volume, there can be no question of free fall of the particles, and, in fact, investigations of what really happens in a sedimenting column of emulsion of this concentration show that the phenomena are rather complicated. What happens is that the whole bulk of the particles tends to fall together, or, as it might alternatively be expressed, the continuous medium tends to slip through the mass of particles and to come to the surface. The mass of particles concentrates towards the bottom with gradual packing of the various sizes into the closest spontaneous arrangement. After a little while, therefore, you get in the sedimenting column a thin layer of more or less pure aqueous phase and, below that, a layer of almost constant concentration, as we go downwards, of all sizes of particles, with the proportion of large ones tending to become greater towards the bottom, and finally a packed layer of particles at the bottom. The following curve was determined for an emulsion of Texas bitumen in 1·5 per cent. potassium oleate, allowed to sediment in a cylindrical column 80 cm. in height, 4 cm. in diameter. It shows the *disperse phase* concentration at varying heights; owing to the high water absorption of the bitumen, it would not have been satisfactory to plot bitumen content against height.

From the practical point of view, this can be overcome by arranging that the storage tanks shall have fitted to them a pipe system, which enables the contents to be circulated by pumping at regular intervals. In this way the bottom packed layer can be re-distributed in the more rarefied emulsion at the top of the column, before it is so tightly packed that it can no longer be handled.

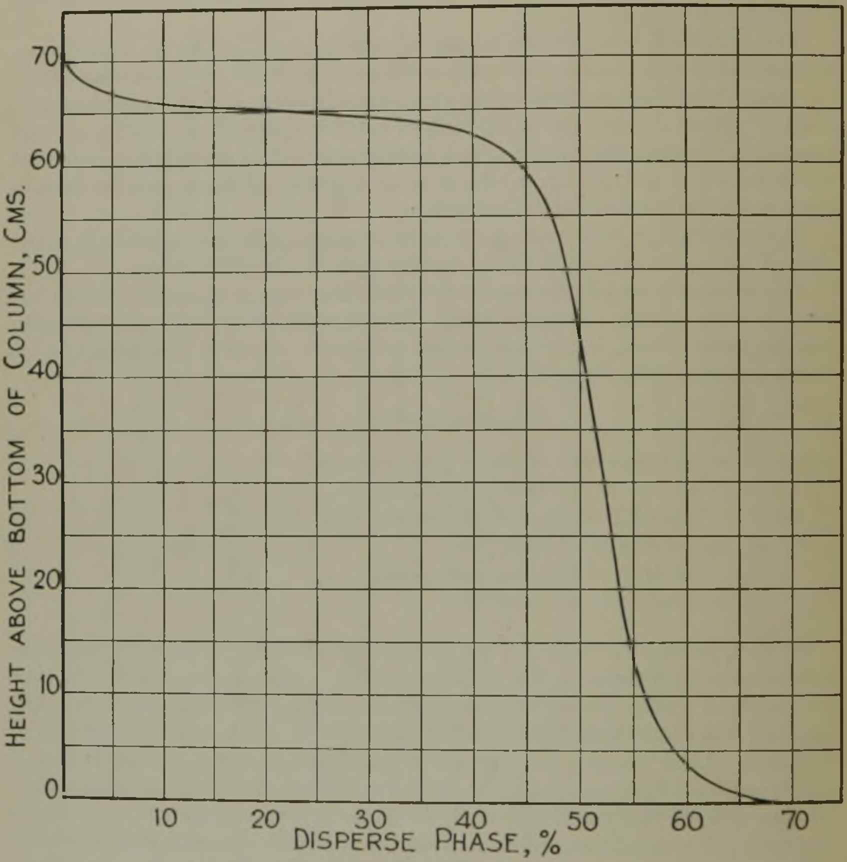

FIG. 6.

SEDIMENTATION OF CYLINDRICAL COLUMN OF EMULSION—DISPERSE PHASE CONCENTRATION AT DIFFERENT HEIGHTS ABOVE THE BASE.

If the emulsion has been decanted off into drums or other containers, then the only means available are the stirring or rolling of the containers. It is when the question of stirring a sedimented container of emulsion arises that we come across some of the most interesting phenomena in the packing of particles. With certain types of emulsion the sediment at the bottom acquires most peculiar properties and, in particular, it is possible to show, with certain stable emulsions, a very pronounced " paste effect ", which is sometimes inaccurately referred to as anti-thixotropy. If the sediment is separated out and poured gently from one container to another, it appears to have the consistency of a very thick cream. If, however, an attempt is made to pour it quickly, it sets solid and will not leave the first container. It is also possible to take this apparently fluid sediment and to subject it to a sharp shearing force, when it will set solid : as, for instance, when a glass rod is jammed into a beaker containing the sediment. The reason for this behaviour lies, probably, in the changes of the configuration of packing which occur when the spontaneous arrangement of the particles is disturbed ; it bears a relation to the effect observed when wet sand is displaced on the sea-shore, and is undoubtedly connected with the phenomen of dilatation. The practical significance of this is that, with the types of emulsion which show this behaviour at its most marked, it may become virtually impossible to stir up a sediment which has accumulated over any length of time. Certain emulsions made with protein emulsifiers show this behaviour very strongly, and it is, in fact, frequently experienced when these emulsions are returned by the customer as containing lumps of coagulated bitumen, that, in fact, the lumps or bitumen layer in such cases may consist of very heavily sedimented emulsion, which can only be re-dispersed with great care. With the normal soap-type emulsions used for the bulk of the work, however, the sediment may, in certain circumstances, become rather stiff for manipulation, but generally it is possible to re-distribute it by stirring or rolling.

The next problem which we always have before us is the question of the road performance of the emulsion. At this stage we confine the discussion to road emulsions, but it should be understood that most of the physical properties so far described are possessed in various degrees by all types of emulsion with a bituminous base, even though designed for other purposes, and later on it is proposed to devote a few remarks to these special emulsions.

In the early days of emulsion manufacture it was assumed that once a satisfactory emulsion had been made, its road performance would be equally satisfactory, and it took quite a little while to appreciate that an emulsion which is good *qua* stability and dispersion may be quite unsuitable for the purpose for which it is designed. It was not realized by what process the emulsion actually set on the road, and there was much talk of emulsions " throwing off " their water, as if the process were an active operation on the part of the emulsion, rather than a passive submission to various factors bringing about setting. In fact, of course, an emulsion does not throw off its water : the water leaves the disperse phase by a series of perfectly familiar physical and chemical processes. In recent years these have been investigated in great detail, and our understanding of the processes of breakdown of emulsions, though still incomplete, enables us to get a very good picture of what happens. The mechanism of break of emulsion may be divided into three main headings :—

1. Evaporation.
2. Chemical Coagulation.
3. Capillary Effects.

1. *Evaporation.*

Generally speaking, in road work or, for that matter, in most industrial applications of emulsions, the bulk of the water is lost by evaporation pure and simple. This evaporation follows very much the same laws as the evaporation of water from a free surface, and it can be seen by reference to Fig. 7 that over quite a range of emulsions, the initial rates of loss of water by evaporation, under constant external conditions, are the same. At a later time in the setting of the emulsion a point is reached at which a sudden change comes over the rate of evaporation, due to the inhibiting effect of the residual magma of bitumen. The point at which this occurs differs to quite

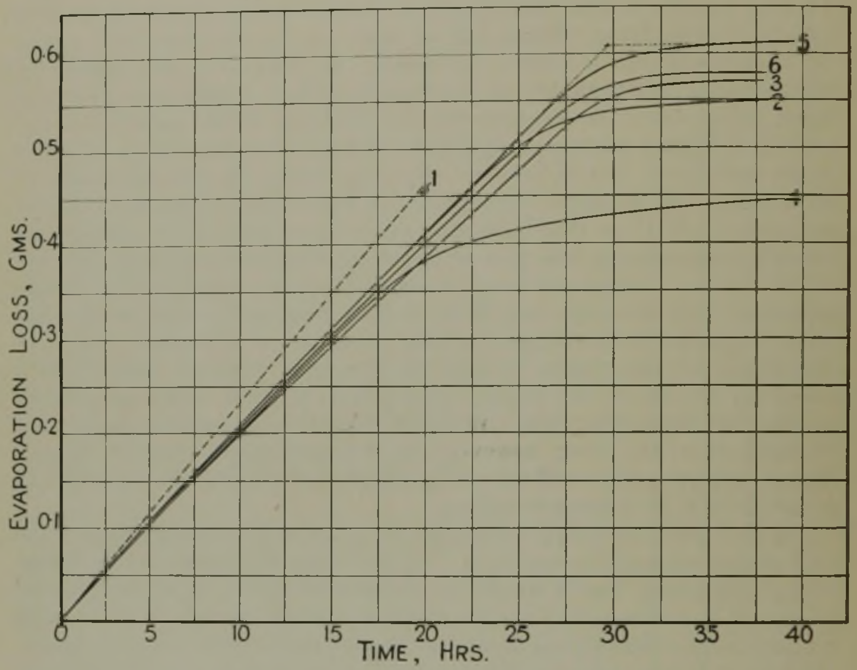

Fig. 7.

INITIAL RATE OF EVAPORATION FROM EMULSIONS.

(Loss in weight *v.* drying time.)

(Film area = 12·9 cm. Temperature = 21·5° C. Relative humidity = 80 per cent.)

Curve No. 1. Distilled water.
,, 2. Labile emulsion A.
,, 3. ,, ,, B.
,, 4. ,, ,, C.
,, 5. Semi-stable emulsion.
,, 6. Stable emulsion.

Note that all the emulsions lose water at a slightly lower rate than distilled water, owing to the dissolved solids in the aqueous phase. The effect is particularly marked in the case of Labile emulsion C which contained an exceptionally high percentage of electrolyte. The initial rates of evaporation are constant for about twenty hours.

a considerable extent among different emulsions, and this is exemplified in Fig. 8.

It is interesting that the position where this rapid change takes place has been proposed as a fundamental characteristic of road emulsions by the Société Chimique de la Route in France. There are several objections which can be made to the employment of this characteristic as a guide to performance, but there is no doubt that it has its theoretical interest.

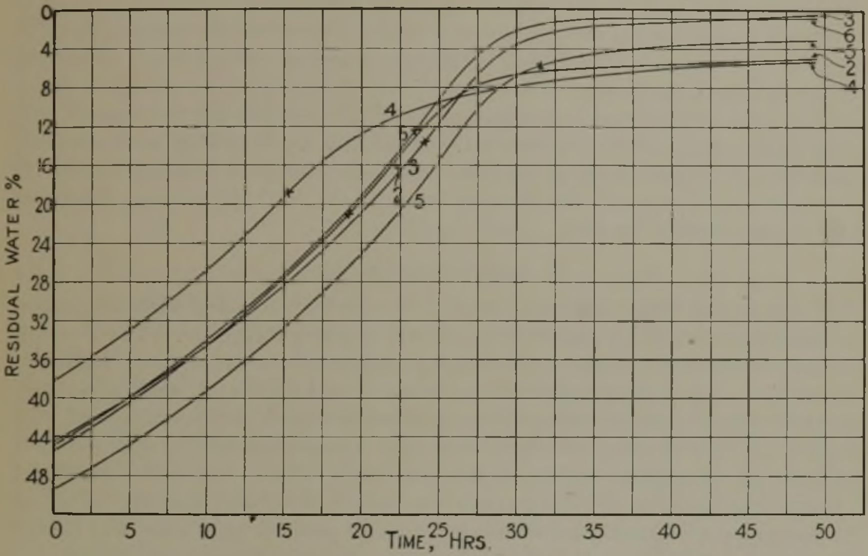

Fig. 8.

EVAPORATION OF WATER FROM EMULSIONS.

(Residual water content *v.* drying time.)

(Film thickness = 1 mm. Temperature = 21·5° C.
Relative humidity = 80 per cent.)

Curve No. 2. Labile emulsion A. Lability = 21·3.
,, 3. ,, ,, B. Lability = 13·7.
,, 4. ,, ,, C. Lability = 18·8.
,, 5. Semi-stable emulsion. Lability = 6·8.
,, 6. Stable emulsion. Lability = 12·6.

Curves show *percentage residual water content* plotted against drying time. Conditions as above.

Note that the initial evaporation when plotted in this way is not linear, but slightly convex to the time axis.

In actual road work, however, it is uncommon for the evaporation of the water to be able to proceed in a quiescent manner. Normally the application of the emulsion is followed by the scattering of stone chips over it, and these are then rolled, or possibly immediately opened to the passage of traffic. In any case, the application of the chips themselves and the action of passing vehicles, or of the roller, are sufficient to disturb the evaporating film mechanically. This has been found to produce an interesting effect on the point at which the bituminous magma ceases to be a collection of packed, isolated particles and commences to assume the properties of adhesive bitumen. This point, of course, is usually referred to as the point of break of the emulsion. It does not mean the point at which an anhydrous film of bitumen is obtained—and different emulsions yield bitumens which commence to show adhesive properties at different residual water contents—but, generally speaking, there is a fairly considerable amount of water remaining in the film at the point at which the normal bulk properties of bitumen begin to be manifested. The point at which a substantial coagulation of the bitumen is first observed under conditions of mechanical disturbance may be called the "Lability Point." We shall discuss this further later in the paper. The effect of the mechanical disturbance, to which reference has been made, is to produce coagulation at an earlier stage: that is, at a greater residual water content than would be the case if the evaporation were entirely quiescent. Referring back to Fig. 8, the points marked with crosses show the lability points for the emulsions the curves of quiescent evaporation of which have been traced, and the relation between the two can readily be seen.

2. *Chemical Coagulation*

In the normal use of the emulsion it comes into contact with the stone surface of the road and also with the newly applied chippings. These stone surfaces are found to exert a breaking influence on the emulsion. In other words, if a chip is suspended in emulsion, it will be found, after a certain lapse of time, that a coating of coagulated bitumen is present round the stone. It was at first thought that this phenomenon was due to the presence of coagulating substances in the stone, such as lime salts or soluble calcium compounds. Investigation has shown, however, that the effect is by no means so simple, and what really takes place is that soap and alkali are adsorbed on to the surface of the stone. In this connection it should be realized that although most stones do not possess any marked porosity in the ordinary sense, they do undoubtedly possess a micro-porous structure, and, therefore, the extent of the coagulating surface of the stone may be very much greater than the mere external surface presented to the eye. Stones vary greatly in their power to coagulate given emulsions, and, what is more, if a series of emulsions is placed in a certain order of stability, when submitted to the coagulating action of a given stone, it will frequently

Table II.

Aggregate.	Percentage of Bitumen Coagulated.		
	Types of Emulsion :		
	Labile.	Semi-stable.	Stable.
Arnold's limestone	8·4	5·5	1·7
Mountsorrel granite	9·0	4·2	1·8
Craig yr Hesg Sandstone	25·3	10·9	2·3
Llandebie Limestone	4·1	—	—
Alderney Granite	10·6	—	—
Wickwar Limestone	15·0	—	—
Forest Rock Granite	16·5	—	—
Llanbedrog Granite	20·7	—	—

be found that by substituting another stone, even when it is of similar general reactivity, the emulsions are frequently placed in quite a different order of stability. The effect, therefore, is quite specific, and may be due to a combination of the chemical nature and reactivity intrinsic to the given stone surface and the dimensions and extent of the micro-pores. Table II shows typical coagulations with emulsions belonging to the three main categories—labile, semi-stable, and stable—with a variety of British road stones.

It will be noted that the variations in coagulative power of the different aggregates are so great that the range of coagulations produced, as between the labile surface-dressing-type emulsion and the semi-stable emulsions which are normally prepared with much higher concentrations of soap, overlap. This is not so evident with the results with stable emulsions, which are not normally affected to anything like the same extent by the stone, and may, in general, be said to be almost completely immune to this coagulating effect.

3. *Capillary Effects.*

This factor was, at one time, thought to be very much more important than is now held to be the case. It will readily be recalled how, in earlier days, the so-called filter-paper test was used as a guarantee of quality of road emulsions. This test was supposed to demonstrate the rate of break of the emulsion; in fact, of course, it did nothing of the kind. All that happens when a drop of emulsion is exposed on filter paper, at any rate for the first five or ten minutes, is that a certain amount of aqueous phase passes out from the central drop into the pores of the paper, due to the capillary forces acting in the fine capillaries. This effect is duplicated, to a certain extent, on the surface of the road, as many road surfaces are either directly porous, as in the case of water-bound roads, or contain a percentage of dust or other fine material, which serves as a species of blotting-paper for the aqueous phase of the emulsion. As a means of reducing the water content, porosity is very much on an equal footing with quiescent evaporation; it separates the water, and the residual bitumen assumes its adhesive state at a time dependent on the characteristics of the original emulsion and on the presence or absence of mechanical disturbance. There is this difference in theory: when the water separates, due to porosity, it carries with it the emulsifying agent, whereas when it evaporates, the emulsifying agent is left behind, and in most cases will cause some retardation in the appearance of coagulation. It is interesting, from the point of view of road construction with emulsions, to discuss the relative importance of the three different main influences which have been enumerated. The problem is, however, very complex, because the rate of evaporation depends on many circumstances, but, in the first place, on the ambient temperature and on the wind velocity at the road surface. Secondly, the degree of mechanical disturbance can never be predicted, and this in turn will have an influence on the rate of coagulation, due to the mechanical disturbance factor. The degree of coagulation due to the stone aggregate depends, of course, on the type of stone, the specific stability of the emulsion to that stone, and, as a practical factor of great importance, on the amount of stone and the amount of surface of that stone exposed to unit quantity of emulsion on the road.

In general, however, an analysis of the normal incidence of these factors leads to the conclusion that the first factor, sometimes referred to as the lability factor, is normally at least as important as the chemical factor, and the porosity factor, in these days of re-treatment of already bituminized roads, is of subsidiary importance. In cases of favourable weather conditions it is easy to see that the lability factor may have an altogether preponderatingly important rôle in producing the final result.

Viscosity of Emulsions.

When allusion was made to the early difficulties encountered, due to a change of bitumen type, it was indicated that one of the chief difficulties introduced with the new type of emulsion was its lower viscosity. At that time there had been small opportunity of giving detailed attention to the influence of the viscosity of the emulsion on its road performance, but a little fundamental thinking soon rendered it evident that this was, in fact, a very important characteristic. Normally, the road surface has a certain camber, and this causes any fluid liquid applied to the crown to tend to run down into the gutters. The less viscous the liquid, the more chance it will have to run away off the effective road surface, before it is covered with chippings or otherwise prevented from doing so. Furthermore, if the emulsion is too viscous, the minimum quantity which can be applied to a given unit of area is reduced and, therefore, its covering capacity may easily overstep that quantity which corresponds to the amount of bitumen necessary to bind the chippings without the presence of excess. Excess, of course, manifests itself sooner or later, by the fatting up of the surface, due to the rise of the bitumen under the pressure of the traffic, until it partly or completely engulfs the stone, which should form the running surface.

Viscosity control, therefore, is obviously important. Once this point had been reached, the next step was evidently to produce emulsions of a range of viscosity found by experience to be the best, as being the mean between the two undesirable consistencies mentioned above. The precise value of this mean is, of course, a matter of opinion, but there is a good deal of experience to show that for normal working in British conditions, and especially in this connection, when used as a surface-dressing emulsion, the figure should lie between 10° and 12° Engler at 20° C. A good deal, however, depends on the precise technique adopted by the workmen responsible for using the emulsion, and a gang trained to use a thinner emulsion could probably produce a good result with an emulsion of 5–6° Engler. Nevertheless, in the view of the author, 10–12° Engler constitutes the best general range to adopt.

It was known at an early stage in the manufacture of emulsions that the most straightforward way of producing emulsions of greater viscosity was to increase the bitumen content. The way in which viscosity rises with increasing bitumen content is shown in Fig. 9, curve 1. It will be seen, in particular, that above a bitumen content of 55 per cent. or so, the slope of the curves rises steeply and, in other words, above this figure great increases in viscosity result from small increases in bitumen content.

However, it was not possible to consider a variation in bitumen content as a final solution of the problem of producing emulsions of varying viscosity, because if any degree of precision is to be obtained in apportioning the quantity of emulsions used to the area of road treated, it is necessary to have an emulsion of standard bitumen content. The problem was, therefore, a rather more difficult one to solve : that is, the increase or decrease in viscosity had to be produced at a given bitumen content. In order to solve this problem, research work was done to trace the origin of the variations in viscosity at given bitumen contents, found in passing from one type of bitumen to another.

In curve 2 it will be seen that the slope is more gradual and, further, that at any given bitumen content the actual viscosity is lower. At first it was thought that the differences experienced might have something to do with the amount of soap adsorbed from the aqueous phase on to the surface of the particles. When, however, careful measurements were made of the concentration of soap in the bulk aqueous phase, and from these a computation made of the amount adsorbed, a striking fact was found in the case of Mexican bitumen emulsion : the concentration of soap in the bulk aqueous phase was actually higher than the original concentration employed, and not lower, as would have been expected, had any considerable quantity of soap been adsorbed. This was true for emulsions made with both sodium and potassium soap. The actual concentrations found are shown in Table III.

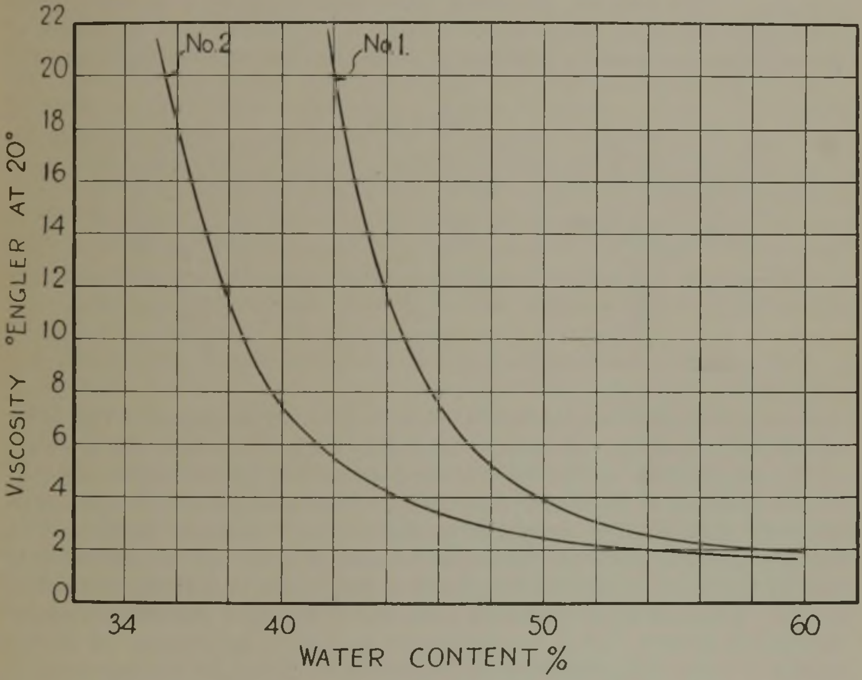

FIG. 9.

VISCOSITY/WATER CONTENT—CURVES OF EMULSIONS.

Curve No. 1. Water absorption = 24 per cent.
,, 2. Water absorption = 12 per cent.

What was the explanation of this? It at once leapt to the mind that in some way or another, as it was impossible for more soap to be present than was actually put in, the converse must be true and, in fact, a certain proportion of water had somehow become fixed, so that it did not function as part of the bulk aqueous phase. A lengthy series of experiments was carried out, which cannot be recorded here in detail, which resulted in the fact that this water was fixed by occlusion in the bitumen particles, and we finally succeeded in showing that this occlusion seemed to be, at any rate as a first observation, the result of the establishment of an osmotic equilibrium between the soap and electrolyte solution constituting the final bulk aqueous phase and the solution contained in the interior of the bitumen particles. This solution, therefore, must have acquired a certain content of osmotically active substances. Finally it was shown that the source of these substances was the presence of a minute amount of micro-crystals of various water-soluble salts in the original bitumen employed. The effect of these micro-crystals of electrolyte (mainly sodium chloride) was to set up, as it were, a rather special type of semi-permeable membrane, constituted by the bitumen of the disperse particles. This semi-permeable membrane must be distinguished clearly from the ordinary Donnan membrane, in that, whilst the latter is permeable to certain ions, but impermeable to others, the present type of membrane is permeable to solvent, but not to solute. Bitumen is, of course, in bulk, one of the most water-impermeable substances known, but it can be shown that films of bitumen of minute thickness—say of the order one to two microns—do exhibit the permeability to water necessary to account for the establishment of this type of osmotic equilibrium.

Table III.

Soap Concentration.	Soap Concentration in Aqueous Phase.	
Initial Emulsifier, % wt.	Sodium Oleate, % wt.	Potassium Oleate, % wt.
1·05	1·13	1·26
1·53	1·63	1·68
2·07	2·21	2·20

We have, therefore, as the result of this work, the fact that the viscosity of this particular type of disperse system is governed mainly by the volume concentration of disperse phase. The difference between an emulsion of one type of bitumen and an equally concentrated emulsion of another type of bitumen, having a higher viscosity, is simply that the more viscous emulsion actually possesses a higher content by volume of disperse phase than the less viscous emulsion, this being due to greater swelling of the bitumen particles in the case of the more viscous emulsion, owing to the presence of water in the interior of the particles, due to the osmotic equilibrium.

Hatschek, in 1911, developed the following formula governing the viscosity of disperse systems ;

$$\eta s = \frac{\eta}{1 - (\phi)^{\frac{1}{3}}}$$

where ηs = viscosity of the disperse system.
η = viscosity of continuous phase.
ϕ = fraction of total volume occupied by disperse phase, where ϕ is assumed to be greater than 0·5.

Sibree and others have subsequently shown that if ϕ is substituted by $h\phi$, where h is a numerical constant for a given type of dispersion, this formula gives a good approximation to the observed results in many different kinds of systems. (In typical bitumen emulsions h shows values of the order of 1·3–1·6.)

Now that the phenomenon of water absorption has been demonstrated in bituminous emulsions of this type, it is possible to bring them into line with the Hatschek expression by interpolating the known percentage of water absorption to get the true percentage volume of disperse phase and, further, by interpolating a numerical factor $h = 1{\cdot}4$ or thereabouts, as has to be done with other types of disperse systems, when using the Hatschek equation. Subject, therefore, to the significance of this factor h being unravelled, it may be said that the Hatschek expression does give a good approximation to the viscosity of disperse systems, even though the viscosity of the disperse phase in these systems may vary from that of air, in the case of Sibree's froths, through that of liquid paraffin to that of the normally high viscosity of asphaltic bitumen of 200 penetration, or even higher.

Subsequently, this discovery has been used to work out a system whereby a bitumen deficient in water-soluble constituents capable of giving these viscosity increasing effects may have this deficiency rectified by the addition of further quantities of suitably dispersed electrolyte, and thus any bitumen may be treated to produce emulsions of any reasonable viscosity, at a chosen bitumen content. This principle has now been used in practice in the production of many thousands of tons of emulsion all over the world, and may be said to be a very typical example of the value of research, originally undertaken from a more or less abstract point of view, in developing an asset of considerable importance to the industry as a whole.

APPLICATIONS OF EMULSIONS.

Having surveyed some of the technical developments which have taken place in the technology of emulsions themselves (and it should here be emphasized that these are merely one or two typical examples of the increase in our knowledge since the early days of the industry), it is now proposed to indicate the manner in which the use of emulsions has developed during the same period.

It was made clear at the beginning that the first idea was to use these products as dust-laying compounds, and from this developed their use as surface-dressing binders. At the time that this development was taking place, grouting of packed stone courses with hot bitumen was a very common procedure, and yielded excellent results in the majority of cases. Here again, however, the difficulty of controlling the exact viscosity of the heated bitumen and of combating the chilling effect when the bitumen touched the road-stone led to difficulties of manipulation. When bitumen emulsion became available, its great fluidity at once indicated it as a product which might be very well employed for the grouting or penetration process. Various adjustments of the working specifications had to be devised to ensure that penetration of the emulsion, while adequate, did not proceed to such an extent that it was able to run out underneath the layer of packed stone, and thus be wasted. This was, of course, achieved by placing a layer of sand below the stone and, in some cases, of working it up as a slurry between the stone, by rolling. A more economical form of grout was devised, usually known as semi-grout, which employed this slurry of sand in such a way that it filled approximately half the depth of the packed-stone layer, the emulsion being used for the remainder.

These processes—grouting and semi-grouting—continue to find employment, even to this day, and although supplanted on many of our main roads by still heavier constructions, due to the high demand of traffic in recent years, grouting and semi-grouting still form a very important item in those countries where the road system is being developed, in particular in some of the British Colonies.

When these processes had become established, a further development of the market took the form of an increased use of cutback bitumens, which, to a certain extent, supplanted emulsion in the form of coated stone carpets. Then, at a later period, these relatively coarse stone carpets were produced with finer gradings, and we now have quite a demand for what are known as fine carpets. These are materials of varying composition, but all adapted to present a final running surface with either a sand-paper texture or, in some cases, with a texture a little rougher than this.

Manufacturers of emulsion, therefore, began to look round for methods of entering into this market, and emulsions were developed, in the first place, for purposes of mixing, in suitable forms of mixer, with graded stone aggregates, to yield carpets similar to those prepared with cutback bitumens. It is rather curious that these carpets have never found any great application in Great Britain, but in other countries, notably in Germany and also, to a certain extent, in the United States of America and Canada, premix carpets and carpets mixed *in situ* on the road surface have developed to a large extent, and sales of emulsion for this type of work have extended greatly.

These emulsions are, of course, usually of the semi-stable type and, although similar in general properties to the labile emulsions which are used for surface dressing and grouting, have higher concentrations of emulsifier, usually of the soap type, and are thus adapted to the greater mechanical strains imposed upon them in the mixing operations.

Another type of emulsion which has more recently come to the fore, in connection with carpet construction, is a special type adapted for use as the tack coat which is normally applied to cause the fine carpet to adhere to the existing surface of the road, and to defeat any tendency there may be for the carpet to push under the roller or traffic. The problem in designing a tack-coat emulsion is that it should be capable of being brushed out to a very high rate of coverage without coagulating under the broom. This implies, of course, a certain amount of mechanical stability, which, however, must not be excessive, or the emulsion will not break quickly enough in unfavourable weather conditions to permit of the superposition of the carpet.

These two types of emulsion, however, have to yield pride of place, in the importance of the quantities sold, to what is known as the stable type of emulsion. These emulsions are so prepared that they have very high stability to mixing with stone aggregates and usually, though not necessarily, there is associated with this high mixing stability a high chemical stability. They can, in fact, be mixed with acids and electrolytes in moderate concentrations, without exhibiting coagulation. The great stability in mixing is used so that they may be incorporated with aggregates consisting largely of fine material. It is possible, for instance, to mix such emulsions, under suitable conditions, with soils, fine sands, fillers, or even with Portland cement. These emulsions first appeared on the market about 1928, and were used during that year for the preparation of soil/bitumen carpets on footpaths, playgrounds, and light-traffic surfaces. It is interesting to note that, even at that date, a considerable area of this type of mix was constructed at Croydon Aerodrome, and that this remained in position for quite a few years, until alterations in the airport caused the carpet to be abandoned. More recently this type of work, in which the natural soil, whatever it may be, is mixed with emulsions, with a view to producing a low-cost bituminized layer, which may form either the actual running carpet, when reinforced with a suitable anti-attrition layer, or, alternatively, may be used as the sub-foundation of a normal road construction, has come to the fore very much in this country, more particularly under the name of "soil stabilization." Actually, a good deal of confusion has, in the opinion of the author, been created by the indiscriminate use of this term, as between this form of bituminous mixture and the more general work on the study of soils, which has been carried out by Terzaghi, Hogentogler, and others. This work is largely devoted to analysing the characteristics of soils and to classifying them into various types, so that methods may be deduced whereby they can be rendered more suitable for supporting the actual running-carpet construction, which forms the useful surface of the road. These ideas may, of course, be applied quite generally, and the load to be supported need not be a traffic load at all, but a standing load, such as the weight of a building or other construction.

Now, one of the problems which has engaged the attention of these research workers on the stabilization of soil is the fact that only a certain number of soils are capable of sustaining any considerable load when exposed to the infiltration of water. Many of these soils are perfectly suitable at low water contents, but if more than a certain quantity of water is allowed to reach them, their bearing capacity falls sharply. If, therefore, means can be found to reduce the rate of infiltration of the water, certain soils, which otherwise would be unsuitable for employment to carry loads, except in the best drainage conditions, become more suitable, and this waterproofing effect may be obtained by using bituminous emulsion of high stability and mixing it with the soil. This is the proper employment of the term "bituminous soil stabilization."

Most of the work, however, which has been done in this country, and even in the United States, where the idea has received wide application, is not, strictly speaking, of this type at all, but consists in the employment of the soil as it is, or with the admixture of locally obtainable cheap aggregates, to produce a low-cost carpet, which has only to be finished with a stone surface layer, to be able to withstand at any rate light traffic. This type of work is better referred to, for the sake of clarity, simply as " soil mix."

The present paper is not one in which the difficulties met with in the use of bituminous emulsion and soil can be discussed in detail, and for the moment all that need be said in this connection is that, in order to ensure a homogeneous mix of the stable emulsion with the fine aggregate, it is necessary to work in the presence of sufficient moisture to give the mixture a fairly damp consistency, as otherwise, even with these very stable emulsions, a certain amount of coagulation occurs, due to the intensive shearing of the disperse bitumen particles by the rubbing action of the aggregate particles in the mixing operation. It is, therefore, the practice to add water either to the emulsion or to the soil or to both, so that the final mix has a consistency such that, when tamped lightly, there is a just perceptible separation of water on the surface. If more water than this is present, no great harm is done from the coagulation point of view, but there is obviously the risk that dilute emulsion will drain away from the mix with the excess of water.

It is really quite surprising what can be done with suitable types of soil and very low final percentages of bitumen, when incorporated by the use of stable emulsions. With an aggregate, for instance, of the grading shown in Table IV, a mix completely stable to prolonged immersion in water may be obtained, with the use of only 3 per cent. of bitumen. In actual fact, a portion of such a mix has been allowed to soak in the author's laboratory for seven years, and is still quite hard and difficult to cut with a penknife. This represents a particularly favourable soil, but with other types of soil similar degrees of waterproofness may be obtained—in some cases, however, only with the use of larger percentages of bitumen.

TABLE IV.

Passing 200 mesh I.M.M.	6·1% wt.
,, 100 ,, ,,	27·3 ,,
,, 80 ,, ,,	12·3 ,,
,, 70 ,, ,,	14·4 ,,
,, 50 ,, ,,	10·7 ,,
,, 30 ,, ,,	10·6 ,,
,, 20 ,, ,,	5·3 ,,
,, 10 ,, ,,	6·7 ,,
,, ⅛″ ,, ,,	6·6 ,,
	100·0 ,,

It will, of course, be understood that although this degree of mechanical stability persists after prolonged immersion in water, it is not possible for the very limited quantities of bitumen indicated completely to waterproof the mixed material. What happens is that the infiltration of moisture is retarded, but that at equilibrium moisture is present to an extent approximately equal to that necessary to fill the voids in the mix; but that the distribution of the bitumen throughout the mix has been effected to such an extent that the individual particles are sufficiently bound together, so that the general cohesion and stability of the mix are not affected by the presence of the water.

The addition of clay to mixes of this type is sometimes advocated, but it should be stressed that, in the case of mixes containing appreciable percentages of true clay, the immersion in water of samples is usually followed by a pronounced loss of bearing capacity. This is due to the fact that the particle size of the clay is so fine that the binding power of the bitumen is inevitably small, and the capacity of the mixed material to withstand the action of water is, therefore, not great. So long as the mixes containing clay are not subjected to immersion conditions, however, and the access of water is only to a restricted extent, the great bearing capacity which may be attained in suitable circumstances, due to the addition of clay, may be an advantage. This type of mix, however, would seem not to be suited to conditions where water has to be reckoned with.

Industrial Stable Emulsions.

As has been stated previously in this paper, the bulk of consideration has been given to emulsions designed for road work. There is, however, another important sphere of use for bituminous emulsions for industrial purposes generally. These purposes include the preparation of insulating layers for the exclusion of moisture, the formation of compositions involving sand, cement, micro-asbestos, and other materials for heat insulation, electrical insulation, and similar purposes.

The type of emulsion used mainly for this work is, however, something quite different from those we have been discussing heretofore. These emulsions are usually prepared employing bentonite or some similar form of colloidal clay as the emulsifier.

Almost any type of bitumen may be emulsified with a suitable clay, provided that appropriate conditions are selected. The clay suspension to be used as the emulsifier is normally made up in a concentrated form at first, containing, for example, 15 per cent. of bentonite; the resulting high consistency facilitates dispersion of the clay. The suspension, or " clay slip " as it is called, is subsequently diluted to the required concentration and, when necessary, is flocculated to some extent by the addition of an electrolyte. The conditions in any particular instance have to be determined empirically, and depend on the properties of the clay and of the bitumen, as well as on the characteristics desired in the finished emulsion.

The manufacturing process normally consists in running the clay slip simultaneously with molten bitumen into a suitable form of mixer, which already contains some clay emulsion, the temperatures being adjusted so that the emulsion is produced at approximately the melting point (R. & B.) of the bitumen. For proper dispersion of the bitumen it is necessary to maintain a high consistency of the material in the mixer, since, to a very large extent, the emulsion itself is the emulsifying machine. In these circumstances the bitumen, which is added in a thin stream, is drawn out into thin threads in the clay suspension, and ultimately breaks up into cigar-shaped particles. The latter are stabilized by clay particles concentrated in the bitumen/water interface, and in a good emulsion retain their shape permanently, owing to the rigid nature of the clay films. The elongated particles characteristic of clay emulsions are shown in Fig. 10; the spherical particles of a normal soap type emulsion are shown in Fig. 11.

A rather pretty demonstration of the rigid character of the stabilizing clay films may be seen under the microscope if soap solution is added to a clay emulsion, and the treated emulsion kept under observation over a sufficient period. The added soap displaces the clay from the bitumen/water interface, replacing the rigid clay film by a non-rigid stabilizing film of soap, and then, as a result of interfacial tension forces, the elongated bitumen particles are slowly drawn up into spherical globules.

As manufactured, the clay emulsions are thixotropic pastes containing 50–60 per cent. of bitumen. They are extremely stable to mechanical and chemical forces, and do not coagulate on drying until practically the whole of the water has been evaporated. The residual films obtained from the emulsions retain the clay emulsifier as a kind of skeleton structure, which prevents flowing of the bitumen under heat. A surprising resistance to flow can be developed, and it is possible to heat such a film until ignition of the bitumen occurs, without flow taking place. This property renders the emulsions particularly valuable for the application of anti-corrosive coatings to metal or other surfaces, and for the waterproofing of all kinds of structures.

Owing to their high stability, clay emulsions can be added directly to the paper pulp for the manufacture of bituminized paper, thus eliminating a second impregnating process, and they find a considerable application in the production of waterproof wrappings, carton boards, panel board, etc. In conjunction with cement, aggregates, and a variety of fillers, they provide mastics and waterproof compositions for roofing and flooring.

The space at our disposal does not permit of more than this very brief summary of the purposes for which bituminous emulsions are used, but sufficient has been said to indicate the wide field which has been opened up.

CONCLUSION.

The general purpose of this paper has been to show the progress of the bituminous emulsion industry and of the emulsions themselves, from the beginnings, which were purely empirical, to the position to-day, where it may be claimed that the industry is on a sound, scientific basis and the products are produced by precision-controlled methods. The emulsions, even in the early days, were found to have a wide field of utility, and the difficulties which had to be overcome were mainly those encountered in exceptional circumstances of application, or where the demands placed upon the finished products were exceptionally heavy. Owing to the increased knowledge of the constitution and behaviour of these emulsions, even these exceptional circumstances may now be dealt with with a great degree of success and, in fact, it may be said that bituminous emulsions are standardized to a degree certainly equal to that of any other product sold in equal bulk.

Concomitant with this development, a sound position has been built up in respect to specifications with which all products of this type are required to comply. The labile type of emulsion for surface-dressing and grouting is dealt with in British Standards Specification No. 434–1935 and this specification is specially noteworthy, in that it contains a first test for performance. This is the Lability Test, and although, in itself, the Lability Test is not a complete guide to performance, in that it deals only with the set of the emulsion due to evaporation and mechanical disturbance, nevertheless this is a good beginning. The bituminous emulsion industry has formed, from its principal members, the Road Emulsion and Cold Bituminous Roads Association, Ltd., and many of the technical advances which have taken place can be traced to the activities of the Technical Committee of that body. Technical co-operation between the various members of the industry is assured, thus providing the maximum degree of assistance and co-operation with the consumer, coupled with the beneficial effect of competition between the different manufacturers, to secure a satisfactory rate of technical and economic progress.

It is not often that it is possible to survey, in so limited a period, the growth from the very beginning to the fully equipped industry, of an industrial development of the degree of importance which has been assumed by the bituminous emulsion industry, and it is therefore hoped that the account which has been presented in this paper may be not only interesting to those in the industry, but also to the wider public constituted by the membership of the Institute of Petroleum.

The author is greatly indebted to his colleague, Mr. W. L. Peard, B.Sc., to whom much of the experimental work referred to is due, for his assistance in the preparation of this paper.

THE RELATIVE VOLATILITY OF PETROLEUM FRACTIONS.*

By R. Edgeworth-Johnstone, M.Sc., M.I.Chem.E., F.I.C.

In designing fractionating columns for complex mixtures by methods such as that of Underwood,[1, 2] it is necessary to know the relative volatility of adjacent narrow fractions. The relative volatility of two substances at any temperature is the ratio of their vapour pressures at that temperature. In the case of petroleum fractions, vapour pressures may be interpolated from a Cox or similar chart and the relative volatility thus calculated. Most vapour-pressure charts are based on data for pure hydrocarbons.

An empirical relation has been found whereby the relative volatility is obtained directly from the absolute temperature and the atmospheric boiling points of the components. Correlated on this basis the relative volatilities of pure hydrocarbons lie approximately on a single curve.

The relation is :—

$$\text{Log}_e\,\alpha = 11{\cdot}5\,\frac{T_b^2 - T_a^2}{2T^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or :

$$\text{Log}_{10}\,\alpha = 2{\cdot}50\,\frac{T_b^2 - T_a^2}{T^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Where :—

α = relative volatility of component A with respect to component B at absolute temperature T,

T_a, T_b = absolute boiling-points of A and B at atmospheric pressure, T_a being the lower (in the case of narrow petroleum fractions, the average boiling points).

Temperatures may be expressed either in degrees Kelvin (Centigrade + 273) or Rankine (Fahrenheit + 460).

In arriving at this expression, relative volatilities were calculated for various combinations of twenty-one hydrocarbons, including normal paraffins, *iso*paraffins, *cyclo*paraffins, aromatics and a few olefins. Vapour pressures were taken from Rechenberg,[3] Perry [4] and the International Critical Tables. The lowest-boiling hydrocarbon included was propylene, b. p. −47° C.; the highest, hexadecane, b. p. 287·5° C. The pairs chosen consisted of hydrocarbons both of the same group and of different groups. The relative volatility of each pair was calculated at several temperatures. These ranged from temperatures corresponding to vapour pressures of 10–20 mm. up to or near the critical temperature of the lower-boiling component when data for the latter region were available.

The correlation obtained is shown in Fig. 1, in which log α is plotted against $(T_b^2 - T_a^2)/2T^2$. Ninety points are represented, although all are

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* Paper received 19th May, 1939.

not visible, owing to overlapping. The greatest deviations from the average curve occur at very low vapour pressures, near the critical temperature, or at high values of the relative volatility.

At temperatures equal to or near the arithmetic mean of the atmospheric boiling points of the components $[(T_b + T_a)/2T = 1{\cdot}0]$, equation (1) reduces to the simpler form :

$$\text{Log}_e\, \alpha = 11{\cdot}5\, \frac{T_b - T_a}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

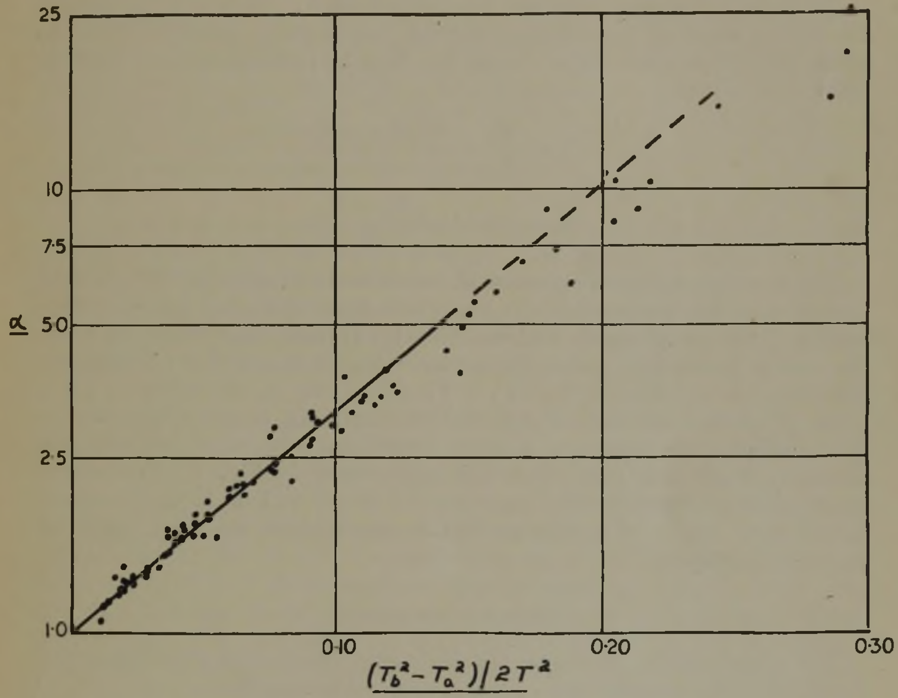

FIG. 1.

RELATIVE VOLATILITIES OF HYDROCARBONS.

This expression, with a slightly different constant, can be derived from the Clausius–Clapeyron equation and Trouton's rule.

Let :

P_a, P_b = Vapour pressure of components A and B at absolute temperature T.

M_a, M_b = Molecular weights of A and B.

L_a, L_b = Latent heats of vaporization of A and B at their respective boiling points.

R = Gas constant (heat units) = 1·986.

T_a, T_b, α are as defined above.

Integration of the Clausius–Clapeyron equation for component A, assuming constant molal heat of vaporization, gives :

$$\text{Log}_e\, P_a = \frac{M_a\, L_a}{R} \cdot \frac{T - T_a}{TT_a}$$

Combining this with Trouton's rule, $M_a\, L_a/T_a = 22$:

$$\text{Log}_e\, P_a = \frac{22}{R} \cdot \frac{T - T_a}{T}$$

A similar equation is obtained for component B. If it be assumed that the latent heats of vaporization remain substantially constant over the range of temperature from T_a to T_b, then the two equations may be combined, whence :

$$\text{Log}_e\, \frac{P_a}{P_b} = \frac{22}{R} \cdot \frac{T_b - T_a}{T}$$

or

$$\text{Log}_e\, \alpha = 11{\cdot}1\, \frac{T_b - T_a}{T}$$

The assumption regarding constant latent heats of vaporization evidently cannot hold for temperatures far removed from the atmospheric boiling points of the components, and equation (3) is then considerably in error. To secure correlation under these conditions it was found necessary to introduce the empirical factor $(T_b + T_a)/2T$, giving equation (1).

In petroleum distillation calculations involving complex mixtures of hydrocarbons, the range of relative volatilities and vapour pressures is normally much less wide than that represented in Fig. 1. For narrow fractions it is believed that equation (1) or (2) will be found to give a satisfactory degree of approximation to the relative volatility under all practical conditions.

ACKNOWLEDGEMENT.

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AN ACCELERATED OXIDATION TEST FOR OILS.*

By W. Francis, M.Sc., Ph.D., F.I.C., and K. R. Garrett, B.Sc.

Summary.

The various modifications of the Michie sludging test that are in use for measuring the oxidizability of an oil are difficult and laborious methods. A new method for determining the oxidizability of oil is described, using a solution of alkaline potassium permanganate under standard conditions as oxidizing agent. The whole determination can be carried out in a few hours with a simple apparatus and the results obtained on a number of different types of oil appear to be capable of correlation with the behaviour of these oils in practice. Not only can the oxidizability of new oils be determined but the state of oxidation of an old oil can readily be ascertained by the new method. The experimental conditions can be modified to increase or decrease the severity of oxidation so as to discriminate more readily between oils of similar oxidizability at either end of the scale.

The authors have recently pointed out the unsatisfactory nature of the existing standard methods for the chemical examination of lubricating oils, particularly in their application to the measurement of the changes occurring in such oils under operating conditions. In an endeavour to improve matters it has been suggested that the standard methods should be modified, and followed by determining the oxidized groupings appearing in the oil during oxidation.

These methods are of value in measuring the effect of oxidation, and especially the rate of deterioration of oils in practice. It is, however, of greater advantage to be able to anticipate the course of events by the evaluation of the liability of oils to oxidation. The authors' attention has now been focused on the measurement of this property.

The oxidizability of oils is usually measured by the Michie test [2] or modifications of it. The general procedure is to pass air at a standard rate through a standard volume of oil in which is placed a strip of clean copper foil. The whole is maintained at a constant temperature, and the sludge formation, change in viscosity, or carbon residue is measured and assumed to give an indication of the tendency to sludge. In the standard tests of the B.E.I.R.A., the I.P.T. or the B.S.I. (*loc. cit.*) the rate of flow of air is two litres per hour, the temperature of the oil is 150° C., and the duration is 45 hr. The sludge formation is estimated by weighing the insoluble matter produced by the addition of petroleum spirit. In the British Air Ministry modification the rate of flow is 15 litres per hour, the temperature is 200° C. and the duration of heating two periods of 6 hr. on consecutive days. The increase in viscosity or carbon residue value before and after oxidation is taken as an index of the oxidizability of the oil.

It is apparent that these tests are difficult and tedious to carry out, and the errors in the determination of the extent of change in the oils are relatively large.

Because of the success obtained by one of the authors [3] in the parallel

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problem of determining the oxidizability of coal by means of its reactivity towards alkaline potassium permanganate solution under standard conditions, it was decided to explore the possibility of adapting this procedure to the determination of the oxidizability of oils. The problem differs from that of determining the reactivity of coal mainly because the available surface of interaction of a given weight of coal is determined by the size, shape, and uniformity of the coal particles, whereas with oil, which floats on the surface of alkaline permanganate, the available surface is the surface area of the aqueous solution. The rate of oxidation of oil depends on the weight of oil taken, its oxidizability, the interfacial area between the oil and alkaline permanganate, the temperature, the rate of diffusion of the oxidation products of the oil from the interfacial surface, and the concentration of alkaline permanganate at the interfacial surface. Since the authors are at the moment interested only in obtaining an index for the oxidizability of an oil, this can be done by fixing the factors arbitrarily in a manner capable of giving a significant reproducible numerical value to this property for the range of oils under examination.

After a preliminary investigation regarding the effect of the above factors on the results, three methods at different temperatures were tried out.

(1) Samples of a turbine oil after varying periods of service were taken and 10 gm. of each were weighed into standard sized 600 ml. beakers; 100 ml. of *N*-potassium permanganate (containing 31·8 gm. per litre) and 25 ml. of *N*-caustic soda were added. After allowing to stand for 72 hr. at laboratory temperature (approximately 20° C.), the contents were filtered under suction through a frittered glass filter (25.G.3). The filtrate was then warmed to 60° C., acidified with sulphuric acid, and titrated rapidly against *N*-oxalic acid in the usual manner. A blank test was carried out with permanganate and caustic soda alone under the above conditions.

(2) 10 gm. of each of the above oils were weighed into thin glass bulbs of capacity approximately 15 ml. Each bulb was broken by dropping it into a round-bottomed flask of capacity 4 litres : 50 ml. of *N*-caustic soda and 200 ml. of *N*-potassium permanganate were added. The flask was attached to a Liebig condenser, by means of a ground-glass joint, and the contents were boiled as quietly as possible for 50 min. The solution was filtered and titrated as in (1).

(3) 20 gm. of each of the above oils were weighed into standard-sized flat-bottomed litre flasks and 40 ml. of *N*-caustic soda added, followed by 150 ml. of *N*-potassium permanganate. Each flask was then placed on a boiling water-bath for 2 hr. The temperature of the solution during this period remained approximately constant at 95° C. The amount of permanganate used was estimated as above.

The results obtained by the above three methods are given in Table I.

The results are comparable, in that the oils are arranged in the same order of oxidizability. While it is considered that method (1) is the most accurate under our experimental conditions, the time taken is too long for a routine test. Method (2) gives significant results in the shortest time, and temperature control is simplified. Unfortunately, however, the reaction is violent with highly oxidizable oils, and severe bumping may alter the interacting surface area to an indeterminate amount.

Method (3) is a compromise, in that the reaction proceeds quietly, and so ensures a constant interfacial surface, whilst the time required is considerably shortened compared with method (1) at atmospheric temperature. For extreme accuracy, of course, the temperature of the solution should be controlled by a thermostat at 95° C.

TABLE I.

Stage of Oxidation.	ml. of *N*-potassium permanganate used.		
	1. After standing for 76 hr. at laboratory temperature.	2. Boiling for 50 min.	3. Heating to 95° C. quiescently for 2 hr.
New Turbine Oil	0·5	2·4	2·3
1.	4·3	13·4	11·0
2.	11·9	35·0	13·6
3.	12·1	46·0	20·9
4.	14·8	47·9	28·3
5.	17·5	51·0	35·6

It is important to titrate as rapidly as possible, after acidifying the permanganate, because the acid permanganate is unstable in the presence of any remaining reducing matter left behind in highly oxidizable oils.

The authors advocate method (3) under controlled temperature conditions as a standard for normal lubricating and insulating oils. The number of mls. of normal permanganate used under these conditions is called the "permanganate number," and this is used as an index of oxidizability. To obtain this for extremely reactive oils, which would decompose all the permanganate under the standard conditions, less oil or more permanganate may be taken. It is sufficient, in such cases, to record the permanganate number as being greater than 150.

Table II contains the results of the examination of a number of oils by the standard method, and compares the permanganate number with the Ramsbottom coke test before and after oxidation by the Michie method.

As would be expected, the permanganate number decreases with increased refining. With highly refined mineral oils the permanganate number is about 2, and with oils from the same source, but not so highly refined, about 16. Vegetable oils decompose all the permanganate, being more reactive and more liable to sludge than mineral lubricating or insulating oils.

It is interesting to observe that some of the products produced by the deterioration of turbine oils in practice are much more oxidizable than the oils themselves. Thus, some of the solid sludge removed from a centrifuge used to clarify such oils, reacted so readily with alkaline permanganate under standard conditions that all the permanganate was used up before the end of the experiment. On repeating, using only 1 gm. of sludge, 72 ml. of permanganate were decomposed. Moreover, some of the oxidation products removed by alcoholic extraction from a used oil, of acidity 425 mgm. KOH/100 gm. oil and permanganate number 120, were remarkably reactive towards permanganate. Under standard conditions of oxidation, but using 0·1 gm. of this resinous material, 85 ml. of permanganate were decomposed. The permanganate number of the extracted oil was only

TABLE II.

Oil.	Description.	Permanganate no.	Ramsbottom.	
			Before oxidation.	After oxidation.
Olive oil.	Vegetable oil, high sludging properties.	>150		
Castor oil.	Vegetable oil, high sludging properties.	>150		
Low-grade American.	Light straight mineral oil used for diluting cutting oils and flushing.	17·1	0·33	3·4
Low-grade American coastal.	Medium oil used for bearings and machinery.	15·0		
Low-grade American.	General purpose heavy lubricating oil.	14·2	0·33	3·4
Mid-continent American dewaxed.	General purpose lubricating oil and turbines.	3·0	0·13	1·8
South American, highly refined by selective solvent process.	Low sludging properties. Cylinder, gearboxes, etc.	2·9	0·17	0·77
American high-grade, selective solvent process.	Turbines, bearings, etc.	2·7	0·11	1·17
Mid-continent American, highly refined, distilled and acid treatment.	Turbines, general lubrication.	2·3	0·14	1·3
American high-grade.	Hydraulic couplings, etc.	1·9	0·11	1·28
Transformer, Naphthene base.	Grade A.30.	1·3		
Transformer, Naphthene base.	Grade B.30.	2·5		
Transformer, Naphthene base.	Grade B.0.	4·8		

14·6, showing that the alcohol-soluble products were responsible for the bulk of the reaction with permanganate. Consequently, if all the oxidation products obtained in service remain in an oil, the determination of the permanganate number appears to be a measure of the degree of oxidation that has occurred.

Unfortunately, from the point of view of checking this point, normal practice is to remove sludge or emulsions from turbine oils by the regular use of a centrifuge. Water-soluble products are constantly being removed from the system, and if the rate of removal of insoluble products is greater than the rate of formation, the permanganate number of the residual oil will not rise after equilibrium has been reached, and it may even fall. This is, in fact, what has occurred with the turbine oils shown in Table III.

TABLE III.

Approx. no. of months in service.	Permanganate no.	ml. of gas at N.T.P. liberated by Grignard reagent.	Acidity, mgms. KOH/100 gm. oil.
0	2·3	2·0	0
4	11·0	9·7	8·9
7	13·6	12·8	15·9
9	20·9	17·7	34·7
11	24·7	21·0	45·3
15	27·3	22·4	64·9
19	33·7	24·4	71·1
22	35·6	24·1	71·1
29	31·1	21·5	65·0

The permanganate number, reactivity towards Grignard reagent, and acidity are compared over a period of 29 months in service. During the first nineteen months the values of all three increased correspondingly, and then remained fairly constant for the next three months. After this period a slight decrease in all three occurred over a period of seven months.

The behaviour of a highly refined oil, containing an inhibitor, is also of interest. The new oil gave a permanganate number of 4·4, the inhibitor itself being mainly responsible for this small reactivity. After three years service the permanganate number was only 4·1, which suggests that little oxidation had occurred, but that some of the inhibitor had been lost. This is confirmed by the Grignard reaction,[1] in which the amount of gas liberated from the new oil was 2·3 ml. and from the used oil 1·3 ml. The appearance and usual tests on the oil confirmed the absence of any marked degree of oxidation; the acidity, for example, only reaching the value of 5 mgm. KOH/100 gm. oil during this period.

The authors feel justified in concluding that the standard method described above gives a measure not only of the relative oxidizability of new oils, but also the extent to which an oil has deteriorated in service. It is offered as an additional method for the examination of oils in the hope that it will be helpful where further evidence on oxidation is required or where a rapid determination of oxidizability is desired.

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[2] B.S.S. No. 148.
[3] W. Francis, *Fuel*, 1933, 128.

A NEW LABORATORY METHOD FOR RATING AVIATION FUELS OF HIGH OCTANE NUMBER.

By R. Stansfield, A.M.Inst.C.E., M.Inst.Pet., and H. B. Taylor, A.F.R.Ae.S.

It has been recognized for some years that laboratory ratings of aviation fuels are unsatisfactory with existing equipment and technique, and many attempts have been made to improve correlation with aero-engine behaviour. The problem has been complicated because of lack of really satisfactory means for examining full-scale performance as regards detonation, and opinion differs sharply on the relative merits of various proposals for full-scale knock testing, upon the results of which any laboratory test must be based.

The first tentative standard method adopted for fuels to meet British Air Ministry specifications was the outcome of tests in single-cylinder aero-engine units, knock being determined under conditions of maximum economy and for fuels of lower octane number than now prevail. The laboratory method based on these results depended on the use of the C.F.R. engine running under Motor Method conditions, except that the mixture temperature was adjusted to 260° F. instead of 300°. As the use of 87 and 100 octane-number fuels became more important it was found that an increase of mixture temperature to the Motor Method value was desirable, and alteration to this method has recently been recommended by the Knock Rating Panel of the Institute of Petroleum.

This change is not considered to be a complete answer to the correlation problem, as it is known that fuels of equal knock rating under cruising conditions may differ considerably when the engine is running under more highly supercharged and rich-mixture take-off conditions where mixture strength is used for limiting detonation.

It is not intended here to give a complete summary of the several proposals for improved ratings, but it is notable that practically every attempt has been influenced by the assumption that lack of correlation with the C.F.R. engine is due very largely to the great dissimilarity between this unit and an aero-engine cylinder. Thus the test engine has been modified by altering cylinder dimensions to permit an aluminium piston to be used at high rotational speeds, with or without increase of jacket temperature; supercharging has been provided for, and the valve system and carburettor have been altered to give greater breathing capacity; the bouncing pin has been replaced by a temperature plug, or a piezo-electric indicating unit, and even audibility methods have been used according to the ideas of the experimenters concerned. British and some Continental work has been influenced largely by the results of single-cylinder aero-engine tests under rich-mixture conditions, while American developments appear to be directed more by full-scale engine tests in which the temperature rise of suitably placed thermocouples is assumed to be the criterion of failure, although pre-ignition and other factors have also received attention.

The development work leading to the method to be suggested is based

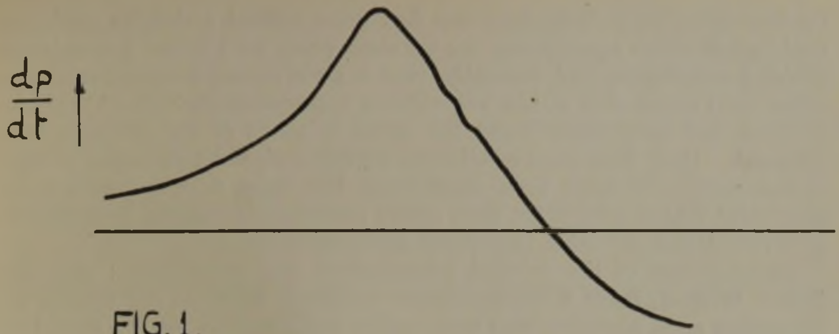

FIG. 1.

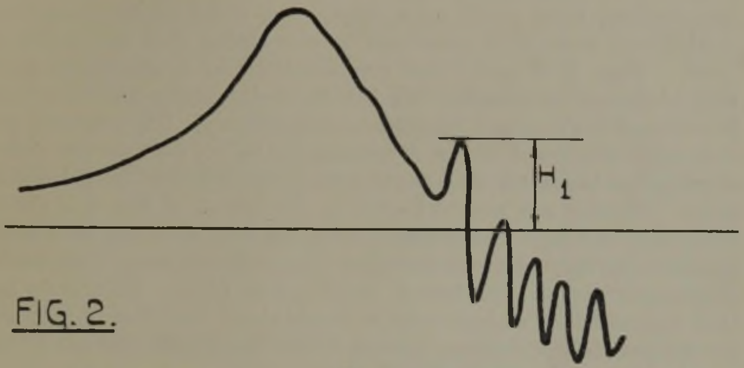

FIG. 2.

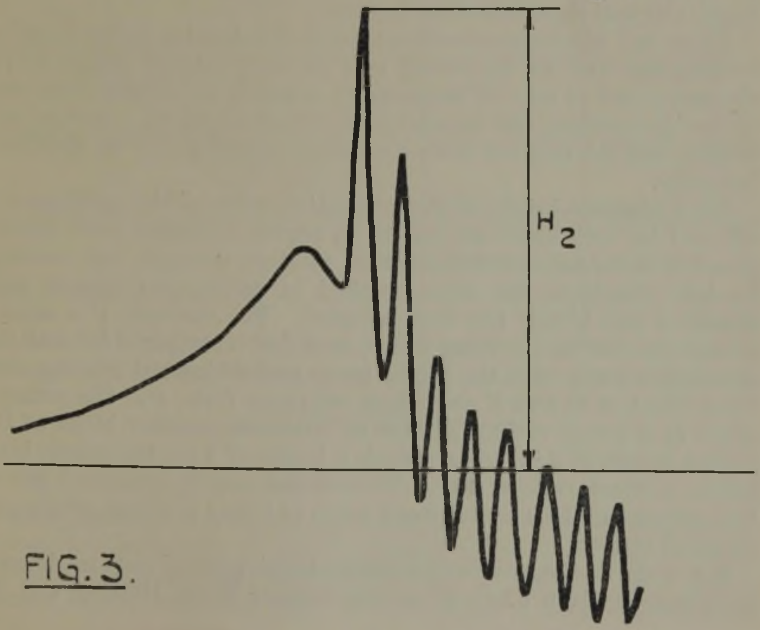

FIG. 3.

on two premises: first, that any fuel must exceed a definite minimum anti-knock value appropriate for its class when used under lean-mixture cruising conditions, and, secondly, that it must exceed a second minimum when used under rich mixture conditions appropriate for take-off, the two minima not necessarily being the same in terms of the reference fuels adopted. Only data from a full-scale British-designed aero engine of large cylinder capacity have been considered, but there does not seem to be any valid reason why more than minor modifications should be needed to give correlation for other important aero-engine types.

Development of the method started from two assumptions: that the Motor Method, itself a weak-mixture test and, so far as our present information goes, agreeing with aero-engine weak-mixture ratings, should be fairly readily capable of alteration to suit rich-mixture conditions, and that instrumentation, such as provided by the bouncing pin, the temperature plug, or oscillograph pressure diagrams, was unsuitable. The latter assumptions were made as a result of a series of instrumentation tests carried out some two years ago in connection with the rating of motor fuels. Figs. 1, 2 and 3 are reproductions of oscillographs showing the rate of change of pressure in a C.F.R. engine under smooth running, light knock, and heavy knock conditions, respectively. The bouncing pin cannot respond to the knock of Fig. 2, because the rate of pressure rise of the general combustion is greater than that of the knock effect at the point of measurement. It may not respond even to the knock of Fig. 3 if the engine is being run at a high compression ratio, because then the pre-knock rate of pressure rise may be great enough to throw the pin away from control of the diaphragm before the knock itself takes place. This does not mean that reproducible ratings cannot be obtained, but they will be influenced by the general combustion process before the knock, and not by the knock itself, and will therefore often be false.

These and other considerations led to the decision to use a cathode-ray oscillograph and an indicating unit showing rate of change of pressure diagrams, and to take as the measure of knock the height of the first wave of the detonation, the maximum observed height in a minute being recorded, and the mean of three such observations giving the required knock intensity.

Since absolute height of the detonation wave on the oscillogram can be affected by very small alterations to engine condition, even though compression ratio, mixture temperature, mixture strength, and running speed be held constant, the usual method of comparison against secondary standard fuel blends has been adopted. For example, if a series of 87-octane-number fuels is being tested, each fuel is compared for peak height of detonation wave with the height given under identical running conditions by a blend of C and F secondary reference fuels, and the rating is first given as a knock ratio. Thus if an 87-octane-number blend of C and F gives a height of 3 in. and a sample a height of 2 in., the sample is rated as having a knock ratio of 0·67. These ratios may be converted into equivalent octane numbers by testing a series of C and F blends which cover the required range.

Fig. 4 shows the results of a comprehensive set of tests made on several fuels ranging from 87 to 91 octane number Motor Method, and the full-scale behaviour of which was known in an important design of air-cooled engine under both weak- and rich-mixture conditions. Considering the curve for fuel A, this sample was run through a jet-type flow-meter to the C.F.R. engine, and the mixture strength adjusted to give maximum knock as measured by the height of the detonation wave of the oscillogram. The mixture temperature was maintained at 300° F. and the speed at 900 r.p.m., as for Motor Method testing. The compression ratio was adjusted

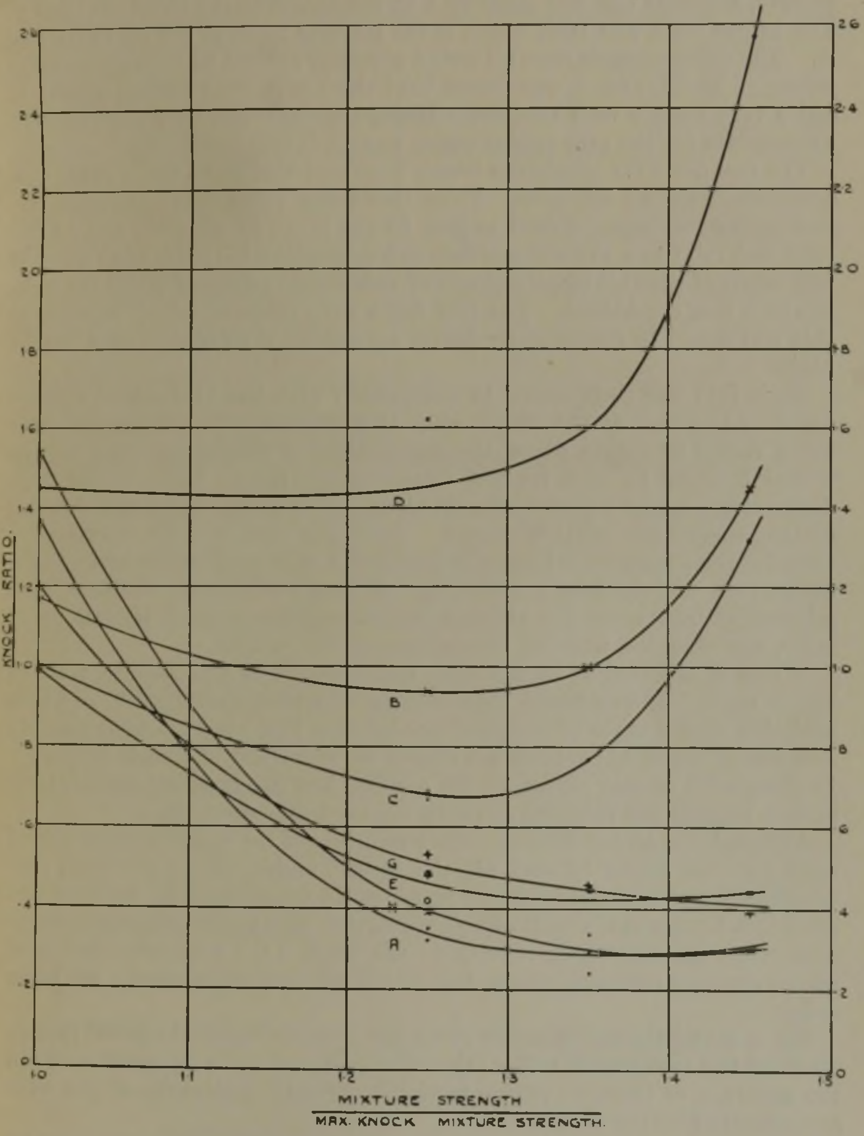

FIG. 4.

so that the detonation wave was about the same height as that of the pre-knock pressure rise, although the setting is not critical. After determining the mean of three separate observations of the maxima occurring in a minute, a similar test was made on a 91·0-octane-number blend of C and F. The height ratio was 1·35, which is the starting point of the curve for fuel A. The other samples were all tested similarly against 91·0-octane-number reference blend, and it was found that the knock-ratio ratings agreed in order very closely with the Motor Method ratings, and they are therefore appropriate for the aero engine under weak-mixture conditions.

The fuel flows for maximum knock were recorded and a mean value was determined for all the fuels. From this mean value were calculated the flow-meter readings required to give 25 per cent., 35 per cent. and 45 per cent. rich mixtures, the richness figures being nominal in so far as no account was taken of possible small changes of volumetric efficiency under the rich-mixture test conditions. The fuel flows were made equal by volume, as this was found to give slightly better agreement than control on a weight basis.

Each fuel was then tested in comparison with the 91·0-octane-number blend of C and F at the 25 per cent. rich mixture, the compression ratio being raised to obtain about the same height of detonation wave for the C and F blend as used for the weak-mixture tests. Some of the fuels depreciated, whilst others appreciated, and tests at the still richer mixture further spread the relative ratings. At 45 per cent. rich the compression ratio for the poorer fuels had to be kept below that used for the better fuels, to prevent unduly heavy knocking. It was established, however, that relative ratings were not affected by the necessary small alterations of ratio, and thus the working conditions are not critical.

A test of one fuel at 55 per cent. rich resulted in a marked increase of knock ratio. It was noted that running was then very erratic, and it is probable that a state of incipient pre-ignition had been reached, possibly one which could have been alleviated by reduction of knock intensity. Investigation of this aspect of the method has not been completed, as it occurs beyond the mixture strength required for correlation.

Although the Motor Method octane numbers of the samples tested varied only between about 87 and 91, the spread under the 45 per cent. rich conditions was about 15 octane numbers as determined by tests on appropriate blends of C and F at this strength. The knock ratio depends, of course, on the secondary reference fuels used, " C " and tetraethyl lead giving entirely different ratios, but rating all fuels in relatively the same order.

Fig. 5 shows the knock ratios at 45 per cent. rich plotted against ratings made on the aero engine under take-off conditions, and agreement is within the accuracy of the aero engine tests themselves. Ratios for 40 per cent. are indicated by the dotted line.

The samples examined include paraffinic, naphthenic, and aromatic types, all with T.E.L. in amounts varying from 2½ to 4 ml. per Imp. Gall.

Should further work confirm the suitability of this type of test, the specification for knock testing of an aviation fuel would include a minimum octane number blend of specified secondary reference fuels which it must match under weak-mixture conditions, and a second minimum number for a match at, say, 45 per cent. rich. Weak-mixture ratings could probably be determined better by rating at a definite engine power drop below optimum, rather than at a rather flatly defined maximum knock, although such

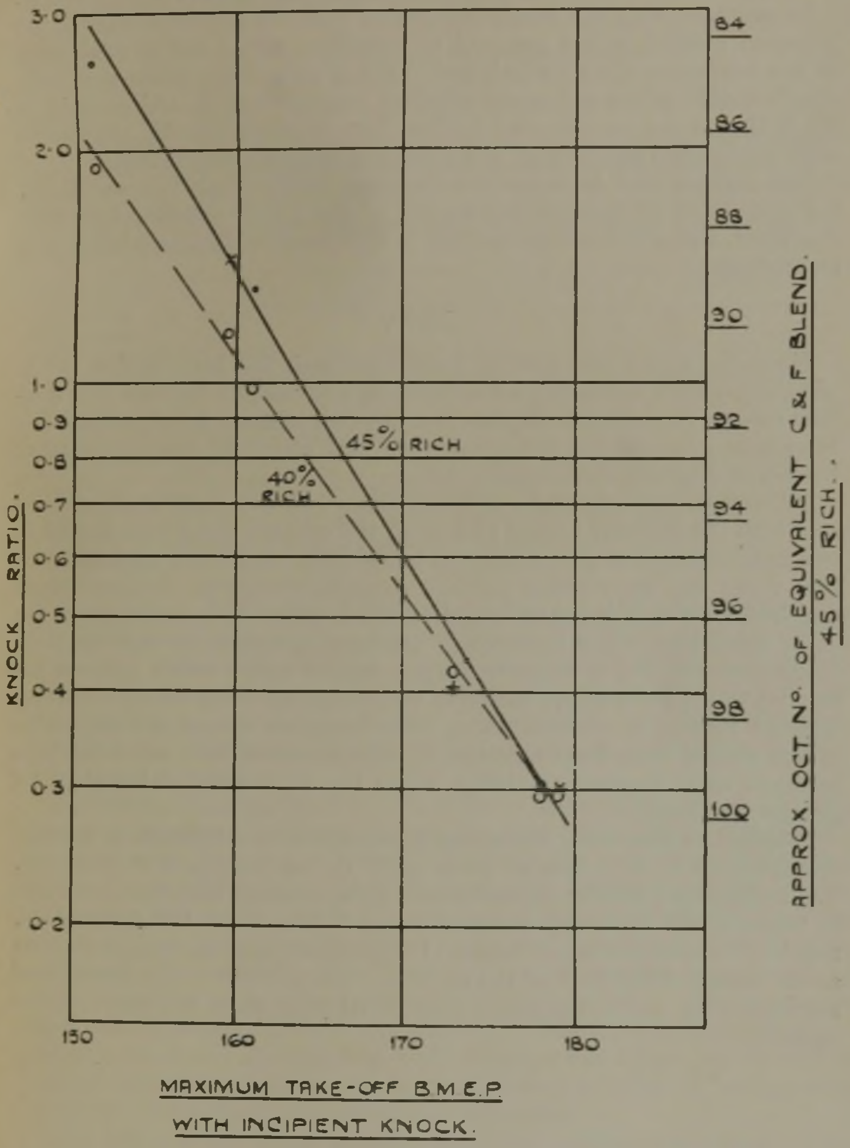

Fig. 5.

a technique requires a dynamometer for load absorption, or the use of a D.C. generator with which the speed falls with fall of engine output.

For the examples given in Fig. 4 the specification might be " not less than 87 octane weak " and " not less than 95 octane at 45 per cent. rich," the latter corresponding to a knock ratio of not more than 0·55 in terms of the 91-octane blend of C and F under the test conditions from which Fig. 4 was obtained. Such a specification would be met by fuels A, E, G and H.

In common with the Motor Method of tests for automobile fuels, the proposed method is not assumed to reproduce actual engine conditions. It is a laboratory device which makes use of an existing engine with only simple modifications and easily obtained instrumentation, and no claim is made that it can be extended further than to obtain suitable correlation with aero-engine fuel ratings under cruising and take-off conditions.

The authors wish to thank the Chairman of the Anglo-Iranian Oil Co. for permission to publish the results of the C.F.R. experimental work described, and which was carried out in the Company's research laboratory at Sunbury.

NOTE.

Since the above was written further research has been carried out in connection with the method described, and correlation between rich mixture ratings on full scale engines and the rich mixture C.F.R. ratings has been shown to exist for 100 octane fuels with about the same accuracy as for the 87 octane number range.

The C.F.R. engine has been adjusted to run with a 19° fixed spark advance and with the inlet air heated to 150° F. the mixture being then heated in the usual manner to give a mixture temperature of 300° F. on a reference fuel under the appropriate mixture strength conditions, the heat input required for this being maintained constant for all fuels tested under the same conditions. The carburettor has been modified, the throttle plate being removed and a properly shaped venturi added which includes the jet and which gives about the same volumetric efficiency as when running without venturi or throttle plate. The flowmeter system and adjustable orifice control have been redesigned. The shrouded inlet valve has been retained as it improves stability, while the unshrouded valve gives no greater test range.

Modified as described, the engine is suitable for testing fuels at mixture strengths up to 45% rich at least up to the equivalent of F plus 2 ml. T.E.L./Imp. gal. without supercharge. Recent ratings have been expressed in terms of the matching blend of C and F with 2 ml. T.E.L./Imp. gal. required to give the same height of detonation wave on the oscillogram as the sample when used at the same mixture strength. This selection of reference fuels covers the entire commercial range from 87 octane number upwards.

ABSTRACTS.

AUTHOR INDEX.

The numbers refer to the Abstract Number.

Geophysics.

849. Care and Maintenance of Seismic Exploration Instruments. E. C. Stuedle. *Oil Wkly*, 29.5.39, **93** (12), 23.—Instrument up-keep embraces : (*a*) normal care which is or should be given to instruments by the field personnel in their daily work ; (*b*) additional care which may be supplied by specially trained personnel detailed for this purpose ; (*c*) methods by which obsolescence and run-down condition of instruments may be minimized ; (*d*) factors of design which affect maintenance ; (*e*) general benefits derivable from a systematic maintenance programme.

Field conditions profoundly affect the problem. Foremost amongst routine care duties come cleanliness and lubrication. The spring adjustment of seismometers is important with regard to record character, and attention must be paid to damping. Good light-sources and clean mirrors help towards good photographic records.

The various items of electrical equipment in the truck require a certain amount of looking after. In cold weather moisture is apt to condense on the metal parts and cause trouble. These effects can be minimized by keeping the interior of the truck warm at night. The complete equipment may include fifty or sixty vacuum tube circuits, and thus a multi-purpose meter is desirable, which may be used as an ohmmeter of various ranges, as a D.C.–A.C. voltmeter and milliammeter, and as a condenser-tester. A tube-tester is also of some value. Facilities should be provided for testing the geophone cables, and all temporary splices or repairs made in the field should be placed in good order before the next day of field work.

Three diagrams show the development of seismic instruments during the past few years.

A systematic programme of inspection and maintenance is essential. An instrument inspector should be in general charge of the instrumental equipment of the company. His duties are outlined. Instrumental design and the layout of equipment should have regard to field conditions. G. D. H.

850. Preliminary Micromagnetic Survey of the Eola Structure. W. P. Jenny. *Oil Wkly*, 29.5.39, **93** (12), 34–35.—The structural interpretation shown on an accompanying map takes into consideration a regional increase in the magnetic intensity which is due to down-dip thickening of the magnetic Wilcox section. The interpretation has been substantiated by drilling.

In the Gulf Coast area it appears that the Lower Miocene acts as the main magnetic stratum. In South-west Texas the magnetic method is credited with the discovery of a number of oil-fields, and ranks among the generally accepted geological tools.

It is probable that in the near future accurate regional magnetic surveys will be accepted as a highly effective reconnaissance method under almost any geological conditions, and that a detailed micromagnetic map of a prospect will be considered one of the essentials before locations are made for wildcats as well as extensions to proved fields. G. D. H.

851. Geothermal Gradients in Californian Wells. R. W. French. *Oil Gas J.*, 27.4.39, **37** (50), 43.—Oil-well temperatures based on true geothermal gradients are important for reservoir content studies. Geological correlation is possible at times, and subterranean water movements have been detected thereby. The transient temperatures in wells affect mud performance and stability, and also the chemical treatment of wells; they indicate the progress of cementation and the position of cement, and are significant with regard to the thermodynamic analysis of flow-tube design and the use of phase-equibria tables.

Maximum registering mercury thermometers and resistance thermometers are commonly used, the latter being the more accurate and satisfactory. Other types are employed. Curves are given which show the distortion effects on the thermal gradient due to mud circulation and production, and which permit the location of cement. Tables give the approximate depth of the 175° F. isogeotherm in the Californian fields, and the temperatures at the bottoms of deep wells in some Californian fields.

G. D. H.

852. Structures in Sparta–Wilcox Trend Disclosed by Magnetics. W. M. Barret. *Oil Wkly*, 15.5.39, **93** (10), 42–43.—Recent results show that the magnetometric method may be well suited for disclosing anticlinal structures in the Sparta–Wilcox trend. The method is capable of covering large areas rapidly at a comparatively low cost. In this area, because of the feeble magnetic properties of the surface materials, deeper magnetic effects are not masked, whilst the basement rocks are so deep that their magnetic effects do not interfere with the anomalies traceable to folding in the sedimentary section. The Wilcox is the shallowest lithological unit in the trend which carries appreciable quantities of magnetic material. Because of its great thickness and properties, the principal magnetic anomalies of local areal extent are probably due to folding of the Wilcox.

In the Cheneyville and Eola fields the present oil-producing areas are embraced by closed contours which represent magnetic "highs" or maxima.

Experience shows that anomalous horizontal-intensity measurements, in addition to vertical-intensity data, are needed in determining the pattern of the structure.

The Sparta–Wilcox trend may cover 25,000,000 acres, of which only a tiny fraction will enclose Wilcox structures of economic importance. 10,000 acres/day can be covered with 1½ ml. spaced magnetometer stations, which are considered sufficient for locating pronounced Wilcox structures. This will cost less than 2 cents/acre.

G. D. H.

853. Geological Mapping from the Air. L. Desjardins and S. G. Hower. *Oil Gas J.*, 11.5.39, **37** (52), 44.—The tracing of outcropping beds is now being done stereoscopically with far greater facility than the equivalent task can be accomplished in the field by the usual plane table procedure. Individual beds present in the stereoscopic model definite characteristics by which they may be recognized and traced. The commonest criterion is the change in slope which they produce. Scarps which in the field are vague, or because of perspective lose their identity to an observer, are traced easily with the aid of a stereoscope. The vertical interval between beds is also characteristic, and helpful in obscure patches. Correlation is facilitated. With colour photography it may be possible to add such criteria as soil and vegetational colours. The location and type of vegetation are significant.

Highly accurate topographical maps can be produced from aerial photographs by mechanical means. Many of the instruments for this purpose are expensive and cumbersome, but the authors have developed a technique which requires only a Zeiss Pocket stereoscope. Allowance must be made for tilt, and with practice, this can be done without instrumental aid with sufficient accuracy for most geological purposes.

From the geological outcrops and the topographical contours, the structural contours can be constructed.

G. D. H.

Drilling.

854. Thixotropy and its Industrial Applications. H. Freundlich. *Chem. & Ind.*, 1939, **58**, 469–470.—In some cases (sols of oxides) thixotropy may be considered as the first stages of coagulation, in other cases (*e.g.*, bentonite suspensions) thixotropy is closely related to the hydration of the particles.

An interesting application of thixotropy is in petroleum drilling mud. Some drilling muds cause trouble by settling to a hard cake, a thixotropic mud forms a soft gel which is readily re-liquefied.

Paints, printing inks, and certain honeys afford industrial examples of thixotropy.
T. C. G. T.

855. Drilling Patents. J. J. Jakosky. U.S.P. 2,150,169, 14.3.39. Appl. 9.3.37. A method for determining variations in an electrical property of the strata at different depths.

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Production.

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L. F. Lamb. U.S.P. 2,150,228, 14.3.39. Appl. 31.8.36. Well packer.

R. C. Baker. U.S.P. 2,150,310, 14.3.39. Appl. 12.13.38. Protective housing for deep well packers.

C. C. Taylor. U.S.P. 2,150,406, 14.3.39. Appl. 22.4.36. Well cleaner, consisting of two swabs encircling a tubing string and means to move the swabs in opposite directions with respect to the casing by movement of the tubing.

J. P. Black. U.S.P. 2,151,416, 21.3.39. Appl. 3.5.38. Perforation cleaner having a number of wire bristles around the periphery.

J. A. Emerson. U.S.P. 2,151,588, 21.3.39. Appl. 28.6.37. Deep-well pump.

O. A. Brown. U.S.P. 2,151,681, 28.3.39. Appl. 5.6.34. Casing perforator of the mechanical type.

H. C. Yarbrough. U.S.P. 2,152,008, 28.3.39. Appl. 24.11.32. Mechanical casing perforator.

B. P. Wininger. U.S.P. 2,152,298, 28.3.39. Appl. 24.8.38. Connector for bailers and sand pumps.
L. V. W. C.

Crude Petroleum.

857. Hydrogen Sulphide in Ishimbaevo Crude. V. G. Plusnin, E. A. Nikonova and S. S. Spasski. *Neft. Khoz.*, February 1939, **20** (2), 46–49.—It has been found that Ishimbaevo and Krasnokamsk (upper horizon) crudes contain dissolved hydrogen sulphide. Other sulphur crudes, however—for instance Chussov, Samarskaya Luka and Krasnokamsk (lower horizon) crude—do not contain hydrogen sulphide.

In the first four of the above-mentioned crudes formation of pyrogenetic hydrogen sulphide starts at temperatures in the neighbourhood of 200° C., and only with Krasnokamsk (lower horizon) crude at about 300° C.

Ishimbaevo crude, during non-destructive distillation, liberates great quantities (up to 7 kg. per 1 ton crude) of pyrogenetic hydrogen sulphide. At 300° C., hydrogen sulphide formation is almost finished within 1 hr. At 350° C., pyrogenetic hydrogen sulphide is formed from elementary sulphur and sulphur compounds of the disulphide type.

Up to 68% of the pyrogenetic hydrogen sulphide liberated at low temperatures from Ishimbaevo crude is formed from sulphur compounds contained in the asphalt-bituminous fractions, and only 32% from those of the kerosine-lubricating oil fractions.

L. R.

858. Examination of Kusyapkulov Crude. E. A. Kazmina. *Neft. Khoz.*, April–May, 1939, **20** (4–5), 58–60.—The Kusyapkulov field is situated in the Bashkir Republic of the U.S.S.R. on the right bank of the Byelaya river, not far from Sterlitamak.

Kusyapkulov crude differs from other crudes of the Sterlitamak rayon by its higher specific gravity, viscosity, and Conradson coke, and also by its considerably higher contents of asphaltenes, resinous substances, and sulphur.

Distillation of the crude resulted in: 16% gasoline–ligroine fractions (I.B.P. 200° C.), 22% kerosine fractions (200–300° C.), 31% gas-oil and lubricating-oil fractions, and 31% bitumen residue.

The gasoline, ligroine, and kerosine fractions have high sulphur contents. The lubricating-oil fractions have a relatively high specific gravity, a high pour point, and high sulphur contents. The residual oil is a high-quality road bitumen (Russ. Standard No. III). L. R.

859. Patent on Crude Oil. C. M. Blair, Jr. U.S.P. 2,159,312 and U.S.P. 2,159,313, 23.5.39. Appl. 13.12.37. Breaking naturally occurring oil-in-water emulsions from crude petroleum using as emulsifier glue and calcium chloride. W. S. E. C.

Gas.

860. Dangerous Gases in Distillation and Refining Processes. E. Le Q. Herbert. *J. Inst. Petrol.*, 1939, **25**, 323–346.—A paper, with twenty-nine references, which discusses the effects of the various gases and solvent vapours that may be encountered in a petroleum refinery and the precautionary means that are adopted. G. R. N.

861. Protection against Dangerous Gases in the Operation of Cracking Units. E. J. M. Tait. *J. Inst. Petrol.*, 1939, **25**, 347–355.—Gas produced in the cracking operation is discussed under the items, gas-masks, drawing samples, pump-houses, trenches, sumps, etc., pressure relief, drop out and drain lines, clean outs and repairs, furnaces corrosion, and safety instructions. G. R. N.

862. Detection of Gas in Field and Refinery in Iran. Anglo-Iranian Oil Co. *J. Inst. Petrol.*, 1939, **25**, 356–358.—The methods employed for the detection of hydrogen sulphide and sulphur dioxide by the Anglo-Iranian Oil Co. are described.

G. R. N.

863. Safety of Electrical Apparatus for Use in Inflammable Gases and Vapours. C. B., Platt. *J. Inst. Petrol.*, 1939, **25**, 368–376.—A report, which deals with design of bells, telephones, and lamps, which are intrinsically safe for use in atmospheres containing petroleum vapours. The difference between intrinsically safe electric apparatus and flame-proof enclosures is indicated. G. R. N.

864. **Flame Arrestors.** H. H. Radier. *J. Inst. Petrol.*, 1939, **25**, 377–381.—The "gravel box" type of flame arrestor is described. G. R. N.

865. **Physiological Effects of Toxic Gases and Vapours.** T. McClurkin. *J. Inst. Petrol.*, 1939, **25**, 382–391.—A paper in two parts, the first dealing with those gases and vapours likely to be encountered in the petroleum industry, and the second with a group of other toxic gases and vapours. G. R. N.

866. **Detection of Toxic Gases in Industry.** R. B. Vallender. *J. Inst. Petrol.*, 1939, **25**, 392–409.—A comprehensive paper on industrial gases with particular reference to their effects on the health of the worker and to the methods that can be employed for their detection. G. R. N.

867. **Detection of Toxic Gases and Vapours in Industry.** R. B. Vallender. *Chem. and Ind.*, 1939, **58**, 330–333.—The sense of smell and the behaviour of animals are both unreliable as general methods for detecting the presence of traces of toxic gases in industrial atmospheres. The need for simple, rapid, semi-quantitative tests, sensitive to very low concentrations of gases and vapours, is pointed out, and the suitability of existing methods of gas determination discussed.

A series of colorimetric tests have been developed, and those for detecting hydrogen sulphide, hydrogen cyanide, arsine, sulphur dioxide, phosgene, nitrous fumes, chlorine, carbon disulphide, aniline, benzine, carbon monoxide, and chlorinated hydrocarbons are described. Lead acetate paper is used for H_2S, H_2SO_4 containing formalin for C_6H_6, iodine pentoxide or palladium chloride for CO, whilst the halide lamp, which produces a green flame in the presence of halide, is used for chlorinated hydrocarbons. Pamphlets describing the tests are to be issued by H.M. Stationery Office on behalf of the D.S.I.R. T. C. G. T.

868. **Handling of Petroleum Spirit and Solvents.** F. N. Harrap. *J. Inst. Petrol.*, 1939, **25**, 359–367.—A summarized account of the various precautions taken by the petroleum industry and its customers against the various risks attached to the handling of toxic gases. G. R. N.

869. **Vertical Retorts with Continuous Water Gas Production.** A. Thau. *Oel u. Kohle*, 1939, **15**, 419–425.—By far the most widespread type of gas-producing oven is the vertical retort; a table is given showing the increasing production from Dessauer vertical retorts from their introduction in 1906 to an output of 16 million cubic metres daily in 1938 (in Germany). More recent developments include independent continuous water-gas producers which can be connected in series with coke-ovens to give gas of the desired calorific value. An outline is given of recent developments in production that have been made by the leading German gas concerns.

T. T. D.

870. **Thylox Process for the Recovery of Sulphur from Gases containing Hydrogen Sulphide.** G. E. Foxwell and A. Grounds. *Chem. & Ind.*, 1939, **58**, 163–170.—The Thylox process is reviewed. The process may be operated to remove 100% of the H_2S in industrial gases, but the authors consider that the most economical procedure is to remove 98% of the sulphide by the Thylox process and the remaining 2% by use of oxide catch-boxes.

The Thylox process depends on the absorption of H_2S by ammonium thioarsenate solution, and the regeneration of the higher thioarsenate, so formed, by oxidation with the liberation of sulphur. The process may be represented :—

$$\text{Absorption}: \quad (NH_4)_3AsO_2S_2 + H_2S = (NH_4)_3AsOS_3 + H_2O$$
$$\text{Regeneration}: \quad (NH_4)_3AsOS_3 + \tfrac{1}{2}O_2 = (NH_4)_3AsO_2S_2 + S.$$

The process is finding favour even in countries like Japan and America, which have natural supplies of sulphur.

Among the examples quoted of plant operating is one which removes 99·99% of the H_2S from a gas containing 410 grains of H_2S per 100 cu. ft., and representing an absorption of 4½ tons of H_2S per day.

The Thylox process also removes HCN.

The economies of the process and the uses of the sulphur produced are outlined.

T. C. G. T.

871. Gassing Accidents. S. H. Wilkes and D. Matheson. *Chem. & Ind.*, 1939, **58**, 316–323.—The authors, as H.M. Engineering Inspectors of Factories, receive reports on all factory accidents, and in many cases take a direct part in the subsequent investigations. In this paper they indicate how and where gassing accidents have occurred during recent years, and the steps taken to prevent them. The medical aspect and the apparatus both for breathing and for testing poisoned atmospheres are not discussed.

Gassing accidents over the period 1932–37 are tabulated. In 1937, of 196 reported accidents, 92 were due to carbon monoxide, and of these 37 were connected with blast-furnaces. Of other toxic gases, chlorine accounted for 19 cases, trichlorethylene 7, benzol 4, petrol and benzine 1, and bitumen, creosote, oil, and tar for 1.

A warning is stressed to those recovering solvents by distillation. The distillate should not be received in a workroom, and, to ensure adequate cooling from the start of the distillation, the control for starting the heat should be locked to the condensing water-control valve. T. C. G. T.

872. Patents on Gas. G. Budan. E.P. 504,579, 27.4.39. Appl. 10.1.38. Device for determining the contents of poisonous gases in air, *e.g.*, war gases, which are not physically perceptible.

T. D. Kelly. E.P. 504,751, 1.5.39. Appl. 1.11.37. Condensing hydrocarbon gases and vapours for storage and transport purposes in light-weight containers using low pressure, by means of absorbents surrounded by solid CO_2 and arranging for the circulation of cold air through and around the condensing vessels.

H. Dreyfus. E.P. 505,121, 5.5.39. Appl. 6.11.37. Manufacture of hydrocarbons and their oxygen-containing derivatives from CO and H_2 at high temperatures using as catalyst Co promoted with thoria.

W. H. Walton. E.P. 505,302, 9.5.39. Appl. 10.3.38. Apparatus for detecting, indicating, or recording the presence of inflammable gas in mines of the type in which the catalytic action at the surface of an electrically-heated Pt or Pt alloy filament, causes a change in temperature of the filament.

Oldham & Sons, Ltd., and H. Holt, Jr. E.P. 505,565, 11.5.39. Appl. 11.11.37. Apparatus for use in detecting inflammable gas and/or vapour.

G. L. Mateer and W. H. Rupp. U.S.P. 2,157,343, 9.5.39. Appl. 18.9.36. Process of recovering gasoline from hydrocarbon gas mixtures.

F. E. Frey. U.S.P. 2,159,434, 23.5.39. Appl. 27.6.36. Separation of isobutene from butene-2 by passing the hydrocarbon mixture containing butene-2 and *iso*butene past one side of a rubber membrane when the butene-2 dissolves in and passes through more readily than the *iso*butene. The gases containing butene-2 in a more concentrated state are then removed from the opposite side of the membrane.

W. S. E. C.

See also Abstract No. 948.

Cracking.

873. Effect of Gravity of Oil on Cracking Plant Costs. W. L. Nelson. *Oil Gas J.*, 6.4.39, **37** (47), 55.—The relation between the equipment cost and profitability of three cracking plants of capacity 1500 brl. per day of reduced crude and the gravity of their intakes (21°, 24°, and 27° A.P.I., respectively) is discussed. Low-gravity intakes produce less gas-oil, so that smaller cracking units are required. A diagram illustrates the total cost and break-up into material, labour, overhead, and profit for reduced crude of different gravities. For 1500-brl. plants operating on 21°, 24°, and 27° A.P.I. reduced crude, the total cost is given as $195,049, $203,310, and $206,643, and the profit in cents per barrel charge as 10·9, 6·6, and 2·7, respectively. For each of the above plants to make a profit of $60,000 per year it would be necessary to obtain reduced crude at 50, 51, and 52 cents per barrel, respectively, and in order to make any profit, the raw gasoline must be evaluated at 3·39 c., 3·67 c., and 3·88 c. per gallon, instead of the 4 c. taken in the previous estimates. The break-up cost of a 1500-brl.-per-day cracking unit is given as : pipe still, stack, etc., 25·2% ; fractionating tower and shell vessels, 8·3% ; heat exchangers, 1·7% ; condensers and coolers, 7·4% ; pumps, 8·8% ; pump-house and instrument-room, 1·2% ; pipe, valves, and fittings, 12·2% ; instruments, etc., 3·2% ; utilities, 0·9%, tools, etc., 0·6% ; supervision and operation, 2·8% ; drafting, 1·7% ; insurance, liability, etc., 4·5% ; overhead and profit 21·0%. C. L. G.

874. Safety in the Design, Construction, and Maintenance of Combination Cracking Units. C. W. Nofsinger and J. V. Hightower. *Refiner*, 1939, **18**, 73 and 123.—Safety records in the petroleum-refining industry disclose, over the last decade, a marked decline in the rate of accidents and fatalities. The above authors give a comprehensive general discussion on the progress in the evolution of safety measures as directed towards the installation of a combination cracking unit under safety in design, pump installations, protection of pipe, control instruments, electrical equipment problems, safety in construction, hoisting machinery, maintenance, and instruments. G. R. N.

875. Use of a Salt-Removal Drum to Reduce Corrosion. J. C. Albright. *Petrol. Engr*, May 1939, **10** (6), 80.—The installation of a salt-removal drum between the charge pump and the main fractionating column of a cracking plant virtually eliminated corrosion in the plant. The oil charge is heated and mixed with a controlled amount of water to dissolve the salt. Heating of the mixture breaks the oil film surrounding the salt crystals. The operation of heating, mixing and settling is automatic when the proper balance has been established. The cost of the operation is more than offset by the saving in the life of the equipment. R. J. E.

876. Patents on Cracking. Houdry Process Corp. E.P. 505,368, 9.5.39. Appl. 9.11.37. Production of motor fuel by catalytic cracking and pyrolysis of hydrocarbons of wide boiling range. The cracking and pyrolysis are carried out in independent stages and the products blended from both stages.

Universal Oil Products Co. E.P. 506,849, 6.6.39. Appl. 1.2.38. Reforming of hydrocarbon-oil distillates of the gasoline boiling range, accompanied by thermal treatment of relatively high-boiling normally gaseous hydrocarbons, including propene and/or butenes, for the production of high yields of gasoline of controlled vapour pressure and good anti-knock value.

C. C. Chaffee. U.S.P. 2,158,353, 16.5.39. Appl. 19.4.35. Production of motor fuel by a combined process of cracking and polymerization of high-boiling normally liquid hydrocarbons and normally gaseous hydrocarbons.

W. T. Hancock. U.S.P. 2,158,365, 16.5.39. Appl. 4.3.38. Oil-refining system in which cracking stock is preheated below cracking temperature and cracked and then followed by fractionation.

V. Voorhees. U.S.P. 2,160,239, 30.5.39. Appl. 10.7.34. Apparatus for the heat treatment of hydrocarbons consisting of a combustion chamber in which the hydrocarbons are rapidly raised to high temperatures by heat-exchange relation with molten material.

H. E. Drennan. U.S.P. 2,160,249, 30.5.39. Appl. 25.7.36. Process of increasing the anti-knock qualities of hydrocarbons boiling in the gasoline range by contacting them in the vapour phase at 500–1500° F. with gypsum at a flow rate to cause only a minor amount of cracking. W. S. E. C.

See also Abstract No. 923.

Hydrogenation.

877. Liquid-Phase Hydrogenation of Pittsburgh Seam Coal. L. L. Hirst and others. *Industr. Engng chem.*, 1939, **31** (7), 869.—Quantitative procedures for the hydrogenation assay of American coals have been developed. This work involved the perfection of mechanical equipment for continuous operation of the experimental plant and the development of relatively simple and accurate quantitative tests. All the work reported was carried out on Pittsburgh seam coal from the Bureau of Mines experimental mine at Bruceton, Pennsylvania. Assay work on this coal has been completed. Further modifications which have been found necessary for the smooth operation of the plant are reported. Data are presented concerning the effect of varying temperature, contact time, pressure, and hydrogen recirculation rate.

The assay comprised determination of the optimum conditions in liquid-phase hydrogenation for the maximum yield of a " middle " oil consistent with the complete regeneration of the vehicle used in making paste with the original coal.

For Bruceton coal the optimum conditions found were, temperature 400° C., pressure 200–300 atmospheres, 2·75 hr. contact time, and hydrogen circulation rate 100 cu. ft. per hour (measured at 20° C. and 760 mm. pressure). Under these conditions a yield of 66% of " middle " oil (containing 20% boiling in the gasoline range and 80% boiling below 330° C.), and 20–25% of hydrocarbon gases (methane–butane) is obtained in a single pass through the converter. The loss 9–14% consists of 6–8% of unreacted carbonaceous material (fusain and opaque attritus) and 3–6% of oxygen, nitrogen, and sulphur hydrogenated to water, ammonia, and hydrogen sulphide. The " middle " oil contains 15–18% of tar acids and from 3 to 5% of tar bases, and the remaining neutral oil contains 6–8% olefines, 67–70% aromatics, and 22–27% saturated hydrocarbons. H. E. T.

878. Patents on Hydrogenation. G. W. Johnson. E.P. 504,349, 19.4.39. Appl. 19.10.37. Process for low-temperature carbonization or distillation of carbonaceous residues containing oil and solids such as are formed in the destructive hydrogenation of coal-tars or mineral oils, in a rotating drum supplied with filler bodies.

P. Marécaux. U.S.P. 2,159,281, 23.5.39. Appl. 26.5.36. Hydrogenation of carbonaceous substances containing sulphur in the presence of a catalyst adapted to transform carbonaceous compounds into carbonaceous products of lower boiling point. The mixture is subjected during hydrogenation to the action of an absorbing substance adapted to absorb H_2S so as to keep the H_2S content of the mixture between 0·1% and 1%.

M. Pier, W. Simon and P. Jacob. U.S.P. 2,159,511, 23.5.39. Appl. 9.1.35. Hydrogenation of carbonaceous substances heavier than gasoline in the presence of metal sulphide catalysts prepared from thio salts. W. S. E. C.

Polymerization.

879. Thermal Poly Process Adapted to Small Gasoline Plant. Anon. (Summary of Paper by D. M. Wilson to Nat. Gas Assoc.). *Nat. Petrol. News*, 17.5.39, **31** (20), R. 194–R. 202.—A small thermal polymerization plant has been in operation for some time, producing 17,000 gals. polymer gasoline from 40,000 gals. butane daily. The plant is typical of those designed for installation at natural gasoline plants. Cost and yield figures in comparison with those pertaining to two larger plants are presented. H. G.

880. Midget Polymerization Units. W. B. Shanley and G. Egloff. *Oil Gas J.*, 18.5.39, **38** (1), 116.—A selection of five out of the fifty U.O.P. catalytic polymerization units in commercial operation, under design or under construction, has been studied from the point of view of differences in cracking stock, effect of combination topping and cracking, variation of olefin content of gases (19–41%) and size of plant (125,000 cu. ft. to 800,000 cu. ft. per diem).

While the total cracked gases may be polymerized, the stabilizer gas represents only one-third of the total volume, but contains two-thirds of the polymerizable hydrocarbons. However, owing to the lower olefin content of the total gas, it is simpler to control the temperature in the catalyst-bed, which falls as the activity of the catalyst decreases. A catalyst life of over 70 gals. per lb. has been attained, 3870 lb. being an average figure. The utilities required for a unit processing 500,000 cu. ft. of gas are: fuel 650,000 B.Th.U. per hr., water 4000 gals. per hour, process steam 550 lb. per hour, and compressor power 35 h.p.

Where the sulphur content of the polymer gasoline is important, H_2S should be removed from the intake, as it reacts with olefins to give mercaptans. As a rule a sulphur content of 0·3–0·4% in the polymer gasoline is permissible, and this may be obtained by treatment with strong caustic solution or by the U.O.P. copper-sweetening process.

Olefin conversions amount to 85–95%, the *iso*butene polymerizing rapidly, butene 2 less so, and butene 1 with some difficulty. Sufficient C_4 fraction is retained in the polymer gasoline to give a vapour pressure of 18·8–30·9 lb.

The effect of catalyst-bed temperature is shown by a table in which an olefin conversion of 95% at 452° F. is reduced to 76·5% at 406° F.

In two of the units the percentage conversion of individual hydrocarbons was: ethylene 44% and 35%, propene 89% and 98%, butene 1 and 2, 71% and 92%, and *iso*butene 92·3% and 94%. Deep stabilization of cracked gasoline is recommended in order to release the maximum quantity of butenes for polymerization, and allow the maximum quantity of unreacted butane to be retained in the polygasoline. The end-point of the gasoline varies with the activity of the catalyst, but is fairly easy to control.

In the case of a reforming unit producing 76% of 70 O.N. gasoline the yield was increased to 84% and the O.N. by 1·5 to 2, on the addition of a polymer plant, the blended gasoline showing, however, an actual road-rating equivalent to 75 O.N.

Several midget *iso*-octane plants are under construction, operating on butane–butane from the stabilizer, which is caustic-treated before processing and selectively polymerized at 700 lb. and 260–325° F. The crude polymer is distilled to give 90–95% of an *iso*-octenes fraction of 85·5 O.N., the *iso*-octenes being hydrogenated at 75 lb. and 325° F. in the presence of a nickel catalyst, yielding mixed *iso*-octanes of 95 O.N. The bottoms may be hydrogenated to give safety aviation fuel. At present midget *iso*-octane plants are uneconomic in the U.S.A. although required in other countries. They also represent a valuable potential source of further supplies of aviation fuel. C. L. G.

881. Patents on Polymerization. Standard Telephones & Cables, Ltd., and S. G. Foord. E.P. 504,765, 1.5.39. Appl. 24.12.37. Method of stabilizing styrene against further polymerization.

Houdry Process Corp. E.P. 505,369, 9.5.39. Appl. 9.11.37. Process of polymerization of hydrocarbon gases containing olefines and cracking or dehydrogenation of gases to produce olefines capable of polymerization.

V. N. Ipatieff and R. E. Schaad. U.S.P. 2,157,208, 9.5.38. Appl. 20.9.37. Polymerization catalyst for the polymerization of normally-gaseous olefines present in cracked gas mixtures. The catalyst is prepared by mixing tetra-phosphoric acid and a siliceous adsorbent and calcining the resultant mixture.

H. C. Schutt. U.S.P. 2,157,220, 9.5.39. Appl. 26.3.34. Motor fuel prepared by blending a stabilized motor fuel containing cracked and polymerized distillates.

C. R. Wagner. U.S.P. 2,157,224, 9.5.39. Appl. 21.4.33. Process of simultaneously polymerizing hydrocarbon gases rich in olefines and reforming naphtha.

C. R. Wagner. U.S.P. 2,157,225, 9.5.39. Appl. 21.4.33. Polymerization of gases rich in olefines at 850–1100° F. and under 500–2000 lb./sq. in. pressure in at least three stages, the second and third stages being at lower pressures than the first.

H. Haeuber and J. Hirschbeck. U.S.P. 2,159,148, 23.5.38. Appl. 30.6.38. Production of hydrocarbon oil by subjecting to polymerization (Friedel Crafts' reaction), gases containing more than 30% of gaseous olefines chiefly butylenes and amylenes, and subjecting the product to both a hydrogenating treatment and treatment with superheated steam in the presence of caustic alakli.

P. A. Maschwitz. U.S.P. 2,159,746, 23.5.39. Appl. 31.5.35. Method for promoting and controlling the polymerization of hydrocarbon gases to heavier hydrocarbons.

R. F. Ruthruff. U.S.P. 2,160,286, 30.5.39. Appl. 17.12.34. Improved combination of an oil cracking unit, utilizing preferably crude oil as charging stock, and eliminating gasoline and heavy fuel oil as the principal liquid products, together with one or two polymerization units functioning to convert gas from the cracking unit into additional liquid products.

R. F. Ruthruff. U.S.P. 2,160,287, 30.5.39. Appl. 17.12.34. Production of gasoline from hydrocarbon gases containing olefines and butane by first separating these gases into a fraction containing ethylene as the predominant constituent which is thermally polymerized to obtain gasoline; a second fraction containing higher-boiling normally gaseous olefines and butane is subjected to catalytic polymerization to produce gasoline. The H_2 and CH_4 from the thermal polymerization, together with the remaining products and those from the catalytic polymerization, are passed to a common fractionating system. The unconverted gases and the gasoline containing substantial quantities of butane are recovered and recycled to the thermal polymerization system. W. S. E. C.

Synthetic Products.

882. Synthesis of Kogasin and Paraffin Wax in Aqueous Phase. F. Fischer and H. Pichler. *BrennstChemie*, 1939, **20**, 247–250.—The synthesis of kogasin and paraffin wax from CO and H by means of catalysts can be carried out with success only within a narrow temperature range. The heat of reaction must therefore be constantly removed with but little temperature fall.

It has been investigated whether the kogasin synthesis could be carried out successfully in the aqueous phase, with the catalyst suspended in superheated water (about 200° C.). Fe, Ni, Co, and Ru were tried as catalysts, but only the latter two were found to be effective, and to retain their activity in weak acid solutions. Ru is best, optimum results being obtained at high gas pressures and temperatures under 200° C. Quantity and quality of products obtained on Co and Ru are similar to those found in the mean-pressure synthesis.

In the aqueous phase the heat of reaction is effectively removed, for, with the pipe sections employed, yields would be very small in the absence of water. Catalyst activity diminishes more rapidly in the aqueous phase than in the dry phase, possibly, because the catalyst collects in less agitated portions of the liquid in the apparatus, and is consequently gradually withdrawn from the reaction.

It is concluded that synthesis in the aqueous phase is practically not feasible, because (*a*) results are not better than in the dry phase, (*b*) more space is needed, (*c*) the apparatus must be lined with acid-proof material, which makes it expensive, (*d*) a considerable amount of energy is consumed for violent agitation, and (*e*) continuous removal of products of reaction is difficult. L. R.

883. Patent on Synthesis. Ruhrchemie A.-G. and O. Evans. E.P. 504,910, 27.4.39. Appl. 27.7.37. Catalytic conversion of mixtures of CO and H_2 at ordinary pressures at 160–175° C. to increase the content of solid hydrocarbons that boil at high temperatures. Cobalt catalysts are used, activated by the addition of thorium oxide or magnesium oxide, and the speed of flow of the gas over the catalyst is not more than 20 litres per litre of catalyst per hour. In this way 50% or more of the CO entering the reaction is converted into paraffin wax. W. S. E. C.

Refining and Refinery Plant.

884. Catalytic Refining Methods. V. N. Ipatieff. *Oil Gas J.*, 30.3.39, **37** (46), 86.—A comprehensive survey of the two processes used for the synthesis of aliphatic hydrocarbons, alkylation and polymerization, in the petroleum industry is given. The alkylation process differs from the Friedel–Crafts type of alkylation in that an olefine is used as alkylating agent rather than an alkyl halide. The mechanism of the reaction is explained by the interaction of an aluminium chloride/olefine complex with the paraffin. Similar results are obtained with boron fluoride as catalyst. The composition of the product obtained by the alkylation of *iso*butane with ethylene under given conditions shows that the hexanes are the predominating fraction. The method adopted for the separation of the hexanes from one another is described. The formation of *iso*pentane is attributed to a secondary reaction consisting of autodestructive alkylation. The failure to alkylate propane is attributed to the absence of a tertiary C-atom, and the impossibility of isomerization to a compound containing such an atom. Support for this theory is given by the results obtained in the alkylation of naphthenes. Aluminium chloride affects the alkylation of *cyclo*hexane by isomerization to methyl*cyclo*pentane. Boron fluoride fails to produce isomerization, and hence does not affect the alkylation of *cyclo*hexane. The mechanism of the alkylation of aromatic hydrocarbons with various catalysts is described.

In the description of the catalytic polymerization of olefines, the effect of variation of reacting condition is fully discussed. The hypothesis of the intermediate formation of unstable esters with the acid catalyst is supported by the isolation and identification of such esters under modified reaction conditions. R. J. E.

885. Efficiency of a Rotary Distillation Column. B. J. Mair and C. B. Willingham. *Bur. Stand. J. Res. Wash.*, 1939, **22** (5), 519–527.—Of the major characteristics which describe a distillation column—the height equivalent to a theoretical plate (H.E.T.P.), the hold-up and the throughput—the latter is of least importance when the greatest possible separation is desirable.

This paper describes tests with respect to these characteristics with a hydrocarbon mixture in a rotary column, in which the type of plate, speed of rotation, and throughputs were varied.

A full description is given of the rotary distillation column which had a rectifying section 56 cm. long and 5·08 cm. diameter. Three types of rotating members were used : (*a*) baskets with fine holes, (*b*) flat plates, (*c*) cones, and tests of separating efficiency were carried out at speeds of rotation from 250 to 1500 r.p.m. and throughputs 1–10 ml. liquid per minute. The hydrocarbon mixture methyl*cyclo*hexane/*n*-heptane served as the test liquid.

The lowest H.E.T.P. was obtained with the conical rotating members spaced 0·64 cm. apart, with which the following average results were obtained : H.E.T.P., 1·04 cm. ; hold-up, 1·3–1·6 ml. liquid per theoretical plate ; maximum throughput, 10 ml. liquid per minute. Within the reproducibility of these experiments there was no variation in H.E.T.P. for throughputs from 2–10 ml. liquid per minute, and speeds of rotation from 250–1500 r.p.m. D. L. S.

886. Theory and Development of High-Vacuum Distillation. C. R. Burch and W. J. D. van Dijck. *J. Soc. Chem. Ind.*, 1939, **58**, 39–42.—Molecular distillation is characterized by the use of permanent gas pressures so low (10^{-6} atm.) as to play no essential part in determining the speed of distillation, or even whether distillation takes place or not.

The historical development of this method of distillation and the theoretical considerations governing the process are outlined, and factors limiting the large-scale application are discussed.

The invention of the "self-pumping still"—*i.e.*, a still in which the distilling vapours themselves force the uncondensable gases to the place at which the pump can handle them—was of great importance for further technical development. Two types of "self-pumping" stills, which remove the limits set by the finite rate of gas flow in the still itself, are described.

Not every distillable product can be distilled in the ultra-high vacuum units. During experiments by the authors it has been found that some oils show slight decomposition, producing only traces of gas, which, however, upset the molecular distillation by causing severe splashing and subsequent contamination of the distillate. This latter problem appears to be the only limitation to the application of molecular distillation on a large scale. T. C. G. T.

887. Carbonization of Acid Sludge. V. K. Shchitikov and G. N. Krutikov. *Neft. Khoz.*, March 1939, **20** (3), 34–38.—Acid sludge has been carbonized in a batch still yielding coke, coking distillate, acid water, and gas. The present report is concerned with an examination of the coke and the coking distillate obtained.

The carbonization process produced, depending on the type of oil treated: 14·2–19·7% coking distillate, 33·3–34·8% coke, and 27·3–37·3% gas + loss. The coke contains on an average 2·65–3·85% ash and 2·21–3·37% sulphur. It is not suitable for electrode manufacture, but can be used as a fuel.

The coking distillate contains: 22·8–26·3% gasoline distillate, 25–29·3% kerosine distillate, and 42·7–49·3% residual oil. By treating the gasoline distillate with sulphuric acid (2%) and with Zikeyev filter clay in the vapour phase, a gasoline of good stability was obtained. With addition of α-naphthol (10 mg./100 c.c.), the gasoline contained after two months storage 5·6 mg. gum, and had an octane number of 79.

Similar treatment of the kerosine distillate did not give satisfactory results. The product was very dark and had a natron test of 3–4.

The residual oil contains 1·45% sulphur and can be used as a boiler fuel. Asphalt produced from it conforms to the Russian Standard No. II. L. R.

888. Design and Operation of Depropanising Plant. J. C. Albright. *Refiner*, 1939, **18** (4), 131.—Hancock Oil Co. at Signal Hill, California have recently installed a new gasoline plant. The chief features are the three distillation columns. In the first column straight-run gasoline is stabilized to a 81·5% recovery and is sent to storage. In the second column pressure distillate is stripped to approx. 91·6% recovery, and also goes to storage. The third tower handles the overhead, chiefly butanes and propane, from the other two towers plus the raw gasoline from an absorption plant. The stabilized condensate from this stage is used to control the vapour pressure and augment the final blend of straight and cracked gasoline. In all three columns the reboiler fluid is heated refinery gas oil. G. R. N.

889. Uses of Oxygen and Acetylene in the Refinery. H. Jouette. *Refiner*, 1939, **18** (4), 161.—A concise account of the uses of oxygen and acetylene, based on practical experience, in welding, salvage, demolition and metal spraying. G. R. N.

890. Portable Heater for Small Heating Loads. F. L. Kallam. *Refiner*, 1939, **18** (4), 163.—The Millard heater is described. It is a readily portable unit consisting of a rigid circular steel shell mounted on an I-beam skid. The only foundation required is a set of timbers or concrete piers. The heater tubes are placed around the periphery of the firing-chamber and are connected by means of conventional junction boxes. Gas or fuel-oil burners can be used, and firing is through the centre of the long combustion chamber or shell without flame impingement on the tubes. Heating is entirely radiant, but higher thermal efficiency can be attained by adding a second circular shell of identical construction, placing it directly above the primary radiant heater, and using it as the convection section. A double heater of this type with a heat release of 9,000,000 B.Th.U. per hour weighs only 40,000 lb. Since the heater can be shop fabricated, air-setting refractory is used. This material is much lighter than firebrick or cast refractories, and does not crumble or spall at furnace temperatures of 2300–2400° F. The heater can be operated up to 300 lb. working pressure with a coil outlet temperature of 650° F. G. R. N.

891. Solutizer Process for Extraction of Mercaptans. D. L. Yabroff and L. E. Border. *Refiner*, 1939, **18**, 171.—Suitable organic solvents or solutizers have been found, which will improve the mercaptan extracting power of aqueous alkaline solution. For commercial purposes a solutizer must not be decomposed or changed in either cold or hot alkaline solutions, must be very soluble in aqueous caustic but only slightly soluble in gasoline, and its vapour pressure at elevated temperatures must be low, so that steam regeneration can be employed. Sodium and potassium *iso*butyrates are good solutizers with the corresponding hydroxides—a typical treating reagent consists of 3*N*-*iso*butyrate salt in 4–6N-hydroxide solution. Several types of gasoline have been treated in a 250-brl. pilot plant. A 95–250° F. cracked gasoline, which could not be sweetened with 40% by vol. of 15–45° Bé. caustic, was readily sweetened by three-stage extraction using 20% of the solutizer reagent. The regenerated solutizer has a high mercaptan content, but has no adverse effect on its subsequent use. Solutizer treatment does not affect octane number, but improves the lead susceptibility of the gasoline. Solutizer reagent removes effectively alkylphenols, leaving the gasoline unstable. This can be overcome by using a mixed solutizer containing alkylphenolate salts, the treated gasoline then having a definite alkylphenol content. G. R. N.

892. Field Installation of Chromium Sheet Linings in Pressure Vessels. J. T. Shaler. *Refiner,* 1939, **18,** 183.—A comprehensive account of the experience of the Standard Oil Co., California, in lining pressure vessels with chromium steel during the past ten years. Primarily installed for corrosion resistance, the linings described also possessed a desirable heat insulating characteristic, which protects the vessel against thermal shock. It is shown that uncontrolled introduction of water into unlined vessels can induce stresses exceeding the proportional limit of the shell metal, whereas the lining limits cooling rates to safe values. Full details and drawings are given.
G. R. N.

893. Multi-Layer Construction of Thick-Wall Pressure Vessels. T. M. Jasper. *Refiner,* 1939, **18,** 193.—The largest vessel of multi-layer construction built by A. O. Smith weighs 110,000 lb. Vessels of this kind are used for hydrogenation at high temperatures, high-pressure chemical processes, etc. In construction, successive layers of steel are wrapped around a cylinder, being tightened and welded together. The outer layers are usually less than $\frac{1}{4}$ in. in thickness ; the innermost may be thicker. The innermost layer must be leak-proof and be chosen for the purpose desired, whereas the outer layers can have perforations. When the layers are in place the ends are machined for a welding groove. The sections are assembled and welded as solid-wall vessels are. One of the advantages of this type of construction is that it gives opportunity for close scrutiny of the material. In addition, the cost of the plant necessary for the manufacturing process is also less. Stress-relieving is not necessary, and is not recommended. When failure of multi-layer vessels takes place under pressure there is deformation, and no shattering data and photographs are given. G. R. N.

894. Metal Spray Protection of Refinery Equipment. D. R. Johnson and E. K. Dewey, Jr. *Refiner,* 1939, **18,** 199.—In January 1934 the Continental Oil Co. metallized two Dubbs reaction chambers to check corrosion. In October 1934 the coating had peeled badly at the domes, so the surfaces were sand-blasted and re-sprayed with ten coats of aluminium to a total thickness of 0·018 in. This proved successful, and since then the average annual metallizing replacement has been 4–5%, a figure that would be lower but for the rotary cleaners. Similar success was obtained in metallizing the lower sections of bubble towers, a lubricating-oil contact kettle, pump-rods, etc. In sand-blasting a surface of metallizing, the blast should be directed at an angle of about 60° to the surface. First-quality blasting sand only should be used. Blasting should only proceed at such a rate that spraying can quickly follow it. All coke or oil must be removed. The air supplied to the metallizing gun must be dry, and the coating must be evenly applied. The best results have come from applying individual coats from 0·0015 to 0·0020 in. thick. Twelve-gauge wire is preferred, but eleven-gauge is under test. Costs of metal spraying depend in the metal and the area to be covered, and may vary from 0·70 to 2·25 dollars per sq. ft. G. R. N.

895. Condenser Tube Alloys Improved by Antimony. Anon. *Nat. Petrol. News,* 17.5.39, **31** (20), R. 208.—It is claimed that small additions of antimony to brass, including aluminium brass and Admiralty Metal, increase water-corrosion resistance. 0·02% sb. added to 65% α-brass prevents dezincification. As little as 0·007% sb. greatly increases water-resistance, although dezincification still occurs. In this respect antimony alloys are superior to those containing arsenic, since the latter does not inhibit dezincification and may induce inter-crystalline corrosion. H. G.

896. Corrosion-Resistant Linings Reduce Shutdown Time. Anon. *Nat. Petrol. News*, 17.5.39, **31** (20), R. 211.—Summary of A.P.I. May papers.

J. T. Shaler. "Field Installations of Chromium Sheet Linings in Pressure Vessels."

D. R. Johnson. "Metal Spray Protection of Refinery Equipment."

R. K. Hopkins. "Pressure Lining of 11–13% Chromium Steel."

The economic loss due to shut-down time can be reduced by the use of water to cool the vessels to a temperature safe for opening. The use of corrosion-resistant linings, by lowering the maximum temperature differential during cooling, greatly reduces the warping hazard. Vessels have been lined *in situ* by a variety of methods and with a variety of materials. Low carbon, 11–13% Cr sheet spot welded into position, and metal-spray coating with 18–8 stainless steel or aluminium are typical examples of processes which have proved to be successful. H. G.

897. Stainless Steel Applications which Reduce Corrosion. K. E. Luger. *Nat. Petrol. News*, 17.5.39, **31** (20), R. 221.—Recent applications of stainless steel to refinery practice include the use of stainless-steel bubble caps, trays, risers, and hold-down bars. Costs have been reduced by reducing tray thickness to as little as 0·0625 in., the necessary strength being imparted by special designing. Immunity from corrosion, the minimizing of coking and reduction of labour costs owing to the weight reduction, and the ease with which coke is removed from a non-corroded surface are the principal advantages gained. Old reaction vessels have been successfully lined with stainless steel "on the job." 18–8 welding-rod has been used for the building up of worn parts such as valve-bodies, pump-plungers, and valves. H. G.

898. Light-metal Fractionating Apparatus. J. N. Belsen. *Oel u. Kohle*, 1939, **15,** 363–366.—Corrosion tests have shown that pure aluminium is attacked less by the sulphur- and cyano-compounds in crude benzol than is cast iron, so it is suggested that aluminium should be used in the construction of benzol plants. In order to keep costs reasonably low, it is essential that fractionating columns, etc., should be constructed of a number of serial units of standard dimensions, so that these units may be produced on a comparatively large scale, instead of each column being made to individual specifications.

The construction of a unit on these lines is described in some detail and the work illustrated with photographs and diagrams.

A de-benzolizing plant capable of dealing with 10 tons of wash-oil per hour weighs only 1 ton when made of aluminium, compared with 7·5 tons if of iron, costs little more initially, and is cheaper to run. T. T. D.

899. Dimensions of Pipe-Stills. W. L. Nelson. *Oil Gas J.*, 11.5.39, **37** (52), 63.—A mathematical analysis of the cost of construction of pipe-stills is presented in order to provide a method of determining the most economical pipe arrangement. This is based on factors such as the higher cost of many short tubes over that of fewer long tubes, and the high cost of a return bend (which is regarded as equivalent to 18 ft. of tubing, 3–4 sq. ft. of roof, 12–13 sq. ft. of floor, foundations, etc., 4–5 sq. ft. of walls, header boxes, etc. C. L. G.

900. Steam and Air used to De-Coke Still Tubes in New Method. T. E. Garrard. *Nat. Petrol. News*, 19.4.39, **31** (16), R. 146.—In the method described the furnace is heated to a temperature of 1100–1300° F., depending on the nature of the coke deposit, and steam at about 100 lb./sq. in. inlet pressure is admitted. The rate of steam flow, which has a maximum of about 3000 lb./hour, is adjusted according to the character of the coke removed in the steam stream. The removal of coke usually commences in about 1 hr. Too high steam pressure and/or rate of steam flow may result in undue erosion of the tubes if the coke is removed in a coarse form. Air is admitted in increasing quantity with the steam as the rate of coke removal diminishes. The last of the coke is thus burned off. The method is claimed to be no more expensive than the conventional methods and may be much cheaper, the noise and dust nuisance associated with the use of rotatory scrapers is eliminated, and continuous welded construction of the tubes is possible. The disadvantages of the system are :—

(*a*) That the coke seal between the old tubes and the heater boxes is burned away, resulting in leaks at those points.

(*b*) Whether or not the high temperatures reached result in accelerated spreading, distortion of the heaters is still debatable. This effect would be very undesirable, but is evidently not great.

(*c*) The system calls for skilled operators. H. G.

901. Entrainment in Plate Columns. E. M. Baker. *Industr. Engng Chem.*, 1939, **31** (6), 717.—The McCabe–Thiele graphical method for determining the number of plates required for the separation of a binary mixture is modified to allow the effect of entrainment to be introduced. P. D.

902. Choice of a Low-Temperature Insulating Material. K. M. Ritchie and C. C. Vogt. *Industr. Engng Chem.*, 1939, **31** (7), 821.—The conditions of service to be met by a suitable low-temperature insulation include, besides those common to most insulating problems, the question of the possibility of moisture condensing inside the lagging, and so spoiling its efficiency. This can sometimes be overcome by placing the lagging on the inside of the chamber.

A general discussion of this and other effects is given. P. D.

903. Heat Insulation. J. Z. Finck. *Industr. Engng Chem*, 1939, **31** (7), 824.—The three means by which heat is transmitted through an insulation—namely, thermal conductivity of the solid material and the air, convection in the air spaces, and radiation—are discussed. Equations are given for calculating the quantities of heat transmitted by these means, together with illustrative examples. P. D.

904. Silica Aerogel. Effect of variables on Thermal Conductivity. J. F. White. *Industr. Engng Chem.*, 1939, **31** (7), 827.—The conductance of silica aerogel rises with temperature, owing to the fact that it is transparent. This may be overcome by incorporating in the gel some opaque material, which may be either reflecting or non-reflecting. It was shown experimentally that the former type was best, the best lagging being produced by the incorporation of 15% silicon, which gives a gel with conductivity near that of still air.

The effect of the apparent specific gravity of the aerogel on the thermal conductivity was also investigated. P. D.

905. Reflective Insulation. G. B. Welkes. *Industr. Engng Chem.*, 1939, **31** (7), 832.—The theory of reflective insulation is given, and the results of tests on aluminium foil insulations are described. Typical figures for heat losses from roofs, ceilings, and walls are also given. P. D.

906. Relation between Catalytic Activity and Size of Particle. E. W. Thiele. *Industr. Engng Chem.*, 1939, **31** (7), 916.—In the case of reaction taking place on the surface of a solid catalyst which is used in the form of porous grains, two regions can be considered. If the reaction rate is high and the grain size or particle size is small, the activity is proportional to the amount of catalyst present, since the whole surface, both external and internal, is operative. As the grain size is increased, the effects of diffusion of the reactants into the interior of the grains and of the product outwards become noticeable, the activity of the centre of the grain decreasing, until in the limit the activity depends only on the external surface of the grains.

The problem is treated mathematically considering the catalyst grains to be flat plates or spheres. Several cases are considered for a first-order reaction, no change of volume, reaction increases volume, and reaction decreases volume.

The case of a second-order reaction with no change of volume using flat plates of catalyst is also treated.

It is shown that for a first-order reaction the ratio of actual activity to maximum activity remains high (*i.e.*, above 0·7) for values of the modulus $x_s\sqrt{(c/rk)}$ less than unity, using consistent units.

x_s = radius of grains (spheres),
c = activity of unit internal surface of the pores,
r = hydraulic radius of the pores,
k = diffusion coefficient.

P. D.

907. Patent on Distillation. A. R. Nevitt. U.S.P. 2,159,566, 23.5.39. Appl. 24.9.36. Distillation apparatus for hydrocarbon oils. W. S. E. C.

Fire Prevention.

908. Modern Fire-Fighting. J. R. Howcroft. *Chem. & Ind.*, 1939, **58**, 323—329.—The use of vaporizing liquids—*e.g.*, carbon tetrachloride—of carbon dioxide, chemical foam, and mechanical foam for extinguishing fires is traced from the infancy of each to present-day equipment and technique. The suitability of each type for special purposes is discussed. T. C. G. T.

909. Recent Developments in Apparatus for Automatic Extinction of Fires. Anon. *Chem. & Ind.*, 1939, **58**, 439.—Automatic sprinklers based on the fusion of low-m.-pt. alloys, or the rupture of a heat-sensitive diaphragm are well known. The technique of light-sensitive cells, which, in the presence of a flame release a fire-extinguishing material, is developing, and lends itself to cases where instantaneous action is vital—*e.g.*, in the manufacture of highly inflammable compositions by kneading on hot rollers.

An interesting apparatus involves the ignition of a small amount of explosive to give instant rupture of a diaphragm and subsequent release of large volume of fire-extinguishing material.

French patents 826,050 and 826,882 are reviewed. T. C. G. T.

910. Modern System of Fire Protection. Anon. *Chem. & Ind.*, 1939, **58**, 439.—A general review of the advantages of the CO_2 method of fire extinguishing. Particular stress is laid on the fact that some fire-extinguishing materials are liable to cause more damage than the fire they extinguish. Such possibilities are obviated by the use of CO_2. T. C. G. T.

911. Some Methods of Fire Extinguishing. A. M. Cameron. *Chem. & Ind.*, 1939, **58**, 522–527.—Methods of extinguishing fires are traced from their infancy, when water alone was used, to present-day technique. Dry-powder extinguishers are still in use. These depend on either the evolution of an inert gas on heating or on the formation of a fire-proof crust on the burning material—*e.g.*, sodium bicarbonate, silicates, phosphates, borax, and microcosmic salt.

The plunger and turnover types of bicarbonate–acid extinguishers are reviewed.

Halogen extinguishers receive due attention, and it is pointed out that carbon tetrachloride has been used with safety on short circuits up to 200,000 volts. The non-conductivity of these materials makes them very suitable for electrical fires. Methyl bromide is finding extending use, particularly for aircraft, although it is more costly than CCl_4.

It is evident that the CO_2 system has many advantages, especially its cleanliness, great dielectric strength, and non-toxicity. It is noted that certain metals—*e.g.*, magnesium and the alkalis—will burn in CO_2.

Chemical foam systems are largely used in the oil industry. An example is aluminium sulphate or ferric aluminium sulphate and sodium bicarbonate. A foam stabilizer such as saponine or liquorice is added. General practice is to keep tanks full of the necessary solutions and to run mains through the tank farms or to use powder which is fed through hoppers into the water-hose. The necessary precautions for this latter technique are outlined.

Mechanical foam has developed over the last twelve years. In this case only a very small quantity of foam stabilizer is required, and it is fed by a special device into the water-jets, together with a controlled amount of air. 2 lb. of stabilizer and 100 gal. of water will produce a 1000 gal. of foam. The stabilizer is carried in a small tank on the back of the fireman.

" Xaust Suds " is a type of mechanical foam which utilizes petrol engine exhaust gas instead of air for the production of the foam.

The " Mulsifyre " system, which is applicable mainly to oil fires, depends on the ability of a number of jets to impinge water on the surface of the burning oil in a manner sufficient to cause a surface emulsion. Water pressures of 40 lb. are required for heavy oils, and a somewhat higher pressure for petrol.

The sprinkler system, alarm valves and stop valves, together with their automatic accessories, are briefly outlined. T. C. G. T.

Chemistry and Physics of Petroleum.

912. Auto-oxidation of Simple Hydrocarbons in Relation to the Auto-oxidation of Lubricating Oils. H. Hock. *II^{me} Congrès Mond. Pétrole*, 2 (Sect. 2), Proceedings II, 803–806.—Auto-oxidation of solid fuels, of tars and tar-oils, and of motor fuels is discussed, the ageing of oils being regarded as connected with auto-oxidation.

The auto-oxidation of mineral oils is complex, but a solution of the problem has been attempted by quantitative determinations of the peroxides contained in the mineral oils. J. L. E.

913. Oxidation of Mineral Oils. N. I. Tchernojoukov. *II^{me} Congrès Mond. Pétrole*, 2 (Sect. 2), 797–802.—The author has investigated the oxidation of individual hydrocarbons and mixtures. Naphthenic hydrocarbons show increasing tendency to oxidize with increasing molecular weight and number of side-chains. The principal oxidation products are acids, mainly insoluble in ether, which form deposits in the course of oxidation. Highly refined oils containing no aromatics and resins are more liable than others to oxidation. The oxidation of mixtures of aromatic and naphthenic hydrocarbons has been studied. The presence of aromatics reduces the tendency of naphthenes to oxidize and prevents the formation of deposits. It is concluded that the stability of oils towards oxidation is essentially determined by the aromatic content. Resinous bodies have been found to act as inhibitors in preventing the formation of acid products. Modern methods of refining which are based on the removal of aromatic hydrocarbons by solvents are consequently not entirely satisfactory. S. R.

914. Oxidation of Naphthene-Base Oils by Oxygen. Parts 2 and 3. K. I. Iwanow. *Petrol. Z.*, 1938, **34** (33), 1–7; (34), 1–6.—The work described in Part 1 (see Abstract No. 164, 1939) was extended by varying the conditions of the experiment singly, the following observations being made :—

1. *Influence of Time* : T. = 150° C.; $p(O_2) = 15$ at.—Rate of production of carboxylic-acid groups was determined, the acids being isolated and their ultimate analysis carried out at successive stages. In addition, unsaponifiable oxygen compounds were isolated, determined, and subjected to ultimate analysis.

The results of this investigation indicate that the rates of oxidation of similarly refined paraffinic and naphthenic oils are equal or nearly so.

In all cases, reaction starts only after a short induction period, then proceeds rapidly, with a subsequent retardation in rate.

The more highly refined fractions are in each case the more rapidly oxidized.

In the case of the low-grade raffinates, little change in yield of acid bodies or in saponification value was observed under these conditions after 3 hrs. up to the final time of 14 hrs. The author attributes this fact to negative catalytic action on the part of tarry reaction products.

Carboxylic acids are the principal products of the oxidation. The rate of production of high-mol.-wt. acids is greater the more highly refined the oil. The quantity of carboxylic acids produced is at first proportional to the period of oxidation, but remains constant or decreases after a few hours. With the highly refined fractions, the quantity decreases after about 4 hrs., the further increase in acidity being due to formation of low-mol.-wt. hydroxy-acids. It is suggested that the latter are oxidation products of the high-mol.-wt. acids.

In all cases the unsaponifiable residue was shown to have a small but definite oxygen content.

2. *Influence of* $p(O_2)$: $t = 3$ hrs. ; T. = 150° C.—Oxygen and also air were employed at various pressures and partial pressures of O_2. The oxidation products from all four fractions were examined as in 1 (above).

It was found that the extent of oxidation is directly proportional to $p(O_2)$. The coefficient is slightly higher with the paraffinic oils. It is also higher the more highly refined the oil fraction.

Examination of the products, as before, shows that alteration of pressure of oxygen (2–15 at.) or air (25–60 at.) does not sensibly alter the course of the reaction in a manner comparable with the effect of changing time at constant $p(O_2)$ (1, above).

The observed proportionality between $p(O_2)$ and rate of oxidation excludes the possibility of heterogeneous reaction. The oxidation is homogeneous, and is brought about by O_2 dissolved in the liquid phase.

3. *Influence of Ratio : Exposed Surface/Volume.*—In the cases of the low-grade raffinates, increase of the surface–volume ratio affects the reaction in a manner similar to increase of time at constant $p(O_2)$ and T. (1, above).

The highly refined fractions were not completely examined. Under certain conditions the reaction proceeded with explosion.

4. *Influence of Temperature.*—Over the range examined (130–160° C.), increase in T. at constant $p(O_2)$ and time produces a strongly marked acceleration of oxidation, and affects the yields, properties, and ratios of carboxylic and hydroxy-acids in a manner comparable with the changes produced by the time variation above. The maximum temperature coefficient of oxidation (= 2) is shown between 130° C. and 150° C., the rate of acceleration being reduced at higher temperature.

5. *Influence of Container Surface.*—Increase in area of oil–glass interface, other conditions remaining equal, was found to retard oxidation. It is concluded that the reaction contains at least one stage in which oxidation involves a chain reaction, the reaction chains being broken at the solid–liquid interface.

Numerous graphs and tables of analysis figures are given, together with an extensive bibliography. C. G. G.

915. 2 : 6-Dimethylheptane : its Synthesis, Properties, and Comparison with an *iso*-Nonane from Petroleum. J. D. White, F. W. Rose, Jr., G. Calingaert and H. Soroos. *Bur. Stand. J. Res., Wash.*, 1939, **22** (3), 315–319.—The isolation from a mid-continent crude of an isomeric nonane, b. pt. 135·2° C., tentatively identified as 2 : 6-dimethylheptane, has already been described. In order to establish more definitely the identity of this material, synthetic 2 : 6-dimethylheptane was prepared by coupling *iso*butyl magnesium bromide with ethyl formate, producing 2 : 6-dimethylheptanol-4 in a 74% yield.

This was hydrogenated in three steps, and the product purified by treatment with 98% H_2SO_4, washing, drying, and refluxing over sodium–potassium alloy, and finally fractionating carefully in a column packed with crushed carborundum.

The purity of the synthetic hydrocarbon was found to be 99·6 mole-%, and its properties, extrapolated to a purity of 100 mole-%, were found to be as follows : b. pt. at 760 mm. Hg. 135·21° ± 0·02° C. ; f. pt. in air − 102·95 ± 0·10° C. ; density at 20° C. 0·70891 ± 0·00003 g./ml. ; refractive index n_D^{20} 1·400 73 ± 0·00005 ; aniline point 80·0° ± 0·3° C.

The properties of the *iso*nonane from petroleum are in good accord with those of the synthetic product. D. L. S.

916. Separation of Hydrocarbons of High Molecular Weight by Adsorption on Silica Gel. C. B. Willingham. *Bur. Stand. J. Res., Wash.*, 1939, **22** (3), 321–327.—Preferential adsorption by silica gel has been used for several years for separating mixtures of hydrocarbons, but no data have so far been reported concerning the effectiveness of separation of hydrocarbons of high mol. wt.

The apparatus used for this work was essentially the same as that described in a paper by Mair and White in 1935, except that both the silica-gel tube and the receiver were equipped with a heating-jacket. The four hydrocarbons used were synthetic materials, and experiments were carried out on binary mixtures. A sharp separation of 5-(7-tetrahydronaphthyl)docosane from 5-(2-decahydronaphthyl)docosane and of n-dotriacontane from 1-(p-diphenyl)octadecane was obtained. Some separation of 1-(p-diphenyl)octadecane from 5-(7-tetrahydronaphthyl)docosane was found, but this was not so sharp as with the two preceding mixtures. No separation of n-dotriacontane from 5-(2-decahydronaphthyl)docosane was obtained.

For the first three mixtures cited above, the capacity of 20 gm. of the gel to absorb preferentially the more aromatic components was found to be 1·8, 3·3, and 0·8 gm., respectively. D. L. S.

917. Heats of Combustion of Tetramethylmethane and 2-Methylbutane. J. W. Knowlton and F. D. Rossini. *Bur. Stand. J. Res., Wash.*, 1939, **22** (4), 415–424.—Reliable values for these thermochemical constants are needed because of the present-day importance of the pentanes. Synthetic tetramethylmethane was purified until the final product contained only 0·3 mole %-impurity with a C/H ratio not far removed from the hydrocarbon itself. The 2-methylbutane was prepared at Brussels, and contained impurities estimated at less than 0·1 mole-%.

Both compounds were thoroughly dried and burnt in purified oxygen. Their heats of combustion in the gaseous state in O_2 at 25° C. and a constant total pressure of 1 atm. to form gaseous CO_2 and liquid H_2O were found to be: tetramethylmethane 3516·53 $\pm$ 0·94 international kilojoules/mole; 2-methylbutane, 3528·03 $\pm$ 0·62 international kilojoules/mole. Converted into kilocalories by means of the generally accepted factor 1/4·1833, these values become 840·61 $\pm$ 0·23 and 843·36 $\pm$ 0·15, respectively.

Combining these values with those previously reported for n-pentane shows that in the gaseous state at 25° C. and 1 atm. the energy content of n-pentane is greater than that of tetramethylmethane by 19·59 $\pm$ 1·29 kilojoules or 4·68 $\pm$ 0·31 kilocalories/mole, and greater than that of 2-methylbutane by 8·09 $\pm$ 1·08 kilojoules or 1·93 $\pm$ 0·26 kilocalories/mole. D. L. S.

918. Type Analysis of High Boiling Hydrocarbon Oils. A. V. Grosse. *Refiner*, 1939, **18** (4), 149.—The author discusses the theory underlying the analysis of paraffinic and mono- and poly-naphthenic oils. The specific refraction method of Waterman and his co-workers is examined, and it is shown that the hydrogen/carbon ratio can be used with greater theoretical justification, accuracy, and simplicity in the determination of the number of rings per molecule in saturated oils than the specific refraction. It is considered that the percentage of paraffinic or naphthenic hydrocarbons present in a saturated oil cannot be determined by existing methods. A naphthenicity index and an aromaticity index are proposed. The former is defined as the difference between the hydrogen/carbon ratio of the oil and that of the paraffin having the same number of carbon atoms, multiplied by 100. G. R. N.

919. High-Octane *iso*Paraffinic Fuels. S. F. Birch, A. E. Dunstan, F. A. Fidler, F. B. Pim and T. Tait. *Industr. Engng Chem.*, 1939, **31** (7), 884.—In the presence of concentrated sulphuric acid the lower olefins, with the exception of ethylene, react with considerable ease with *iso*butane to yield products consisting essentially of *iso*paraffins. The reaction carried out in the liquid phase at temperatures in the range — 10° to 30° C., is exothermic, the heat of reaction being of the order of 500–600 B.Th.U.'s/lb. of unsaturated C_4 hydrocarbon reacting. From the reaction product a fully saturated fraction (boiling from 27° to 185° C.) may be isolated by distillation, consisting almost entirely of *iso*paraffins from *iso*pentane to *iso*decanes and higher. The high octane rating, roughly 90+ of this fraction, coupled with its low sulphur content, renders it an excellent material for 100-octane aviation gasoline. Propylene, *iso*butene, 1- and 2-butene, trimethylethylene, and the lower polymerides of *iso*butene, di- and tri-*iso*butene all react smoothly with *iso*butane to give good yields of saturated products. Of the paraffins used in the reaction, *iso*butane, *iso*pentane, and *iso*hexane (2-methylpentane) reacted smoothly, although the octane number of the saturated product decreased rapidly with increasing length in carbon chain of the *iso*paraffin used in the reaction. By repeated fractionation, indications were obtained of the presence of 2 : 4 and 2 : 5-dimethylhexanes and 2 : 3 : 4- and 2 : 3 : 3-trimethylpentanes, and further small quantities of *iso*pentane, 2 : 3-dimethylpentane, 2 : 3- and 2 : 4-dimethylpentanes and 2 : 2 : 5-trimethylhexane have been isolated from the reaction mixture in the poly*iso*butene–*iso*butane reaction.

The effect of varying the reaction conditions, upon the yield and nature of the product is outlined. It has been demonstrated that the unsaturated four-carbon fraction obtainable from normal cracking operations is a satisfactory starting material for commercial operation when used with an *iso*butane concentrate from natural gasoline stabilization. The acid consumption and the heat evolved in the exothermic reaction are also discussed. H. E. T.

920. Attempts to Prepare the Methylene Radicle by Thermal Decomposition of Hydrocarbons. F. O. Rice. *J. Amer. chem. Soc.*, 1939, **61,** 213.—An attempt to prepare methylene by passage of methane or other hydrocarbons over heated filaments resulted in the production of a large enough supply of dimethyl telluride from Te mirrors to identify it (m. p. $-19{\cdot}5°$). The attempt to prepare ketene by passing a mixture of carbon monoxide and methane or other hydrocarbons over a hot filament was unsuccessful. The conclusion is that trivalent carbon radicles are the primary products of organic dissociations, and even in the few cases in which methylene is the primary product it passes readily into the trivalent state. R. D. S.

921. Kinetics of Decomposition of *n*-Butane. I.—Normal Decomposition. L. S. Echols and R. N. Pease. *J. Amer. chem. Soc.*, 1939, **61,** 208–212.—This is the first of a series of papers on this subject, the investigation being prompted by suspected complications in the pyrolyses of propane and the butanes, which, from flow experiments at 1 atm., appear to be homogeneous dissociations of the first order. It was found that pure nitric oxide inhibits *n*-butane decomposition, an effect that is partly transient, thus confirming the belief that the mechanism is a radical chain reaction. Later, it was found that propylene, a reaction product, also effects transient inhibition. Kinetic data were obtained from pressure measurements at constant volume. The normal decomposition was investigated between 480 and 535° C. and from 100 to 600 mm. pressure, and it was found that the reaction was not strictly of the first order; initially, an order of 5–6 is required, and comparison of times to 10% decomposition for different initial pressures indicated an order of about 1·3. It was demonstrated that the complexity of the reaction was not due to impurity in the butane employed. A semi-empirical equation is given to fit the data. R. D. S.

922. Bromination of Trimethylethylene. (1) W. E. Vaughan and F. F. Rust. *J. Amer. chem. Soc.*, 1939, **61,** 215–216. (2) J. B. Conn, G. B. Kistiakowsky and E. A. Smith. *Ibid.*, 1939, **61,** 216–217.—When 1 vol. chlorine and 2 vols. *iso*butene reacted together at 70°, Vaughan and Rust found 99% consumption of chlorine, 93% by substitution; but when these gases were passed together over granular calcium chloride at 109° the chlorine completely disappeared, 19% of it producing hydrogen chloride by substitution. These authors, therefore, cast doubts on the validity of the figure for the heat of catalytic addition of bromine to trimethylethylene obtained by Conn, Kistiakowsky and Smith (*J. Amer. chem. Soc.*, 1938, **60,** 2764–2771; *J. Instn Petrol.*, Abstr. No. 310, 1939), as the latter tested the effluent gas in their experiments for unreacted halogen and for substitution by test-papers and relied on refractive indices as criteria of the purity of the products, there being no literature value for trimethylethylene dibromide. By such tests the last-named authors detected substitution occurring during dynamic bromination of *iso*butene and *cyclo*hexane, although trimethylethylene seemed to react cleanly. Vaughan and Rust, in an attempt to confirm this, passed bromine, trimethylethylene, nitrogen, and carbon dioxide over calcium bromide–asbestos at 82°. Test-papers showed no unreacted bromine or acid, and the catalyst was found to be uncontaminated with liquid condensate. After topping of the product to remove unreacted olefin the residue was fractionated. This showed definitely that the product of reaction is a mixture, and the difficulty of avoiding substitution reactions when halogenating tertiary olefins.

In reply, Conn, Kistiakowsky and Smith admit the correctness of the criticism, but believe that the error thus introduced is rather small, as the catalyst they used was inactive owing to previous extended use, so that the secondary reactions described above may easily have been less pronounced in their experiments. Even if the yield of monobromides was considerable, they argue that this could not seriously have affected their thermal data, and so the original estimate of the over-all error is adequate. R. D. S.

923. Cracking of Kerosine as Function of Pressure and Temperature. C. Otin and S. Savencu. *Monit. Pétr. roum.*, 1939, **40** (10), 635–639; (11), 705–708.—A kerosine was heated for varying periods of time at different temperatures and pressures, alone and with catalysts, and after each treatment the properties of the product were compared with the original. First, it was heated alone for 2, 4, 6, 8, and 10 hrs. (1) at 170° C. and atmospheric pressure, (2) at 115° C. and 10 kg./cm.^{2} pressure, (3) to an initial temperature of 240° C. at 20 kg./cm.^{2} pressure. On examination of the physical and chemical constants of the products, including distillation, the authors concluded that the only factor favourably influencing the yield of light products was temperature. Next, the kerosine was heated to various temperatures for 2 hrs. at normal, at 10, and at 20 kg./cm.^{2} pressure with 5% concentration of finely divided, chemically pure metals, oxides, chlorides, and sulphates. Except for chlorides, these had only a feeble catalytic effect on the cracking. The chlorides of magnesium and iron had a noticeable influence, but aluminium chloride had a most pronounced effect. To investigate the latter more fully, the time was also varied to 4, 6, 8, and 10 hrs. with 5% aluminium chloride and at pressures of 1, 10, and 20 kg./cm.^{2}; and 1% and 10% concentrations of aluminium chloride were used at the same pressures for 2 hrs. In all these experiments increased time and pressure tended to increase the yield of light bodies, but the effects of temperature and increase in proportion of catalyst were the most profound. Of other catalysts tried only aluminium bromide gave results comparable to aluminium chloride.

The authors' conclusions are that only temperature has a favourable effect on cracking, particularly if no catalyst or a badly chosen catalyst be employed; but if the catalyst is correctly chosen, then time and pressure may also have a marked effect.
R. D. S.

924. Comparative Efficiency of Catalysts in Polymerising Unsaturated Hydrocarbon Gases under Pressure. D. Rudkovskii, G. Shevtsova and G. Pemeller. *Petrol. Engr*, April 1939, **10** (7), 65.—Laboratory-scale experiments for comparing the efficiency of catalysts in the polymerization of olefines are described. Of the catalysts examined, clay had a poor catalytic action and was rapidly poisoned. Molten zinc chloride was highly active, but was quickly poisoned by solution of polymerization products. Zinc chloride deposited on chamotte carrier proved a very effective catalyst, but rapidly deteriorated owing to the deposition of coke. Phosphoric acid on a solid carrier was the most efficient of the catalysts examined. Its efficiency is explained by the assumption that intermediate phosphoric esters are formed which soon decompose with regeneration of the acid and growth of the olefine molecules. Of the three phosphoric acids the pyro-acid was the most effective. R. J. E.

925. Industrial Use of the Alkaline Waste Liquors Derived from Refining Cracked Naphthas. C. N. Dacu. *Monit. Pétr. roum.*, 1939, **40**, 151.—Mercaptans and phenolic compounds were extracted (on a laboratory scale), by methods which lend themselves readily to industrial applications, from alkaline solutions derived from treating cracked naphthas.

By entrainment with steam at about 100–110° C. approximately 2·5% mercaptans were obtained, boiling within the range 120–250° C.

Subsequently, after obtaining the mercaptans, the phenols were extracted from the same solution by the following methods :—

(*a*) Entrainment with superheated steam.
(*b*) Treatment with sulphuric acid of various concentrations.
(*c*) Treatment with hydrochloric acid of various concentrations.
(*d*) Treatment with carbon dioxide.

Of the above methods (*b*) gave the highest yields, with about 27% of phenols on the original solution. The optimum sulphuric-acid concentration, in respect to yields and resulting phenol quality, was found to be 20%. Method (*d*), however, is more likely to find application in refinery practice (about 19% phenol yield) because of the availability of CO_2 in the stack gases. G. S.

926. Aromatisation of some Homologues of *cyclo*Pentane and Paraffins. B. A. Kazanski and A. F. Plate. *Nat. Petrol. News*, 5.4.39, **31** (14), R. 134.—It has been shown that *cyclo*pentane and its simplest homologues are hydrogenated in the presence of platinized carbon in an atmosphere of hydrogen at a temperature of 300–310° C. The higher homologues such as normal and secondary butyl*cyclo*pentane and *iso*amyl-*cyclo*pentane suffer not only hydrogenation, but a measure of aromatization. In an atmosphere of CO_2 or nitrogen, yields of aromatics as high as 35% have been obtained. Is it assumed that the side-chain is cyclicized, the hydrindane formed rupturing in the presence of excess hydrogen, to form *O*-ethyltoluene. *N*-octane in an atmosphere of nitrogen yields 10% of aromatics, the permanganate oxidation products of which are benzoic and phthalic acids. Methyl-, ethyl-, and propyl-*cyclo*pentane do not show this reaction. H. G.

927. Preparation of Low-Temperature Hydrogenation Catalysts. B. Dudley Sully. *Chem. & Ind.*, 1939, **58,** 282–284.—The disadvantages of the Raney catalyst have led to the development of a nickel catalyst by other means. The catalyst has been developed primarily for the liquid-phase hydrogenation of crotonaldehyde to butyl alcohol. Nickel carbonate is precipitated from a solution of the sulphate by the addition of sodium carbonate. The nickel carbonate is readily reduced at 310° C.

The colloid mill has been adapted for the preparation of mixed copper and nickel catalysts, the carbonates being passed through the mill in a mother-liquor of sodium sulphate.

The activity of the catalysts is assessed by testing the rate of hydrogenation of *iso*-pulegol to menthol. A suitably active catalyst will complete 80% of this hydrogenation in 40 mins. under the conditions of test. T. C. G. T.

928. Inflammation of Mixtures of Air with Diethyl Ether and with Various Hydrocarbons at Reduced Pressures : Green Flames. M. S. Hsieh and D. T. A. Townend. *J. chem. Soc.*, February 1939, 332–337.—This investigation was carried out to examine more fully the nature of " green flames " which certain mixtures of diethyl ether and air produce at low pressures, the nature of their visible emission and the inflammable ranges of ether–air and hydrocarbon–air mixtures. The latter were determined in a horizontally-mounted glass tube electrically heated with asbestos-covered nichrome wire. The normal flames were initiated by a high-tension spark. As the pressure was reduced the limits of inflammability approached one another and green flames were produced, being most intense at the critical pressure where the higher and lower limits coincide (90 mm. at 20° C. ; 80 mm. at 100° C. ; 78 mm. at 150° C., corresponding to 5% ether in air). Similar phenomena were observed with *n*-hexane–air, propane–air, and methane–air mixtures. The latter series give three pressure limits of inflammability within a very narrow range of mixtures near 12·8% methane in air. It is inferred that the emission of green flames is common to all hydrocarbons.

The green flames are attributable to the Swan bands arising from C_2 molecules which emit at 4381 and 4737 Å in the green region of the spectrum, and are favourably influenced by deficiency of oxygen and by reduced pressure. The C_2 molecules are present in an excited state at temperatures and/or pressures below which there is any evidence of aggregated carbon, but how they arise is speculative. R. D. S.

929. Mechanism by which " Cool " Flames may give rise to " Normal " Flames. Part I. Inflammable Ranges of Ether–Air Mixtures in Closed Vessels. M. S. Hsieh and D. T. A. Townend. *J. chem. Soc.*, February 1939, 337–340.—The ignition of certain hydrocarbons is brought about in the temperature range 300–400° by a two-stage process, the normal flame occurring after the passage of a cool flame and after a definite short time interval. If the pressure is sufficiently high, the higher hydrocarbons ignite in the cool-flame range by a one-stage process, ignition being almost as violent as detonation ; thus correlating engine-knock with the probable spontaneous ignition of the unburnt charge ahead of the flame. It was fairly well established that spontaneous ignition arising from prior cool-flame formation is the same, whether the cool flames are initiated by hot-wire in the cold or by heating. At the minimum ignition pressure the inflammability range was greater, the higher the temperature. The minimum pressures for normal ignitions were much higher than for cool flames. The authors consider that the initiation of normal flames in the cool-flame range at a critical pressure is a sudden development of pressure greater than that which can be

ascribed to cool flames. When the limiting pressure for normal flames in the cool-flame range was reached, ignition occurred some distance after the cool flame passed down the tube and the normal flame travelled forward to, and replaced, the cool flame. The authors believe that the superposition of the normal-flame range on the cool-flame range arises by a similar process for artificial as for spontaneous ignition.
R. D. S.

930. Mechanism by which " Cool " Flames may give rise to " Normal " Flames. Part II. Inflammable Ranges of Higher Paraffin Hydrocarbons in Air : Establishment of " Cool " Flame Ranges at Ordinary Temperatures and High Pressures. M. S. Hsieh and D. T. A. Townend. *J. chem. Soc.*, February 1939, 341–345.—The general tendency of increasing pressure on mixtures of combustible gases with air and oxygen is to widen the limits of inflammability, chiefly at the upper limit. Previous work on higher paraffin hydrocarbons showed also that not only was the widening progressively greater as the series was ascended, but in each case, on the attainment of an adequate pressure, which decreased in the same order, it became accentuated abruptly. The higher paraffins behave in a similar manner to ether in spontaneous ignition experiments in the cool-flame range; hence, from the relationship between spontaneous ignition and inflammability, observed in the preceding paper, the corresponding cool-flame inflammation ranges ought to exist with higher paraffins at ordinary temperatures in a way similar to those known to exist with ether–air mixtures. Further, owing to (*a*) minimum pressures and (*b*) time-lags for spontaneously developed cool flames, both being greater for hydrocarbons than for ether–air mixtures, and to (*a*) and (*b*) decreasing as the paraffin series is ascended, the cool-flame ranges should be located at progressively decreasing initial pressures in the same order. All these predictions were confirmed in re-determinations of the limits of inflammability of hexane, butane, and propane : at 100° C. the cool-flame ranges were : above 5 atm., above 9 atm., above 12 atm., respectively.
R. D. S.

931. Mechanism of Additions to the Double Bond. Part VI. Kinetics of Gaseous Associations. G. A. Benford and A. Wasserman. *J. chem. Soc.*, March 1939, 362–367.—The velocity coefficient (k) of a bimolecular reaction can be expressed in terms of a steric factor (P) and a collision frequency (Z) so that $k = A_e^{-E/RT} = PZ_e^{-E/RT}$, where E is the activation energy. For gaseous reactions involving atoms or diatomic molecules $P =$ about 1 and $A = Z$ approximately, but in the diene synthesis in the gaseous phase P is probably < 1. Experiments are described in which gaseous *endo*-di*cyclo*pentadiene was formed from the association of gaseous *cyclo*pentadiene. A study of the kinetics of the reaction between 79° and 150° at initial pressures between 154 and 735 mm. confirms the impression that P is much smaller than unity. A qualitative explanation for this is tendered.
R. D. S.

932. Mechanism of Additions to the Double Bond. Part VII. Chemical Equilibrium in Solution and in the Gaseous State. G. A. Benford and A. Wasserman. *J. chem. Soc.*, March 1939, 367–371.—The constants of two association equilibria (*a*) $C_2H_4 + H_2 \rightleftharpoons C_2H_6$; (*b*) $2C_5H_6 \rightleftharpoons C_{10}H_{12}$ (di*cyclo*pentadiene) were compared in the gas phase and in solution by using van't Hoff's equation involving the solubilities of the reactants and of the products. The reactants and the products of equilibrium (*a*) possessed numerically smaller heats of solution and larger statistical weight of the condensed molecules than the molecules of association (*b*). It was shown that the heat changes of both gaseous associations are not much altered by the presence of the solvent, and also that the statistical weight of ethane is of the same order of magnitude in both states, but that the statistical weight of di*cyclo*pentadiene is somewhat larger in solution than in the gas phase.
R. D. S.

933. Mechanism of Additions to the Double Bond. Part VIII. Equilibrium of Gaseous Associations. B. S. Khambata and A. Wasserman. *J. chem. Soc.*, March 1939, 371–375.—The non-exponential factor (a function of the translational, rotational, and vibrational partition functions) of the equilibrium constants of the association of gaseous *cyclo*pentadiene to gaseous di*cyclo*pentadiene was determined from the kinetics of the formation and decomposition of di*cyclo*pentadiene in B.P. paraffin. The kinetic measurements were carried out between — 1° C. and 175° C. and the solubilities between 27° C. and 111° C. The translational, rotational, and vibrational partition functions were calculated for both reactant and product, and it was deduced that at 80° C. the vibrational partition function of di*cyclo*pentadiene is at least 500 times the square of that of *cyclo*pentadiene. Qualitative confirmation of this calculation is adduced by consideration of models. R. D. S.

934. Mechanism of Additions to the Double Bond. Part IX. Kinetics of the Association of *cyclo*Pentadiene in Carbon Tetrachloride Solution and in the Pure Liquid State. G. A. Benford, H. Kaufmann, B. S. Khambata, and A. Wasserman. *J. chem. Soc.*, March 1939, 381–387.—The study of the mechanism of the association of *cyclo*pentadiene in carbon tetrachloride solution showed that the kinetics of the reaction were not measurably influenced by the presence of oxygen, peroxides, or acetonitrile, and that the reaction is of the second order at all temperatures. In the pure liquid state, however, the second-order velocity coefficients are constant at — 2° C., but they increase at temperatures up to 39·4° C. This is considered due to the fact that at the beginning of the run the " solvent " is *cyclo*pentadiene, but at the end it is di*cyclo*pentadiene. The mechanism of the association is bimolecular in both carbon tetrachloride and the pure liquid state. R. D. S.

935. Mechanism of Cracking. Part 1. Kinetics of Inverse Diene Synthesis in Solution and in the Pure Liquid State. B. S. Khambata and A. Wasserman. *J. chem. Soc.*, March 1939, 375–381.—The kinetics of the decomposition of *cyclo*pentadienebenzoquinone and of *cyclo*pentadiene-α-naphthaquinone were measured in benzene solution and the cracking of di*cyclo*pentadiene was studied in B.P. paraffin solution and in the pure liquid state. The experiments were carried out at atmospheric pressure between 49° C. and 175° C. In solution all these inverse diene syntheses are of the first order. No induction period occurred in the decomposition of *cyclo*pentadiene, nor did peroxidic intermediate compounds, glass powder, Hg, PbO_2, MoS_2, and SnS affect the rate, indicating that the decomposition is not a chain reaction. The non-exponential factors of the velocity coefficients are of the order of magnitude of interatomic vibration frequencies, and it was concluded that the mechanism of the inverse diene synthesis is unimolecular in solution and in the pure liquid state. R. D. S.

936. Physics of Flames and Explosions of Gases. B. Lewis and G. von Elbe. *J. Appl. Phys.*, 1939, **10** (6), 344.—This paper presents a concise summary of our present knowledge. The subjects dealt with include ignition, flame propagation, detonation, flames resulting from the diffusion of one of the reactant gases into the other, and the state of the burnt gas. P. D.

937. " Transformation " and Detonation. O. Herstad. *Oel u. Kohle*, 1939, **15**, 385–388.—In the ordinary state, a drop of liquid on a hot surface is in contact with the surface on one side, and with a mixture of air and vapour on the other ; in the " transformed " state the drop of liquid is separated from the surface by a thin film of vapour. (For earlier work on this subject see Abstracts Nos. 836 and 1423 of 1938.)

The author claims that his experimental work has shown that for a complete solution of the problem, knocking must be considered in relation to the transformation properties of the fuel. In investigating the ignition properties of fuels, the author condemns the drop method of analysis, since, owing to variations in physical properties between different liquids, drops from the same orifice will have different weights and volumes, and different rates of formation. Consequently, as the test apparatus has a combustion space of fixed dimensions, the same ratio of fuel vapour to air will not be obtained on adding drops of different liquids, and strictly comparable results for the ignition temperatures will not be obtained.

A diagram is given of four typical S.I.T. curves as obtained on the " Zundwertprüfer," one of which exhibits the " Zundlücke " first described by Jentzsch. The explanation of this phenomenon by Zerbe and Eckert is refuted and replaced by one based on the transformation concept. The author shows that the temperature at which transformation sets in in the case of gas oils may vary by 100° C. according as the surface on which the drops impinge is polished (300° C.) or rough (400° C.). Citing this as proof of the number of apparatus constants necessarily inherent in the Zundwertprüfer, the author, while agreeing that the test engine is not ideal for the determination of ignition qualities, prefers the results obtained from it to those obtained with the former apparatus, although he finds it of interest in investigating transformation. T. T. D.

938. Phase Equilibria in Hydrocarbon Systems: Latent Heat of Vaporization of Propane and *n*-Pentane. B. H. Sage, H. D. Evans and W. N. Lacey. *Industr. Engng Chem.*, 1939, **31** (6), 763.—The latent heat was determined experimentally over the temperature ranges 100–170° F. (propane) and 80–200° F. (*n*-pentane). The results are compared with experimental and calculated values obtained from the literature. P. D.

939. Separation Processes. Point Transformations of y versus x diagrams. M. Randall and B. Longtin. *Industr. Engng Chem.*, 1939, **31** (7), 908.—Methods are given for transforming the x versus y equilibrium diagram to give $(y - x)$ versus y, $(y - x)$ versus x, $(y - x)$ versus $(y + x)$ and $(y - x)$ versus $(2x - y)$. The usefulness of some of these, particularly the $(y - x)$ versus x diagram when using the McCabe and Thiele method of designing fractionating columns for volatility ratios near unity, is emphasized. P. D.

940. Enthalpy-Concentration Charts from Vapour-pressure Data. W. Haltenberger, Jr. *Industr. Engng Chem.*, 1939, **31** (6), 783.—The enthalpy-concentration chart for a liquid solution may be constructed from a knowledge of heat capacities at one concentration and heats of dilution over the concentration range. Experimental data for the latter are scarce, but calculated values may be obtained from vapour-pressure data. The method is described and illustrated by the construction of the enthalpy-concentration chart for sodium hydroxide solution up to 50% by weight of NaOH. P. D.

See also abstract No. 958.

Analysis and Testing.

941. Testing of Used Motor Lubricating Oils by A.S.T.M. Methods. G. Blank. *Oel u. Kohle*, 1939, **15**, 341–346.—The following A.S.T.M. methods of testing used oils are described and discussed: (i) Material Insoluble in A.S.T.M. Naphtha and Chloroform; (ii) Ash; (iii) Conradson Carbon Residue; (iv) Water Content; (v) Deposits; (vi) Diluent Content; (vii) Viscosity; (viii) Neutralization Number; (ix) Saponification Number; (x) Specific Gravity; (xi) Flash Point. T. T. D.

942. Contamination of Lubricating Oil by Water. M. G. Damany. *II^me^ Congrès Mond. Pétrole*, 2 (Sect. 2), 791–795.—The author describes an apparatus designed for use on board ship for the detection of water in lubricating oil. The apparatus consists of an electrical condenser through which the oil is pumped and a valve circuit for indicating variation in capacity of the condenser due to the presence of water. R. R. F.

943. Miniature Grease Penetrometer. G. Kaufman, W. J. Finn and R. J. Harrington. *Industr. Engng Chem., Anal.*, 1939, **11** (2), 108.—Because of the relatively large amount of sample required, the A.S.T.M. grease penetrometer is unsuitable for testing the consistency of small amounts such as used grease from ball or roller bearings. A miniature penetrometer was designed to determine the consistency of samples weighing about 3–5 gm. The instrument is described, and follows the lines of the official tester, the cone and plunger being made of aluminium and having a total weight of 20 gm. Data obtained on both instruments indicated that the relationship, if any, varied with the texture of the grease, the particular soap used, or the viscosity of the mineral oil. It was concluded that the miniature instrument should be regarded as a valuable adjunct to the official tester. G. R. N.

944. Mineral Oil Deterioration. A. G. Assaf and E. K. Gladding. *Industr. Engng Chem., Anal.*, 1939, **11** (3), 164.—Oxidized petroleum oils such as used insulating oils have been studied by the Grignard reagent (methylmagnesiumiodide) method of Larsen. The present paper describes improvements in the apparatus and procedure. It also gives results which show the accuracy of the quantitative determination, by the Grignard reagent of the types of compounds—ketones, esters, and peroxides—which may occur in oxidized mineral oils. G. R. N.

945. Determination of Undissolved Sludge in Used Oils. H. Levin and C. C. Towne. *Industr. Engng Chem., Anal.*, 1939, **11** (4), 181.—After examining various solvents the authors find that commercial pentane is the most suitable for separating undissolved sludge from used or oxidized motor oils. The procedure is as follows : separate 10-gm. amounts of the sample before and after percolation through absorbent cotton (at 60–75° C.) are agitated in conical flasks with 100 ml. pentane. After standing overnight the deposited sludge is filtered off through a Gooch crucible and washed with 100 ml. pentane, then dried at 110° C. for 1 hr. From the difference in the weights of insoluble matter the undissolved sludge is calculated as follows :—

$$C = 1000\left[A - \left(B\,\frac{10 - A}{10 - B}\right)\right]$$

where A = sludge undissolved by pentane, original sample (gm./10 gm.).
B = sludge undissolved by pentane, clarified sample (gm./10 gm.).
C = undissolved sludge (mg./10 gm.).

When A is low (0·1) for practical purposes $C = 1000(A - B)$.

The method gives results reproducible within 5% on the sludge basis when the sludge content is high, but duplicate tests within 4 mgm./10 gm. are considered its limit of reproducibility. G. R. N.

946. Determination of Dissolved Sludge in Used Oils. F. W. Hall, H. Levin and W. A. McMillan. *Industr. Engng Chem., Anal.*, 1939, **11** (4), 183.—The criterion set up for characterizing dissolved sludge in used oils was the material insoluble in liquid propane, using as the sample the oil obtained by percolation of the used oil through absorbent cotton. A suitable laboratory apparatus is described in which 4 gm. of the clarified sample are contacted with 64 ml. liquid propane, then washed with this solvent in a closed system under pressure. After removal of the propane the insoluble material is dissolved in warm benzol, the resulting solution being filtered into a small beaker, then evaporated on a steam-bath. The insoluble material is finally dried at 110° C. for 1 hr. The method has yielded results reproducible within 5% on samples containing large amounts of dissolved sludge, and within 5 mgm./10 gm. on samples containing small amounts. Results have shown that frequently the dissolved sludge is greater than the undissolved sludge (cf. preceding abstract). G. R. N.

947. Thermostatic Bath for Low Temperature Viscosity Determinations. E. L. Baldeschwieler and L. Z. Wilcox. *Industr. Engng Chem., Anal.*, 1939, **11** (4), 221.—A thermostat, which can be operated at from − 10° C. to − 60° C. with a temperature control of ± 0·03° C., is described. It consists of a cooling-coil and bath, a Hoeppler ultra-thermostat, and a Dewar type flask in which a Ubbelohde viscometer is set up. Alcohol–water mixture is used as the recirculating fluid, whilst *iso*propyl alcohol plus solid carbon dioxide is the refrigerant. G. R. N.

948. Apparatus for Microanalysis of Gas. C. H. Prescott, Jr., and J. Morrison. *Industr. Engng Chem., Anal.*, 1939, **11** (4), 230.—This article describes modern refinements of apparatus and technique for the rapid analysis of minute amounts of gas. On samples of 5–25 cu. mm. at normal temperature and pressure, analyses may be made with errors for each component within 2% of the total sample. The errors are within 5% on quantities of gas as small as the proverbial limit of 1 cu. mm. The methods described are available for the gases, water, carbon dioxide, hydrogen, carbon monoxide, and oxygen or methane. One hour is required for a complete general analysis. Under special conditions the least detectable quantity of a component may be pushed to a limit of 0·025 cu. mm. equivalent to the carbon monoxide in 1 sq. cm. of a monomolecular film. G. R. N.

949. Composition of High-Solvency Hydrocarbon Thinners. E. H. McArdle and others. *Industr. Engng Chem., Anal.*, 1939, **11** (5), 248.—Data gathered by ten laboratories working in six co-operating groups show that the refractive index–sulphuric acid extraction method for determining the aromaticity of commercial high-solvency hydrocarbon thinners, the evaporation rates of which are similar to that of toluene, and which are substantially olefin free, provides results which are reasonably accurate, as shown by comparison with synthetic blends, and can be duplicated by several stations with a precision of ± 0·5%. Although the method does not determine the naphthene or paraffin content with equal accuracy, the relatively greater importance of aromaticity is demonstrated by a reasonably good concordance in the viscosities of solutions of film-forming materials in the commercial thinners and their synthetic matches. The above method is not recommended for the proximate analysis of low-solvency thinners. A nomograph connecting composition, average boiling point, and refractive index for an aromatic free naphtha is given. G. R. N.

950. Measuring Oxidation of Lubricants. V. R. Damerell. *Industr. Engng Chem., Anal.*, 1939, **11** (5), 265.—A simple test for measuring the thickening produced in hypoid lubricants by heat treatment is described. It consists of noting the time of flow of a 5-gm. sample of the oil placed in a cylindrical glass crystallizing dish, 80 mm. diameter, 40 mm. deep, when the latter is first placed on one side, set upright, then placed on the other side. Two horizontal lines in ink on the sides of the dish determine the extent of the flow to be recorded. Four advantages for this method are claimed, viz : (1) the change in flow time of the entire sample is determined, showing in a simple manner the tendency of the lubricant to thicken in practice ; (2) the method is time-saving ; (3) the apparatus is simple ; and (4) the sample may be reheated as many times as desired, giving a curve (flow time or percentage increase in flow time *v.* time of heating) instead of a single result. G. R. N.

951. Stedman Packing for Close Fractionation. L. B. Bragg. *Industr. Engng Chem., Anal.*, 1939, **11** (5), 283.—The conical type of Stedman packing is made of wire cloth which has been embossed and trimmed into flat, truncated conical discs. A semicircular hole is cut out of one side of the cone and extends about two-thirds of the distance from the edge of the cone to the flat in the centre. The discs are welded together alternately back to back and edge to edge to form a regular series of cells with the holes, which serve as passages for the vapour located alternately on opposite sides of the section of packing. In operation the liquid flows along the screen and seals the opening of the mesh, then out towards the walls of the column on a cone that is concave downward, then back to the centre of the column on a cone that is concave upward, which is welded to the first cone at the outer edge. The lower cone is welded to another still lower cone at the centre, and the liquid flows through the mesh at the point of junction. The vapour enters the space between two cones which are welded around the outer edges, through the vapour hole in the lowest cone. It then flows through the space between these two cones, practically at right angles to the axis of the column and out through the vapour opening in the upper cone of the pair. The vapour then divides and flows around the point where two cones are joined back to back and across to the side of the column where it first entered the packing. Thus there is continual mixing and separation of liquid and vapour, so that channelling is negligible. This packing was tested (in three sizes) using benzene–ethylene dichloride as the binary mixture, and it is shown that at comparable vapour velocities it is superior to all other types of packing. G. R. N.

952. Glass Helices for Fractionating Columns. R. W. Price and W. C. McDermott. *Industr. Engng Chem., Anal.*, 1939, **11** (5), 289.—Glass helices are frequently used at the present time as packing for laboratory fractionators. Suitable methods for their manufacture in the laboratory either require considerable skill or special equipment. The authors describe a straightforward procedure in which only the ordinary tools of the laboratory are required. G. R. N.

953. Determination of Lead Tetraethyl in Gasoline. G. Calingaert and C. M. Gambrill. *Industr. Engng Chem., Anal.*, 1939, **11** (6), 324.—50 ml. of the gasoline, 50 ml. of a straight-run kerosine, and 50 ml. of concentrated hydrochloric acid are refluxed in a special glass apparatus for 30 mins. After cooling, the acid is drained off, then 50 ml. water are added to the gasoline–kerosine and refluxed for 5 mins. After cooling the water is separated and added to the acid. The aqueous solution so obtained is evaporated to dryness. The lead chloride is treated with nitric acid until a white salt is produced. It is next dissolved in dilute nitric acid and the lead is determined either gravimetrically as the chromate or volumetrically as the molybdate. It was found that this method yields results with a mean error of only − 0·012 ml. $PbEt_4$ per gallon of gasoline, as against − 0·054 for the bromination method, the improvement being particularly noticeable in the case of cracked gasolines. G. R. N.

954. Traces of Copper in Gasoline Determined by New Test. G. H. Short and W. A. Schulze. *Nat. Petrol. News*, 19.4.39, **31** (16), R. 162.—The test is quasi-quantitative, and depends on the formation of a copper complex of diphenylthiocarbazone, and hence the gradual change in colour of the reagent, which, in solution, is green. The reagent is prepared by dissolving diphenylthiocarbazone in C.P. benzene to obtain a concentration of 2 mgm. per 100 ml. solution. 100 ml. of the gasoline are filtered through paper into a glass vessel and 1 ml. of the reagent is added and the mixture stirred gently. The time for the colour to change from the original vivid green to yellow is determined in minutes. The rate of colour change decreases with increasing amounts of copper present. Precautions to be taken to avoid the vitiation of results are :—

(*a*) The test must be carried out in the minimum of light compatible with proper observation.

(*b*) Alkaline solutions, mineral acids, mercaptans, and metals other than Cu affect the rate of colour change.

(*c*) Water, if present, and especially if of p_H greater than 7, accelerates the rate of colour change.

(*d*) Contact with air and the inclusion of air in the gasoline by shaking or too vigorous stirring should be minimized.

(*e*) The test should be carried out at a reasonably constant temperature. H. G.

See also Abstracts Nos. 971, 792, 973 and 978.

Motor Fuels.

955. Patents on Motor Spirit. Standard Oil Development Co. E.P. 504,470, 26.4.39. Appl. 3.11.37. Improvement of motor spirit by adding 5% or more of a normally liquid ether which is miscible with the hydrocarbon, having the formula ROR′, in which R is a branched aliphatic hydrocarbon group and R′ is an ethyl group, *e.g.*, tertiary butyl ethyl ether and a small amount of lead tetraethyl.

Standard Oil Development Co. E.P. 504,837, 2.5.39. Appl. 3.11.37. Method for the improvement of motor fuel as described in E.P. 504,470 in which tertiary butyl secondary butyl ether is added.

I. Lovens. E.P. 506,230, 24.5.39. Appl. 23.4.38. Preparation of a product to be added to liquid fuels for use in internal combustion engines to increase their efficiency, by treating a vegetable non-drying oil such as olive oil, dissolved in white spirit, benzol, toluol, etc., with a quantity of oxygen and of hydrogen.

N.V. de Bataafsche Petroleum Mij. E.P. 506,574, 31.5.39. Appl. 15.10.38. Removal of mercaptans from motor spirit by means of aqueous caustic alkali containing diamino alcohol.

D. L. Yabroff and E. R. White. U.S.P. 2,156,577, 2.5.39. Appl. 8.2.37. Removal of mercaptans from petroleum distillates by means of an aqueous solution of alkaline metal hydroxide containing a substantial amount of a dissolved salt of aminocarboxylic acid having 4–7 C atoms.

E. D. Sutton. U.S.P. 2,157,223, 9.5.39. Appl. 17.6.35. Sweetening hydrocarbon oil by mixing it with an aqueous alkaline plumbite solution containing an oil-insoluble soap in the solution.

M. Mueller-Conradi and R. Uloth. U.S.P. 2,159,175, 23.5.39. Appl. 24.1.35. Process of dividing liquid hydrocarbon mixtures boiling within the b. pt. ranges of benzine into fractions of different octane values by treatment with acetonitrile.

H. E. Bode. U.S.P. 2,160,116, 30.5.39. Appl. 16.8.37. Method of treating naphtha to remove mercaptans by mixing 100 parts of naphtha containing 1% of mercaptan, 2 parts of dextrose, and 2 parts of HCl (sp. gr. 1·19), to precipitate glucose mercaptan.

W. J. D. van Dijck. U.S.P. 2,160,607, 30.5.39. Appl. 1.7.35. Refining of cracked distillates to remove sulphur compounds by solvent extraction with thiopene aldehyde or cyanothiophene.

D. L. Yabroff and E. R. White. U.S.P. 2,160,632, 30.5.39. Appl. 7.5.37. Separation of mercaptans from hydrocarbon distillates by treatment with an aqueous solution of ethylene glycol containing not less than 25% of water. The solution is saturated with an alkali metal hydroxide, the amount of glycol being sufficient to prevent salting out of the alkali metal mercaptides from the solution. W. S. E. C.

See also Abstracts Nos. 953, 954.

Gas, Diesel and Fuel Oils.

956. High-speed Diesel Fuels Less Acute. M. G. Van Voorhis. *Nat. Petrol. News*, 19.4.39, **31** (16), R. 156.—The advances made in high-speed diesel-engine design are reflected in the more general character of fuel specifications and in the elimination from the specifications of special items which have often involved the refiner in difficulty. The widening of the viscosity specification makes it possible, in some cases, to meet the demands for certain grades of domestic heating oil and diesel oil with a single grade. Viscosity, in certain instances, has been eliminated altogether from specifications. Opinion is divided as to the value of cracked gas oil as a diesel fuel, but at present more than sufficient straight-run oil is available.

The correlation of specification requirements with ignition quality is still unsatisfactory, and even the cetane number, although the best index, is not the ideal criterion. The cleanliness problem is solved technically, and the education of the distributor and user is all that is necessary to eliminate trouble from this source entirely. H. G.

Lubricants and Lubrication.

957. Arylstearic Acids from Oleic Acid. A. J. Stirton and R. F. Peterson. *Industr Engng Chem.*, 1939, **31** (7), 856.—Various analogues of phenylstearic acid have been prepared by the Friedel–Craft reaction with the intention of their being tested as addition agents to lubricants. The following compounds have been prepared: *p*-tolylstearic, *p*-chlorophenylstearic, *p*-bromophenylstearic, *p*-methoxyphenylstearic, *p*-phenoxyphenylstearic, and *p*-xenylstearic acids. Other possible uses under consideration include the uses of such compounds in the manufacture of soaps, wetting agents, and waxes. The alkyl oleates behave in a similar fashion to oleic acid in the Friedel–Craft reaction with an aromatic compound. The preparations illustrate the generality of the reaction of oleic acid or an oleate with aromatic compounds. H. E. T.

958. Effect of Fatty Acid Derivative on Lubricants. Part III. A. W. Ralston and E. J. Hoffman. *Nat. Petrol. News*, 19.4.39, **31** (16), R. 150.—Acylated courmarone and indene resins prepared by the condensation of fatty acid chlorides with resin fractions materially lower the pour points of paraffinic lubricating oils to which they are added. The mechanism of the lowering is shown to be due to a modification of the crystal size and crystal structure of the constituent wax, which suffers a continuous change from the clearly defined crystalline to the amorphous state with increasing amounts of the additive.

When tested on a Stephen's consistometer the treated oils show smaller temperature increases than do untreated oils, indicating lower internal friction and greater lubricating value. H. G.

959. Trends in Lubricating-oil Manufacture. G. F. Fitzgerald. *Petrol. Engr*, Mid-year 1939, **10** (10), 105.—The recent widespread transition to the solvent refining of lubricating oils has necessitated more attention being paid to the rigid supervision of plant to maintain optimum conditions in dewaxing and extraction ; and has necessitated very high capital outlays, particularly for control equipment. Two-thirds of the world's dewaxing capacity uses benzol ketone, whilst propane dewaxing is next in importance, providing a method of removing resins as well as wax, and thus increasing the yield of the neutral oils and reducing filter losses as well as improving quality. Solvent extraction has greatly increased the range of crudes that can be used for lubricating-oil manufacture. Furfural is the most widely used solvent, Duosol, phenol, and SO_2–benzol following very closely, with chlorex approximately one-fourth of that of furfural. Furfural is generally preferred owing to the normal temperatures (150–250° F.) used in extraction. For paraffinic oils the removal of 5–10% extract improves the viscosity index by about 1 for each per cent. extracted. For naphthenic oils the extract losses are greater, but are counterbalanced by the lower cost of the crude material. Solvent-treated oils are now replacing to some extent the purely paraffinic oils previously demanded, owing to their greater oxidation stability and lower liability to form gum and carbon.

De-resination and de-asphaltization are also being effected by distillation with a close-cut petroleum product—used as a " carrier "—enabling cylinder stocks and bright stocks to be run to less than 2% bottoms. This method is stated to be more economical than solvent refining, and yields distillates of lower carbon residue. For the decolorizing of lubricating oils, Fuller's earth is being replaced by bauxite and activated earths of improved quality. Attempts have been made, with some success, to refine in the still with clay added to the charge the clay dropping to the bottom of the tower.

Research is being carried out on extreme pressure and diesel-engine lubricants, on the chemical composition of lubricants, the catalytic effect of metals on lubricating-oil deterioration and inhibitors to prevent this, as well as inhibitors to lower pour point, prevent varnish formation and bearing corrosion, to increase oiliness, and to raise the viscosity index. C. L. G.

960. Formation of Products Insoluble in Chloroform by Artificial Oxidation of Lubricating Oils. Dixmier and Lyon. *II^me^ Congrès Mond. Pétrole*, 2 (Sect. 2), 731–738.—Tests are described on used lubricating oils. An approximate relationship is given between the percentage weight of compounds insoluble in petroleum ether and compounds insoluble in chloroform. Unused oils were heated in sealed glass bulbs at temperatures varying from 140° C. to 410° C. with and without copper catalyst. Compounds insoluble in chloroform are formed only at the higher temperatures (350–400° C.), but these contain much less oxygen than those obtained from the used oils. It is suggested that the chloroform-insoluble material is formed in practice by alternate heating and cooling in an oxidizing atmosphere. R. R. F.

961. Carbonization of Lubricants. J. Damian. *II^{me} Congrès Mond. Pétrole*, **2** (Sect. 2), 739–744.—The production of carbon from lubricating oils in internal-combustion engines is discussed.

An apparatus is described in which the carbonization of lubricants at temperatures between 200° and 550° C. in the absence of flame and under conditions similar to those occurring in the cylinder of an engine may be studied ; a curve for the variation of carbon deposit with temperature is given. J. L. E.

962. Oils for Internal Combustion Engines. F. Van Lierde. *II^{me} Congrès Mond. Pétrole*, 2 (Sect. 2), 745–749.—A classification of lubricating oils based on viscosity index, stability, and pour test is described.

The viscosity index and stability afford information relating to the behaviour of the oil in service and to its resistance to dilution and oxidation ; the viscosity index and pour test provide indication of ease of starting and engine wear. J. L. E.

963. Oxidation of Mineral Oils at High Temperature. A. Maillard. *II^{me} Congrès Mond. Pétrole*, 2 (Sect. 2), 751–755.—A study of asphaltic, carbonaceous, and mineral contents of samples of oil from crankcases of marine diesel engines and internal-combustion engines has been made.

The results obtained showed that deterioration of oils leads to products differing from those usually obtained by ordinary methods in the laboratory ; experiments are being carried out on oxidation at high temperature in order to ascertain the conditions which most nearly approach those found in practice. J. L. E.

964. Methods and Equipment Used in the Development of Lubricants for High Output Service with Special Reference to Aviation Oils. C. H. Baxley and J. P. Stewart. *II^me Congrès Mond. Pétrole*, 2 (Sect. 2), 757–769.—A single-cylinder air-cooled engine consisting of parts with dimensions similar to those used in multi-cylinder engines has been modified to give conditions of oil temperature similar to those experienced in practice. Temperatures of oil and mechanical parts are reproducible and the amount of oil in circulation, in particular that thrown to the cylinder walls, is carefully controlled, since this is found to be critical in the deterioration of the oil. Special selection of mechanical parts, even within specification limits, is essential, since these affect the time for ring-sticking. Operating factors such as mixture ratio and temperature are controlled. R. C. W.

965. Condition of Lubricating Oil after Use in High-speed Oil Engines. A. T. Wilford. *II^me Congrès Mond. Pétrole*, 2 (Sect. 2), 771–779.—Tests on used oils indicate that carbon content, ash, diluent, and increases in viscosity and acidity of an oil depend on engine type and oil consumption rather than on the oil itself. Used oils are less resistant to laboratory oxidation tests, and the hard asphalt content of used oils shows qualitative agreement with that obtained after laboratory oxidation tests. A figure of 8%-wt. of carbon is considered as critical when considering engine failure. R. C. W.

966. Selection and Care of Oils for Steam Turbines. G. Baum. *II^me Congrès Mond. Pétrole*, 2 (Sect. 2), 781–789.—The properties on which turbine oils are generally selected and the standard test regulations specified by various Standardizing Committees are critically discussed.

Refining processes are dealt with, but it is emphasized that careful treatment of the oil during its period of service is more important than its chemical treatment during refining. Care of the oil in service is discussed, and the importance of efficient oil coolers and collectors, etc., is stressed.

Reference is made to the possibility of regenerating oil after deterioration with age. J. L. E.

967. Studies in Lubrication. V. The Theory of Thick Film Lubrication of Flooded Journal Bearings and Bearings with Circumferential Grooves. M. Muskat and F. Morgan. *J. Appl. Phys.*, 1939, **10** (6), 398.—An extension of the method previously developed for finite length bearings fed with lubricant sources (*J. Appl. Phys.*, 1939, **10**, 46) is applied to flooded bearings of finite length. The results are expressed in three graphs : (*a*) journal eccentricity against Sommerfeld criterion, S ; (*b*) relative load-carrying capacity against eccentricity ; (*c*) coefficient of friction against S. In each case a series of lines of constant bearing length to bearing diameter ratio $\bar{\omega}$ are plotted. It is shown that eccentricities and friction coefficients, for fixed values of S, decrease as $\bar{\omega}$ increases, whilst the load-carrying capacity for fixed eccentricity increases.

The effect of a central groove is to give two bearings each with characteristics determined by the value of $\bar{\omega}$ for the two halves. The main advantage of such an arrangement must therefore lie in the cooling produced by the increased flow of oil and in overcoming negative pressures which might result in film rupture in the case of a flooded bearing. P. D.

968. Patents on Lubricating Oil. Ruhrchemie A.-G. E.P. 504,350, 19.4.39. Appl. 19.10.37. Synthetic production of lubricating oils by condensation of hydrocarbons containing olefines using aluminium chloride as condensation agent. The hydrocarbons used are benzines obtained by cracking at 460–510° C. and under 4–12 atm. pressure, mixtures of hydrocarbons obtained synthetically from CO and H_2 by the Fischer–Tropsch process, and boiling above 150° C.

H. D. Elkington. E.P. 505,141, 5.5.39. Appl. 10.6.38. Refining of lubricating oil with or without the addition of a diluent by treatment with strong acid and separating the acid sludge in the presence of a hydrocarbon treating agent of low mol. wt. at temperatures above the critical temperature of the agent.

H. D. Elkington. E.P. 506,228, 24.5.39. Appl. 10.6.38. Refining of lubricating oils with or without the addition of a diluent, by means of concentrated sulphuric acid.

H. G. Tovote. E.P. 506,532, 30.5.39. Appl. 30.11.37. Process and apparatus for improving the pour point of hydrocarbon mixtures containing wax.

F. M. Archibald. U.S.P. 2,157,315, 9.5.39. Appl. 28.11.36. Removing ash-forming constituents from a residual petroleum oil containing soaps dissolved therein (derived from acid refining followed by alkali wash), by adding sulphuric acid in the form of acid sludge.

S. W. Ferris. U.S.P. 2,157,821, 9.5.39. Appl. 3.7.33. Refining of lubricating oils by means of nitrobenzene and a low-boiling hydrocarbon diluent, *e.g.*, naphtha.

L. R. Evans. U.S.P. 2,158,358, 16.5.39. Appl. 34.2.37. Dewaxing hydrocarbon oil in the presence of a wax crystal modifying substance, *e.g.*, crude montan wax, aluminium stearate, etc.

F. X. Govers. U.S.P. 2,158,360, 16.5.39. Appl. 29.3.32. Manufacture of low pour test high v.i. lubricating oil from wax-bearing mineral oil by means of liquid SO_2 and monochlorbenzol.

F. X. Govers. U.S.P. 2,158,361, 16.5.39. Appl. 16.9.32. Solvent extraction of hydrocarbon oil using an aliphatic ether selected from the group consisting of *iso*-propyl and ethyl ether.

E. C. Knowles. U.S.P. 2,158,370, 16.5.39. Appl. 3.3.37. Dewaxing hydrocarbon oil by means of evaporative cooling.

E. G. Ragatz. U.S.P. 2,158,425, 16.5.39. Appl. 4.1.36. Method and apparatus for the vacuum distillation of lubricating oils.

D. E. Carr and M. L. Wade. U.S.P. 2,158,671, 16.5.39. Appl. 26.8.35. Dewaxing of hydrocarbon oils using propane and an oxidized wax.

D. E. Carr and M. L. Wade. U.S.P. 2,158,672, 16.5.39. Appl. 15.12.36. Dewaxing of hydrocarbon in which the oil is first subjected to the action of oxygen-containing gases at 150–500° F. for a time which is insufficient to oxidize more than 5% of the oil. The oil is then dewaxed.

W. B. McCluer and M. R. Fenske. U.S.P. 2,159,444, 23.5.39. Appl. 23.6.34. Solvent extraction of hydrocarbon oil using methyl ethyl ketone.

T. A. La Brecque. U.S.P. 2,159,994, 30.5.39. Appl. 14.11.36. Reclaiming apparatus for hydrocarbon oils.

W. W. Kraft and W. J. Bloomer. U.S.P. 2,160,103, 30.5.39. Appl. 23.4.35. Distillation of residues containing small percentages of asphalt in the presence of a diluent, to recover lubricating-oil stocks.

B. G. Aldridge and E. G. Ragatz. U.S.P. 2,160,256, 30.5.39. Appl. 10.7.34. Vacuum distillation of oils.

B. S. Greenfelder and M. E. Spaght. U.S.P. 2,160,573, 30.5.39. Appl. 27.8.38. Separation of wax in dewaxing processes for hydrocarbon oils, in the presence of a diluent containing N_2 bases separated from a cracked mineral-oil distillate boiling between 115° and 330° C.

W. S. E. C.

See also Abstracts Nos. 912, 913, 941, 942 and 950.

Asphalt and Bitumen.

969. Recovery of Bitumen from Solutions and Mechanical Mixtures. H. Kamptner. *II^{me} Congrès Mond. Pétrole*, 1937, 2 (Sect. 2), 637–644.—The effect of various organic solvents on the properties of bitumen recovered from solution is considered. Carbon disulphide and benzol are recommended.

The author discusses the effects of distillation processes and gives details of an apparatus for vacuum distillation wherein the bitumen solution is exposed as a thin film, thus reducing time and temperature of distillation.

A special apparatus for centrifugal extraction of bituminous mixtures is described. W. P.

970. New Methods for Examination of Liquid Asphaltic Bitumen. M. C. Siegmann. *II^{me} Congrès Mond. Pétrole*, 1937, 2 (Sect. 2), 645–652.—Two methods have been worked out to meet the following needs :—

(*a*) To recover and examine the whole of the binder present in a road (at any stage in its life) made with a cut-back asphaltic bitumen.

(*b*) To determine with reasonable accuracy the amount and quality of the basic asphaltic bitumen and of the volatile fluxing distillate in such a binder, or in any cut-back asphaltic bitumen of unknown origin.

The methods used are briefly as follows :—

(*a*) Extraction with CS_2 followed by fractionation quantitatively to separate the CS_2, leaving the whole of the binder.

(*b*) Closely defined and carefully controlled steam distillation.

Although the methods are tentative, it is stated that no others are known which can give equally reliable information. C. F. J.

971. Penetration of Bitumen. P. Woog, J. Givaudon and L. Daulin. *II^{me} Congrès Mond. Pétrole*, 1937, 2 (Sect. 2), 655–657.—An investigation of hysteresis effects associated with the penetration test. It is shown that prolonged periods of cooling at atmospheric temperature (*e.g.*, 14 hrs.) result in figures 15% low. Free circulation of air during air cooling is stressed as well as thorough agitation of the water-bath.

An exact procedure is given. C. F. J.

972. Apparatus for Determining the Electric Strength of Filling Compounds for Jointing Boxes. G. W. Nederbragt. *II^{me} Congrès Mond. Pétrole*, 1937, 2 (Sect. 2), 653–654.—The apparatus is fitted with flat electrodes which can be fixed and maintained at any desired distance.

Filling compounds such as asphaltic bitumens can be examined in the two following ways :—

1. A prescribed constant voltage is applied, and it is ascertained whether this can be maintained for a given length of time without breakdown taking place.
2. The voltage, starting from a low value, is increased at a constant rate until breakdown occurs. C. F. J.

973. Ductility of Asphaltic Bitumens. J. P. Pfeiffer and R. N. J. Saal. *II^{me} Congrès Mond. Pétrole*, 1937, 2 (Sect. 2), 665–671.—The author discusses to what extent ductility measurements are a measure of cohesion of asphaltic bitumens.

The behaviour of an asphaltic bitumen in the ductility test is governed by the rheological properties of the bitumen, but the problem is so complicated that exact analysis is not yet possible. The judgment of bitumen in terms of ductility at one temperature or one rate of elongation may be very misleading. W. P.

974. Physico-chemical Researches on Bitumen Emulsions. E. Vellinger and G. Radulesco. *II^{me} Congrès Mond. Pétrole*, 1937, 2 (Sect. 2), 659–664.—The degree of dispersion of bitumen emulsions (prepared in a high-speed mixer) is determined by the p_H of the aqueous phase. NaOH solutions in the absence of other emulsifying agents give stable emulsions only over a narrow range of p_H, the range depending on the type of bitumen. Addition of other emulsifiers (*e.g.*, oleine) considerably widens the p_H range over which fine dispersions are obtained.

At the p_H giving the finest dispersion, stability is a maximum, and sedimentation a minimum; sedimentation may be modified, however, by the electric charge on the particles.

In certain cases there is a maximum viscosity at a certain p_H of the aqueous phase. The viscosity can be increased by the addition of stearic or sulphonic acids, the former producing structural viscosity and marked thixotropy. Sulphonic acids do not give thixotropic emulsions, but tend to produce scum, particularly at low p_H.

Coagulation of emulsions by gravel, etc., decreases with increasing p_H and fineness of dispersion. Addition of salts to control p_H results in a rapid fall of viscosity, and is therefore not a practicable method of adjusting stability.

Storage stability generally improves with increasing fineness of dispersion, but no definite correlation is to be observed. W. L. P.

975. Emulsions in Industry. H. L. Bennister and A. King. *Chem. & Ind.*, 1939, **58**, 220–223.—The authors discuss the paper industry with particular reference to the sizing of either the pulp or the finished product. Reference is made to the use of rosin, paraffin, carnauba, or montan wax emulsion as *beater-sizing* materials for admixture with the pulp. These emulsions are generally broken down in the pulp by the addition of alum. Papers made in this way are deficient in mechanical strength, although some of the modern synthetic waxes give better results.

For the preparation of special papers by means of bituminous emulsions, soap, glue, and clay are the emulsifying agents generally used, emulsions are added to the pulp at the beater stage and must be stable. Clays are considered better than soap, in spite of the increased weight of the paper, and sulphite lyes appear to be better than either. Coarse emulsions prepared by emulsifying with colloidal pastes of carbon dust, silica gel, or metal hydroxides are also satisfactorily employed. It is stated that the emulsifier for wax and bitumen should be inert and should cause the dispersed product to adhere to the films, but this does not appear to have been achieved at present.

The adoption of *surface-sizing* with emulsions, particularly with wax, has enabled the undoubted advantages of wax to be utilized without subsequent loss of paper strength. Satisfactory emulsions and methods of application at high speeds do not appear to have been obtained yet. Other emulsified materials used include nitrocellulose, for which new type emulsifying agents such as sodium butyl-naphthyl sulphonate are used; plasticizers must be used, and synthetic resins are normally required to impart special characteristics. Rubber latex is not generally satisfactory.

H. G. W.

976. Manufacture and Use of Asphalts for Low Cost Road Construction in Canada. J. E. Easterbrook and R. K. Stratford. *IIme Congrès Mond. Pétrole*, 1937, **2** (Sect. 2), 687–692.—A survey is given of road development and of commercial production of asphaltic bitumen in Canada. The change from sheet-asphalt construction to low-cost types necessitated experimental and development work which is briefly surveyed.

W. P.

977. Manufacture of Bitumens for Use in Road Construction. L. Hemmer and R. Flavigny. *IIme Congrès Mond. Pétrole*, 1937, **2** (Sect. 2), 673–685.—The important properties of a bitumen in relation to road construction are consistency and adhesivity. Consistency is discussed in terms of conventional tests and of composition while adhesivity is discussed in terms of surface equilibrium, particularly in the system bitumen–stone–water. Variation in adhesion with the type of stone and the possibility of improving adhesion by treatment of the bitumen are discussed.

The emulsification of bitumens is discussed in relation to their origin and method of preparation but it is shown that emulsification is also greatly affected by the nature of the process and emulsifying agents used.

The production of more suitable bitumens for road construction has become increasingly possible with improved technique of production. W. P.

978. A New Laboratory Test for the Durability of Road Binders. H. C. Bennett and D. W. Parkes. *Chem. & Ind.*, 1939, **58**, 565–572.—The so-called " rubber-strip test " of these authors is an effort to embody in a single test all those properties which contribute to the durability of a road-binder. Preliminary correlation with accelerated carpet tests on the road showed that the most satisfactory were those in which the binder was found to be ductile after weathering, and that a measure of the ductility before weathering was no guide to its behaviour after weathering. The best results were obtained with a standard base tar, oiled back with a very heavy oil, and this was found to be most suitable for open-type carpets, but unsuitable for other types of road work. The test in its present form consisted in applying a film of binder 18 mm. square by 0·005 in. thick automatically (or by hand) on a sheet of rubber. The test strips were then artificially weathered by placing them absolutely level in a ventilated oven at 40 ± 0·5° C., and the critical temperature observed at which the film cracked completely across when elongated 33%, details and diagrams of the apparatus being given. Each binder was weathered for five periods up to 72 hrs., and the critical temperature plotted for each period against the time of weathering. In general, good correlation had again been observed between the behaviour in service and the type of curve obtained in this test, and it was found that binders with high critical temperatures, *after weathering* and showing curves with steep slopes, did not give satisfactory results in use. This will be confirmed by further work. Further investigation has shown that the durability of binders is scarcely affected by the quantity or viscosity of the oiling-back oil, within the range 100–300 sec. (B.R.T.A. at 30° C.), but was strongly influenced by the quality, and that, if a heavy-oil binder was stored at an elevated temperature, deterioration occurred, not revealed by standard distillation tests, but shown by high critical temperature curves in the rubber strip test. It is pointed out that the significance of the figures will depend on the method of curing the binder on the road, but in types of road construction where the binder was submitted in the form of a thin film to maximum atmospheric exposure, it had, however, been proved that the test in its present form gave a very fair idea of durability.

H. G. W.

979. Examination of Road Wear. H. Booth. *Chem. & Ind.*, 1939, **58**, 501–507.—The author points out that it is desirable to measure numerically any kind of change that occurs on a road, so that it can be plotted against time, traffic, and weather to ascertain the real cause and to correlate it exactly with the proper accelerated laboratory test. Visual inspections are carried out at sufficiently close intervals to note any sudden changes in the road surface and photographs taken, if necessary. In road tests all the measuring instruments are used at the beginning of the test at short intervals, and these intervals gradually increased until the largest advisable, which may be three-monthly, are found. The *slipperiness* of roads, particularly on wet surfaces, is measured by the sideway force coefficient of a motor-cycle with a skew wheel on the side-car up to about 50 m.p.h. and with a high-speed car up to 70 m.p.h. Rapid auxiliary methods of estimating slipperiness are the texture print of the surface and the roughness index (obtained by spreading standard sand as far as possible over the surface), and these are particularly useful for showing the gradual smoothing or disintegration of a road. The latter has been found that on a normal road this figure falls to a reasonably steady value after 12 months. The *disintegration* of the road is measured by weighing the amount of stone thrown to the side of the road daily, and the results show that the amounts lost are in general a function of temperature and are greater the colder the day. Alternatively, the rate of formation of pot-holes can be used as a criterion of road disintegration. *Surface irregularity* is measured on a sixteen-wheeled carriage by a single indicating wheel in the centre by (*a*) a profilograph or (*b*) a rise integrator, which measures the total unevenness upwards as per mile, or (*c*) a classifier, which counts the number of rises between successive fixed amounts differing by 0·1 in., and is found to decrease on a normal road to a constant figure after about 6 months; transverse profiles are also taken to give the change in level after making. Reference is made to various other methods for examining the state of a road surface, such as (*a*) photographic views for accidental damage and repairs and to find out whether severe breaking contributes to road failure, (*b*) plaster casts of the road surface, (*c*) deflection of a sheet of rubber by direct pressure to measure surface roughness, (*d*) counting the stones lost from a surface, and (*e*) tentative methods of measuring road hardness. The paper concludes with a brief account of the statistical records that are made of certain influences that affect road wear—namely, traffic tonnage and transverse distribution of traffic (using the axle counter), road-surface temperature and the duration of wet and dry surface conditions (using the wet road clock). In general, the four most heavily loaded 1-ft. strips on a 30-ft. carriage-way are about 4 and 10 ft. away from each kerb. H. G. W.

Special Products.

980. Dehydration of Organic Liquids with Activated Alumina. R. B. Derr and C. B. Willmore. *Industr. Engng Chem.*, 1939, **31** (7), 866.—The application of activated alumina to the drying of organic liquids is discussed. Experimental results on the drying of ethyl and butyl acetates, pyridine and gasoline, are reported. A commercial scale unit at present in operation for the drying of benzene and toluene is described, and applications of drying by activated alumina to catalytic processes and the production of high-grade water-free organic solvents are indicated. H. E. T.

981. Oils for Transformer and Switch-gear. H. Richter. *II^me^ Congrès Mond. Pétrole,* **2** (Sect. 2), 693–698.—The selection and treatment of oils to be used for transformers and switch-gear are dealt with; the effect of ageing is discussed, and the importance of appropriate care of the oil is emphasized. J. L. E.

982. Catalytic Change in Mineral Oils used for Transformers. M. M. Muller. *II^{me} Congrès Mond. Pétrole,* **2** (Sect. 2), 698–706.—Changes in mineral oils have been studied by following the absorption of gaseous oxygen in the oils heated to various temperatures below 150° C.; the effect of catalysts (copper and copper stearate) has also been studied.

At temperatures below 150° C. over-refined oils absorb much more oxygen than do less highly refined ones; above 150° C. the volume of oxygen absorbed by all oils is about the same.

The results obtained are applied to a study of oil stability. J. L. E.

983. Use of Anti-oxidants in Transformer Oils. E. Vellinger and N. Saito. *II^{me} Congrès Mond. Pétrole,* **2** (Sect. 2), 707–712.—The stabilization of over-refined transformer oils by the use of anti-oxidants has been studied systematically at several temperatures and concentrations.

Twenty-two common anti-oxidants were considered, and the effect of the source of the oil on the efficiency of several of these was determined.

Finally, the decrease in efficiency of anti-oxidants in the presence of oxidation catalysts such as Cu and Cu stearate was demonstrated. J. K.

984. Action of Sparks and Electric Arc on Mineral Oils. A. Maillard and Chibaeff. *II^{me} Congrès Mond. Pétrole,* **2** (Sect. 2), 713–716.—The action of an electric arc on mineral oils has been studied. Variations in the physical properties of the oil and the quantity of carbon produced have been determined.

After a sufficiently large number of discharges, enrichment of the oil by heavy products soluble in it and formation of an insoluble deposit occurred.

In a high-tension system such as was used explosions could occur with the combustible gaseous mixtures without the actual presence of sparks. J. L. E.

985. Patents on Special Products. W. A. Farenholtz, G. Hubbe and H. Hubbe. E. P. 506,104, 23.5.39. Appl. 8.6.38. Production of oxidation products (*e.g.*, of fatty acids and alcohols) from hydrocarbons of high molecular weight, by oxidation with gaseous oxidizing agents.

C. A. Jacobson. U.S.P. 2,156,591, 2.5.39. Appl. 29.6.36. Manufacture of carburized silica from coal-tar and finely divided siliceous product of the nature of diatomaceous earth. W. S. E. C.

Detonation and Engines.

986. Diesels. L. J. Logan. *Refiner*, 1939, **18** (4), 165.—A general survey of the use of the diesel in U.S.A. In 1938 the use of diesel oil by the railroads to power passenger trains increased 82%, although the total quantity of all fuels consumed in passenger service declined by 6%. Operating economies of 50% or more apparently explain the increased use. Based on car-mile operation in passenger service, diesel oil cost 1 cent, as against 2–3½ cents for other fuels. In yard-switching or goods service diesel-oil economy was even more clearly demonstrated, with costs per locomotive hour of only 28 cents, against comparative fuel costs of 1 dollar or more. The use of diesel engines in power-stations, tractors, trucks, and pumping-stations is also discussed.
G. R. N.

987. Utilization of Waste Heat from Diesel Engines. H. J. Fountain. *Diesel Eng. Us. Ass.*, Pub. No. S. 151, paper read 8th March, 1939.—The general method at present in use for the utilization of waste heat from diesel engines is the absorption of the heat from the exhaust and jackets in water contained in a boiler, the design of which is determined by the purpose for which the waste heat is to be used. For heating and drying the required heat may be obtained by circulating the jacket-water in pipes through the buildings. Where diesel-electric plant is fitted and there is a demand for heat, a silencer-electric boiler is recommended for improving load factor and heat output at light loads. Where electric power is the primary consideration, an additional steam-driven generator is indicated. For refrigeration or air-conditioning plants, high-pressure steam can be generated in silencer boilers and used in conjunction with refrigerators of the steam-jet type.

The complete layout of a comprehensive heat-utilization scheme for power, heat and cooling, adopting some of the above principles, is outlined and the cost of operation indicated. Details are also given of many specific examples of utilization of waste heat in engineering works, power-stations, railways, and in other land and marine installations. The author finally indicates the directions in which utilization could be made of the vast quantities of waste heat available from aeroplane engines.
T. E. P.

988. Piston-ring Blow-by on High-speed Petrol Engines. C. G. Williams and H. A. Young. *Engineering*, 1939, **167** (3830), 693; (3831), 723.—A wide variety of tests were carried out on one four-cylinder and also on two 500-c.c. O.H.V. single-cylinder engines, one air-cooled, and the other water-cooled. A brief description of the plant and of each test as it was carried out is given and the following conclusions are reached. The general tendency is for blow-by to be constant or to rise slightly until a critical engine speed is reached above which it rises very rapidly and becomes excessive. This rapid increase of blow-by is attributed to "ring flutter," or vibration of the rings in their grooves. High B.M.E.P.s tend to increase the critical speed for "flutter," whilst large side clearances of the rings and low radial pressures lead to flutter at comparatively low speeds; for this reason good design indicates narrow high-pressure rings with small side clearance, although some compromise is required. Reduction of blow-by at high speed can be achieved by reducing the clearance behind the rings, thus limiting their amplitude of vibration, and also by having very large ring gaps (0·15 in.), which prevent breakage by the ends of the rings butting together, although such large gaps cause increased blow-by at low speeds. The viscosity of the lubricating oil has no effect whatever on the amount of blow-by past the rings. Ignition timing has the effect of increasing blow-by as the spark is advanced.

The authors have liberally illustrated this article with diagrams and curves, and from their conclusions put forward a tentative theory for "ring flutter." T. E. P.

989. Influence of Speed on Heat Loss in Petrol Engines. W. T. David. *Engineer*, 1939, **167** (4354), 765.—The author investigates the influence of speed on the heat losses to the cylinder head and barrel, exhaust valves, ports, and passages in petrol engines in connection with the design of cooling arrangements.

The results indicate that the rate of heat loss through the cylinder head and barrel is practically constant and independent of speed, whilst the rate of heat loss to the exhaust system (*i.e.*, exhaust valves, ports, and those parts subjected to scrubbing by the exhaust gases) varies almost directly with the speed. For this reason the sleeve-valve engine with short ports is much easier to cool than a poppet-valve engine with long exhaust passages.

Figures for the distribution of heat to cooling water at various speeds are tabulated for engines of both poppet and sleeve-valve types. T. E. P.

990. Laboratory Method for Indicating Road Performance of Motor Fuels. H. G. Smith. *Refiner*, 1939, **18**, 177.—The main difficulty in developing a laboratory method to assess the road performance of motor fuels lies in the time element for loading the engine and picking up speed. An inertia–load system for absorbing power by means of a suitably designed flywheel with shaft on roller bearings affords a time interval of about 90 sec. for observations. The A.I.L. test unit (acceleration–inertia–load) employs a 2550-lb. alloy steel flywheel having an inertia of the order of an average weight car upon acceleration, in combination with a 240-h.p. hydraulic dynamometer for decelerating the engine. The motor fuel to be tested is rated successively in a Standard Ford V-8, 85-h.p. unit, a standard Chevrolet unit, and a standard Plymouth unit. Secondary reference fuels A, C, and F, ranging from 40 to 90 octane number, are used to bracket the fuel. To establish a working basis a straight-run aviation gasoline of 70·5–71·5 octane number is always initially tested.

After normal running conditions are obtained, the water is drained from the dynamometer so that the entire loading of the engine is affected by the inertia of the flywheel. The engine fuel supply is switched to the sample under test. At 8 m.p.h., with the transmission in high gear, the throttle is opened to the point of maximum knock, and knock intensity is determined at increasing speeds up to 35 m.p.h., the ratings being none, trace, light, light medium, heavy medium, heavy, or destructive. The procedure is repeated with blends of the reference fuels that bracket the test fuel. The octane number of the sample is then determined from the C.F.R.–A.S.T.M. calibration curve. The A.I.L. road rating is the average of the ratings in the three different types of engines. The results on 246 samples rated by a complete series of tests in all three engines indicated a reproducibility of ± one octane number. G. R. N.

Coal and Shale.

991. Coal Dust as Engine Fuel. Anon. *Chem. Trade J.*, 31.3.39, **104**, 311.—In a survey of the development of the coal-dust engine the view is expressed that it is now ready for service trial. The use of wear-resisting steels has resulted in extensive reduction of cylinder wear, whilst contamination of the lubricant is avoided by the provision of special stuffing-boxes. It is claimed that the problem of the choking of the dust-valves is almost solved. The principle of the operation of the engine is described. R. J. E.

992. Additive for "Dust-proofing" Oils. Anon. *Nat. Petrol. News*, 17.5.39, **31** (20), R. 214.—According to the annual report of the British Fuel Research Station, the addition of 0·5% rubber or of a commercial substance of mol. wt. 50,000–100,000 (understood to be an *iso*butylene polymer) greatly improves the efficiency of oils used for dust-proofing coals. The function of these additives is to close the entrances to the pores, prevent the penetration of the oil into the coal, and so to reduce the quantity of oil required. Little evidence has been found to support the claim made in some quarters that the oil treatment of coal improves the combustion characteristics and weathering. H. G.

993. Low-temperature Carbonisation, Ltd. Anon. *Chem. & Ind.*, 1939, **58**, 492–494.—A general description of the plant and process at the "Coalite" Works at Bolsover.

The coal, mined in the adjoining colliery, is washed to about 3% ash. From the washing plant the coal is conveyed to concrete bunkers. There are sixteen of these, and each is 70 ft. high. As several seams of coal are used and they have to be blended in very precise proportion, each type of coal is isolated in its alloted bunker. The coal is blended by adjustment of the speed of electrically operated conveyors running from each bunker. The final mixture passes by elevators and conveyors to the retort feed-bunkers, situated above the eight batteries of retorts which hold about 500 tons of coal—approx. 24 hrs. supply.

Condensed crude oil from the retorts passes to storage tanks, whilst the uncondensed gas passes to electrostatic precipitation chambers, where it is subjected to a static discharge of 80,000 volts in order to remove all suspended matter. The gas is then stripped of petrol and returned to gas-holders for use as fuel on the plant. Ammonia may be extracted as the sulphate, and there is a good demand for this fertilizer in the locality.

The crude oil is split into four oil fractions and pitch in a pipestill unit. Most of the oil fractions are rich in phenolic bodies, and these are removed by caustic-soda washing.

The washed oil is worked up for petrol and diesel oil.

The cresylate is subjected to a series of purification treatments and then hydrolysed by acidification with CO_2 generated from coke in producers. The cresylate acids are 99–100% pure. Caustic soda is produced on the plant, and there will eventually be four causticizers each of 11,000 gal. capacity.

Owing to the temperature employed and the method of distillation, the germicidal value of some of the tar acids is almost four times as great as that of standard products from other sources. T. C. G. T.

BOOK REVIEWS.

Theory of Lubrication. By Mayo Dyer Hersey. 2nd Edition, 1938. Pp. xi + 175. J. Wiley & Sons, Inc., New York, and Chapman & Hall, Ltd., London. Price 12*s*. 6*d*.

The book is based on a series of lectures on the mechanics of lubrication, given at Brown University in 1934, and repeated at Yale University and Massachusetts Institute of Technology in 1935. These lectures aimed at giving the scientific background of modern lubrication.

The book is addressed to the graduate, and not directly to the undergraduate. However, although there is much in the text which is advanced knowledge, there is also much which can be read and appreciated by the intelligent student. Engineers will find the subject interesting and helpful. The wave of simplification which traverses the several lectures must encourage the timid reader to carry on, although at first sight the mathematical aspect may be formidable.

The first chapter is devoted to an historical introduction. The second chapter deals with viscosity and its relation to friction. As viscosity is the most important property of a lubricant, a true concept should be available. To show the practical nature of the subject, a numerical example is given. Then follows a chapter on hydrodynamic theory. Generally, reports on this theory are pretty hard reading, so it becomes pleasant to read of it with a little less tension.

Temperature rise in bearings has always been a matter of consideration, but to-day it is a high light in engine design. Whilst we may not know and cannot ascertain surface temperatures within the bearing unit, we can content ourselves with, and make good use of, such material as is available when considering temperature distribution in the metal and in the oil film.

Oiliness has been a fundamental problem since 1896, when Kingsbury was struggling with this unsolved problem. Many tests, both static and kinetic, have been advocated in the attempt to evaluate relative oiliness of different lubricants. Some of them have contributed to what appears to be a crystallization of the phenomenon. The variables and difficulties in the experimental work are clearly outlined by Hersey.

Many of us glance through a book and form hurried opinions, but the author of "Theory of Lubrication" has given a summary towards the end of the book to enable the reader to obtain a panoramic view. Finally, as a postscript, he continues with a chapter on Recent Developments. It is therefore correct to say that the book is up to date to the end of 1937.

The opinion of the reviewer is that the book is exceedingly well written, and must make a lasting impression on the mind which is interested in the science of lubrication.

E. A. Evans.

Piping Handbook. By J. H. Walker and S. Crocker. Third Edition, 1939. Pp. xi + 897. McGraw-Hill Publishing Company, Ltd., London, W.C. 2. Price 36*s*.

The well-known "Piping Handbook" by Messrs. J. H. Walker and Sabin Crocker has been revised and brought up to date in the third edition just received. This exhaustive treatise covers a wide field of engineering practice as applied to pipework, and embodies authoritative information culled from numerous specialists in the various phases of this important subject.

The rapid advance of modern industrial process continues to call for higher temperatures and pressures, and many long-established standards have, in consequence, been modified or abandoned to meet present-day conditions. These departures are described at length in the "Piping Handbook," and valuable information is given on the metallurgy of piping materials and their selection to suit specific duties. The outstanding change in our time has undoubtedly been the universal adoption of welding both in works fabrication of piping and fittings and the elimination wherever possible of screwed or bolted joints in installation. This procedure has necessitated the introduction of many new standards, and a wealth of information is given in the handbook on production methods, stress relieving, dimensions, weights and test requirements, etc. The different types of flanged joints, screwed connections and proprietary joints and couplings now in use are classified and their merits discussed in relation to their particular application.

Very full information is given on the layout of piping systems with regard to flexibility, and the provision of supports and anchors to take care of the stresses encountered from temperature and pressure differences. The mathematical solution of numerous examples is given, and the data are of the greatest value to pipe-work designers and draughtsmen. Examples are also included of typical layouts and the essential requirements of systems dealing with a variety of gases and liquids. These examples are obviously the outcome of experience, and are therefore of practical value in avoiding the pitfalls so frequently met with in the transportation of fluids in pipes.

On the subject of flow of fluids in pipes the authors' adoption of the rational flow formula making use of Reynolds numbers for the solution of these problems is welcomed. Of flow formulæ, empirical or otherwise, it can be said without exaggeration " Their name is legion," and their indiscriminate use leads to results so conflicting as to be of no practical value. The relevant data in tabular and graphical form for the determination of significant factors and reduction to self-consistent units are most useful, and likewise the various practical examples show clearly the procedure to be adopted in the solution of flow problems.

The authors are to be congratulated on having compiled in a single volume so complete a survey of pipe practice of the present day, and on presenting this information to engineers in such a clear and concise form. J. R. Harkness.

Robbery Under Law. By Evelyn Waugh. Pp. 286. Chapman & Hall, London. 1939. Price 10*s*. 6*d*. net.

Mr. Waugh says that he went to Mexico to write a book about it in order to verify and reconsider impressions formed at a distance. The fact that his more intimate impressions were gathered during a visit of less than two months' duration raises the question whether any writer, however skilled he may be in observation and deduction, could possibly tell a true story about so complex a subject with material so rapidly acquired.

In his introductory remarks Mr. Waugh anticipates this question and supplies his answer, which is to the effect that such is the habit of professional writers, and that in this they are less presumptuous than the barrister or the medical specialist, who, with even less foreknowledge of the conditions surrounding their clients' case, can conduct a litigation or diagnose a disease.

Mr. Waugh's comparison is not a just one, however, and his book betrays him, for a very great number of his statements could only have been based on hearsay evidence which neither the lawyer nor the doctor would dream of accepting as a foundation for conducting the case of their clients.

Nevertheless for a reader who has resided in Mexico for any length of time and has had the opportunity of acquiring a real and intimate acquaintance with the life and character of its inhabitants, this book can be accepted as a very fair and accurate summary of the present state of affairs in that unhappy country.

For readers who have not had this opportunity many of Mr. Waugh's disclosures will appear unbelievable, but if they should feel any doubt about the possibility of such happenings as those described they should read " The Rosalie Evans' Letters from Mexico," a book which recounts the tragic history of a woman, the American wife of an English coffee-planter, who attempted single-handed to defend her dead husband's property in Mexico and who was murdered as a result, in spite of strenuous efforts by the British Government to secure protection for her from the Mexican Government. This episode occurred fifteen years ago, and is not mentioned by Mr. Waugh, but it is historically important, because it led to the withdrawal from Mexico of the British chargé d'affaires after he had vainly tried to protect Mrs.

Evans and had already become *persona non grata* to the Obregón Government because of his frequent protests against the unlawful seizure by that Government of British property and interests.

The recent barefaced theft of the foreign-owned oil properties has focused the attention of the civilized world upon the present, and still more corrupt and rapacious Cardenas régime. Mr. Waugh devotes 43 pages to an admirable and lucid exposition of the events leading up to this shameful episode, and of the heroic but vain struggles of the Companies to defend the legitimately acquired interests of their shareholders.

In a succeeding chapter, entitled " The Good Neighbour," the author discusses the interrelationship of the United States and Mexico from the time of the early English colonists to the present time. This chapter is amazing in its revelations and almost incredible in its implications.

Mexico is depicted here, not as a country of uncivilized Indians recently freed from the Spanish yoke and struggling to establish itself as an independent self-governing nation with the kindly advice and assistance of its northern neighbour. On the contrary, the Mexicans are shown to have been possessed of a civilization and culture far in advance of that prevalent in the United States during the colonial period, whilst the Good Neighbour is portrayed as a mischief-making busybody largely responsible for the unfortunate country's present troubles.

This arraignment of the United States before the bar of public opinion is a serious matter, and may well raise in the reader's mind the question whether Mr. Waugh is not going outside the province limited by his personal impressions when he accuses a United States Ambassador of being " tied up " with American commercial interests, of using the embassy as headquarters of those interests, and of deliberately setting himself to destroy the Madero administration because the latter was opposed to or in competition with such interests.

Further than this, Mr. Waugh makes out that in the two blackest crimes of recent Mexican history—the murders of Madero and Father Pro—there was in each case an American Ambassador at hand who alone could have averted it, and he finishes this chapter with the remark, " Once more, at a crucial moment in Mexican history, when a choice was imminent between further violent experiment and a return to saner counsels, the United States have lent their influence to the disorderly side."

Now, these and several other matters dealt with in this chapter could not have been enacted under the personal observation of Mr. Waugh. It is doubtful whether some of them—for instance, the circumstances surrounding the death of Madero and Pino Suarez—came within the personal cognizance of his informants, whoever they may be.

The remaining chapters of the book make gloomy reading to those who have known Mexico in quieter and more prosperous times. The country has already relapsed into stark anarchism, it is moving towards conditions which may easily provoke a world conflict.

Already, according to Mr. Waugh, the Monroe doctrine is being challenged by Germany all over South America, German and Italian business firms control important industries all over the continent, the air lines are predominantly German, with control of the landing-grounds, Italians are training the Bolivian army and the Lima police force, whilst in Mexico, on the Guatemala border, German planters have imported large quantities of arms and maintain a private defence force. It is far from fantastic to believe that in the event of political conditions in Mexico being propitious, Germany is prepared to intervene with vast, ready-made plans for taking control.

For the petroleum interests these pessimistic prognostications have a special significance; already the governments of other oil-producing countries in South America are showing a tendency to adopt a leftward policy, probably stimulated by pro-Nazi propaganda. Already they have seen that the Monroe doctrine has relapsed into a dog-in-the-manger attitude which opposes the intervention of foreign Powers in defence of their legitimate interests, but does nothing material to protect those interests under its implied guarantee.

This book should undoubtedly be widely read. Its readers may not agree entirely with Mr. Waugh's interpretation of his impressions, they may even see a ray of hope in his affirmation that there is a religious revival in progress that is transforming the Mexican Church; driven into the catacombs, the Church is recovering its spirit, but whether this recovery can become effective in time to save the country from utter disintegration, political, social and moral, only time can show.

J. McConnell Sanders.

Das Erdöl im Weltkrieg. By F. Friedensburg. Pp. 131. Maps 4. Tables 34. Ferdinand Enke Verlag, Stuttgart. 1939. Price R.M. 10.

Statesmen and journalists alike have frequently stressed the part played by oil in deciding the outcome of the World War of 1914–18. Some have assigned to it the credit for the victory of the Allies—others have maintained that the competition for oil supplies was the main cause of the prolongation of hostilities. Numerous popular and sometimes sensational articles have been written during the last twenty years, but up till now no reliable and systematic analysis of the numerous international sources of literature on the subject, appears to have been made. The present book purposes not only to represent, by a careful sifting and examination of sources of information, a reliable estimation of the part played by oil in the course and outcome of the last war, but also to afford practical information regarding modern defence policy, presumably from a German point of view, regarding the supplies of this increasingly important raw material in any future conflict.

That the full significance of oil supplies was not appreciated at the beginning of the last war is shown by the failure in all countries to ration the civil consumption of petroleum products. Only a few people at first suspected, and then did not clearly realize, that the enormous increase in arms and munitions would lead to a revolution of the petroleum industry. This lack of foresight was due possibly to the generally accepted idea that the war would last only a few months. Gradually, however, the specific military requirements of petroleum made themselves felt in all the belligerent countries, and within a year rose to unforeseen magnitudes.

The author carefully analyses the question of oil supplies in connection with the various phases of the history of the war : the campaigns in Galicia, Roumania, and Mesopotamia ; the advance of the Turkish army into the Caucasus, the closing of the Dardanelles, the submarine war, the English blockade, and the fight to maintain the neutrality of the non-belligerent countries. The disastrous effects of the underestimation of the importance of oil by Germany, resulting in her inability to develop her mechanized army, to build tanks, oil-fire her ships, expand her air force, or lubricate her industrial machinery is written with a bias which will, perhaps, not appeal to English readers. The author, however, in his final chapter concludes that while petroleum alone cannot be held responsible for the final outcome of the last war, it played a very considerable part in deciding the victory of the Allies—a fact which no one can dispute.

The interdependence of military requirements and industry—in other words, the significance of supplies of raw materials, and in particular that of petroleum in time of war—is a lesson surely learned by all countries. There can, however, be no harm in repeating the lesson—and this book should commend itself not only to those interested in the inside history of the last war, but to all those interested in any—we hope mythical—war of the future.

B. M. H. Tripp.

PUBLICATION RECEIVED.

Trinidad and Tobago. Mines. Report of the Inspector of Mines and Petroleum Technologist for 1938. Council Paper No. 53 of 1939. Printed and Published by A. L. Rhodes, Government Printer, Trinidad and Tobago. Price 72 cents.

A summary of the progress made in the petroleum, asphalt, and quarry industries during 1938. The production of crude oil, number of wells drilled, refinery operations, pipe-lines laid down, tank-storage capacity, and exports of petroleum and its products from the islands are all given. Statistics relating to the industries are given in several tables, and there is a detailed account of the petroleum industry in Appendix B. There are also eight graphs comparing the present position (1938) with past years as far back as 1911, and in one case 1890.

INSTITUTE NOTES.

August, 1939.

SUMMER MEETING, 1940.

The Council has accepted the invitation of the Committee of the Northern Branch to hold the Summer Meeting of the Institute in 1940 at Manchester from May 6th to May 9th. Further particulars will be notified to members in due course.

ANNUAL DINNER.

The Annual Dinner of the Institute will be held at Grosvenor House on Monday, December 11th, 1939.

LIST OF MEMBERS.

A new List of Members will be published early in 1940. Members are invited to forward to the Secretary notification of changes in degrees or diplomas to follow their names which have occurred since the List of Members was last published in 1936.

STANDARDIZATION COMMITTEE.

Dr. F. H. Garner has been appointed Chairman of the Chemical Standardization Committee of the Council, in succession to Prof. J. S. S. Brame who retired from the Chairmanship of this Committee at the end of 1938.

TRANSFERS TO FELLOWSHIP.

The Council has approved transfer to Fellowship of the following :—

Bihoreau, C.
Brooks, B. T.

Cadman, Lord

Edgar, G.
Egloff, G.
Ellis, C.

Faragher, W. F.
Fenske, M. R.
Francis, C. K.
Fraser, Sir William

Grote, W.

Halle, H. J.

Haslam, R. T.
Holland, Sir Thomas

Kogerman, P. N.

Lederer, E. R.

Mackenzie, K. G.

Pratt, W. E.

Smith, Sir Frank E.
Stratford, R. K.
Swanson, H. R.

Tillman, R.

CANDIDATES FOR ADMISSION.

The following have applied for admission to the Institute or transfer to another grade of membership, and in accordance with the By-Laws the proposals will not be considered until the lapse of at least one month subsequent to the issue of this *Journal*, during which any Fellow, Member or Associate Member may communicate by letter to the Secretary, for the confidential information of the Council, any particulars he may possess respecting the qualifications or suitability of any candidate.

The object of this information is to assist the Council in grading candidates according to the class of membership.

The names of the candidate's proposer and seconder are given in parentheses.

Davies, Thomas Trevor, Chemist (*Shell Marketing Co., Ltd.*), 77, Sunnyside Road, London, N.19. (*J. S. Jackson ; J. Parrish.*) (*Trans. to A.M.*)

Doughty, Walter David, Chemist, c/o C. C. Wakefield & Co., Ltd., 30/32, Cheapside, London, E.C.2. (*E. A. Evans ; G. H. Thornley.*)

Ellis, Dennis Wilson Villiers, Engineer, P.O. Box 4907, Johannesburg, South Africa.

Gilbert, Stanley William Terrence, Engineer (*Standard-Vacuum Oil Co.*), 11, Park Court, Park Circus, Calcutta, India.

Harris, Robert, Engineer (*Standard-Vacuum Oil Company*), Post Box No. 181, Bombay, India.

Kane, John, Chemist (*Shell Marketing Co., Ltd.*), 11, Crondace Road, Fulham, S.W.6. (*J. S. Jackson ; J. Parrish.*) (*Trans. to A.M.*)

Steinitz, Ernst W., Engineer (*Central Motor Institute, Ltd.*), 16, Howley Place, London, W.2. (*F. Kind.*)

Williams, John Henry, Engineer (*Iraq Petroleum Co., Ltd.*), A 3 Bungalow, Baba Gurgur, Kirkuk, Iraq. (*E. Thornton ; R. B. Southall.*)

ARTHUR W. EASTLAKE,
Honorary Secretary.

PERSONAL NOTES.

Mr. F. A. Chuter has returned to Iraq.

Mr. G. A. Richards has left for Southern Nigeria.

Mr. C. W. Woolgar is returning from Venezuela.

Correspondence or *Journals* forwarded to the following members have been returned, and the Secretary would be pleased to receive any information regarding their present address : G. E. Barber, E. C. Brown, K. Burton, E. B. Chapelle, A. L. Davis, V. C. S. Georgescu, J. J. L. Hamilton, A. Hammersley-Heenan, J. R. Horth, A. D. Jones, J. Lander, I. Lusty, A. MacLean, G. P. Melville, C. A. Moon, S. Nicol, G. A. O'Neill, R. G. Reid, N. D. Rothon, H. G. Spearpoint, M. L. Steinschneider, and P. F. Thurlow.

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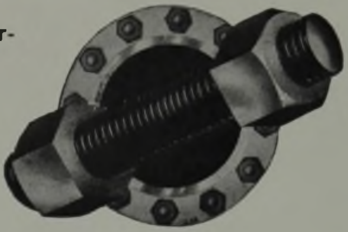

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Colombia.—H. Rappart, PUERTO-BERRIO.

Argentine.—G. Guichardot, COMODORO RIVADAVIA, Km. 27.

Morocco.—M. Texier, Société de Prospection Electrique, PETITJEAN.

Rumania.—A. Poirault, 18 Strada I. C. Bratianu, CAMPINA, (Prahova).

Germany.—Firma von Flotow, Schillerstrasse 36^1, HANOVER.

Dr. B. Paul, Kobenzlgasse 30, VIENNA.

Hungary.—M. Scheibli, Vadaszkürt Tür Istvan U.5, BUDAPEST.

Iraq.—L. Beaufort, QAIYARAH.

British India.—A. Couret, DIGBOI, Assam.

Burma.—L. Bordat, KHODAUNG.

Netherland East Indies.—R. Sauvage, PLADJOE, Sumatra.

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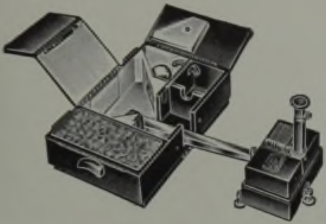

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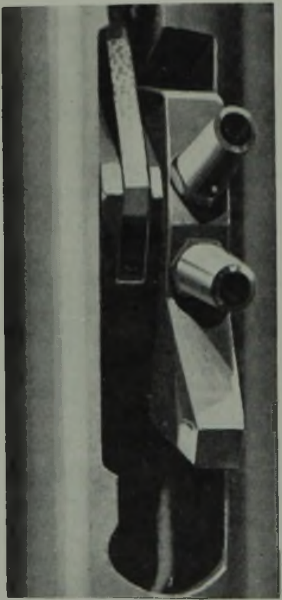

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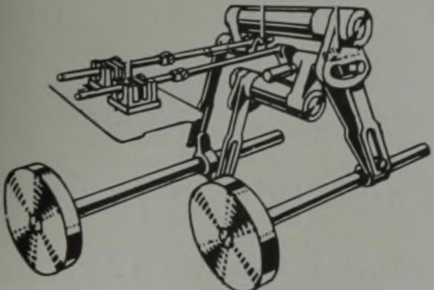

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