THE INSTITUTE OF PETROLEUM.

A MEETING of the Institute of Petroleum was held at Manson House, 26, Portland Place, London, W. 1., on Wednesday, March 12, 1947.

MR T. DEWHURST (Past-President), inviting Professor A. O. Rankine, O.B.E., D.Sc., F.R.S., to preside, said : Geology is the science of the earth, and the earth is one of the smaller planets, having a volume of 260 thousand million cubic miles.   The land surface is 55,000,000 square miles ; and if we assume that a thickness of, say, 10 miles is accessible to geological examination, this amounts to 550,000,000 cubic miles, or about 0·21 per cent. of the total volume.   Therefore, although geology is the science of the earth, geologists have to rely on geophysics for information regarding about 99·8 per cent. of its total volume.   Even if we were to assume a thickness of 20, 30, or 40 miles as being accessible to geological examination, this would affect only the decimal figure and would not change the general picture.

Moreover, considerable areas of the earth's wrinkled and cracked epidermis are covered by ice sheets, desert sands, wind-borne deposits such as loess, wide stretches of alluvium, deltas, swamps, etc., and even where the solid geology is exposed, the surface rocks may be young and barren formations which overlie and conceal older formations containing deposits of economic value.   Again geologists are dependent mainly on geophysics for information bearing on these blanketed areas.

The Egbell oilfield, situated in the Vienna basin, was discovered in 1917, and the application of geophysics to the search for petroleum dates from the recognition that that oilfield was situated on a torsion balance high.   As this discovery occurred during the First World War, it is a difficult matter to be certain of details ; but it is very probable that Professor de Böckh was the first to recognize this coincidence and to appreciate its significance. After the First World War Professor de Böckh visited Great Britain to explain to me this new method of search, and he was then a most enthusiastic pioneer of the method.

The First World War gave an enormous impetus to the search for petroleum, and the torsion balance and seismic refraction methods were pressed into service and were well established by 1924.

The introduction of each and every new method of exploration has been followed by a spate of new oilfield discoveries, and this proved to be the case with successive introduction of the torsion balance, the seismic refraction method and, later, the seismic reflection method.

This evening we are to hear an account of modern developments in geophysical procedure, and we are very fortunate indeed in having with us Professor Rankine, who has kindly undertaken to introduce Mr Van Weelden and subsequently to lead and to guide the discussion on the paper. It would be supererogatory and certainly presumptuous on my part to say anything about Professor Rankine ; but I do thank him for being present, and have very much pleasure in inviting him to take charge of this meeting.

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PROFESSOR A. O. RANKINE, having formally occupied the chair, said : Some time ago I had to decline an invitation by our President to occupy the chair on this occasion, because I thought then that I should be absent from the country. However, I was determined to come if I could. But until a few moments ago I had no indication that I was to be called upon to introduce Mr Van Weelden, although I am very glad to do so.

One of the great regrets of my life is that I did not get to know him earlier. We have discovered in recent years that, not only are we both geophysicists, but we like the same sort of things in other directions, and we have very happy recollections of a visit we made together to Germany some eighteen months ago, when we went over there to see what the Germans had been doing in geophysical work. If Mr Van Weelden is, and I am sure he is, as good a geophysicist as he is a companion, then he is very good indeed.

He is one of the outstanding geophysicists in the world, and he is in charge of the geophysical work of the Shell Oil Company, which has very widespread interests. He has visited most parts of the world in connexion with this work, and we have often met in the course of co-operation between his company and my own, the Anglo-Iranian Oil Company, as well as the Burmah organization. So that I do know how reliable a man he is to hold the balance evenly and fairly as between exaggerated expectations and deductions on the one hand, and complete scepticism on the other, with regard to what geophysics can do. He is just the right kind of man to introduce this subject and to tell us how things have been developing in quite modern times. Therefore, I have very great pleasure in introducing him to you and in inviting him to deliver his discourse.

The following paper was then read :

MODERN DEVELOPMENTS IN GEOPHYSICAL PROSPECTING.

By Ir. A. VAN WEELDEN *

A DISCUSSION of modern developments in geophysical prospecting for oil may conveniently be split into three main sections. These sections are :

 I. New methods ;

 II. Increased accuracy, resolution and general effectiveness of existing, proved methods ;

 III. Extension of established methods to novel conditions and surroundings.

NEW METHODS.

In spite of the very great advance in scientific methods during the war years nothing seems to have been discovered which would lead to a completely new approach to the problems of prospecting for oil. There are,

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however, several types of investigation which may be called " new " in so far as they have not yet reached maturity and general commercial acceptance.

Electrical Methods.

Electrical methods have been very useful in well-logging for many years, but for surface prospecting they have not attained the penetration and the accuracy required. An immense amount of theoretical study has been applied to the problems because the method holds out the possibility of the direct detection of oil on account of its high resistivity as against that of salt water. The practical observation of data in the field, however, does not yet give sufficiently accurate information for the solution of relatively simple problems. The main drawback is lack of penetration, and although for very shallow work, say several hundred feet, good results are obtained in ore-mining or civil engineering problems, for oil exploration, where depths are measured in thousands and tens of thousands of feet, this method is of little practical value.

Telluric earth currents have been the subject of study, especially in France, and more recently in the United States. They hold out the promise of greater penetration, but the results of the work, so far, do not extend much hope that the method will be widely adopted in the near future. Considerably more research must be done before the method can be considered as a standard new method. For those who desire to read more in detail about this particular subject reference should be made to Dahlberg's article in *Geophysics*, Oct. 1945, p. 494.

Soil Analysis.

Much experimental work has been carried out on the question of analysis of the soil for minute quantities of hydrocarbons which may be present there. Attention has also been given to the associated problem of measuring the radio-activity of soil samples. A very interesting paper on the subject of soil analysis as applied to geophysical prospecting has been given by Sylvain J. P. Pirson at Chicago recently under the title of " Disturbing Factors in Geochemical Prospecting "; it is published in *Geophysics*, July 1946.

Early work with this method was started in the field in an empirical way. Theoretical studies were confined to the chemical aspects of analysis proper, but the problem of the origin of the various substances and their significance in terms of oil geology was neglected. Some successes were claimed, but various students came often to contradictory results, and it is felt that more basic research is necessary before field work on a large scale is undertaken. It may be a future method, but at present can hardly be considered as a method that has " arrived."

Electronic Devices.

War-time work on aircraft detection led to a great development in the field of ultra-short wave radio. Devices such as Radar depend for their operation on the extremely high reflection characteristics of these very short waves, and it is this very attribute which makes them unsuitable for

geophysical work, where one of the essentials is that the energy in detectable form shall have sufficient ability to penetrate the subsurface of the ground to interesting depths before being returned for observations with the information required. In other words, a proper balance between penetration and reflection is needed, and Radar is too much on the side of reflection. Certain unsubstantiated claims have been put forward by amateur inventors with this type of equipment, but nothing has yet been proved to give satisfactory results. Not only that, but theoretical considerations covering the spectrum of wave-lengths between the shortest radio wave and the infra-red hold out very little hope of these being of any use for our purpose.

However, the general increased experience with and knowledge of electronic devices may lead to improved designs of equipment in various methods already in use.

IMPROVEMENTS IN EXISTING METHODS.

Turning to improvements in the accuracy, resolution and technique of existing methods, we shall first consider gravity methods.

Gravity Methods.

Early gravity surveys were carried out almost exclusively by the Eötvös torsion balance, but in recent years it has been almost completely superseded by various types of gravity meters. The gravity meter has been proved to give greater accuracy over the wide areas associated with prospecting for oil at a much lower cost than the torsion balance used to do. The gravity meters themselves have improved greatly in accuracy and in ease of operation. The principle of operation has remained the same, but in the past ten years the accuracy of readings has been stepped up from three-tenths of a milligal to three-hundredths of a milligal, corresponding to an improvement in accuracy of observation from 1 milligal to 1/10 milligal, or even better.

The torsion balance was capable of reading to 1 Eötvös $= 1 \times 10^{-9}$ c.g.s. unit. The accuracy of the readings was, however, somewhere between 2 and 5 E. In order to build up an isogam map the torsion balance values had to be multiplied by the distance separating the stations; then if a perfectly smooth, uniform gravitational surface between two observation points 500 metres apart is assumed, the accuracy of the measurement of gravity difference between those points will be at best

$$2 \times 10^{-9} \times 500 \times 10^2 \text{ c.g.s. units}$$
$$= 1 \times 10^{-4} \text{ cm/sec/sec} = 1/10 \text{ milligal.}$$

It is seen, then, that the gravity meter with its 1/10 milligal accuracy is at least as good as the torsion balance, even when the latter is working under nearly perfect, and most improbable, conditions.

Moreover, gravity meters are much less influenced by small topographic irregularities, local heterogeneities, than are torsion balances. If a man lies down beside a torsion balance (watchmen have been known to do it when the instrument was making automatic observations at night) the effect on the reading will be about 10 E, while a similar disturbing mass beside a gravity meter would introduce an error of less than a thousandth

of a milligal. Some people even want to change the unit of measurement because of the increased accuracy now obtainable with the gravity meter. That subject is beyond the scope of this paper, but it does give some idea of the advance which has been made.

The practical limits of accuracy of the method for our purpose are now being approached. An error in the elevation of the ground of ten centimetres already gives an error of three-hundredths of a milligal in the Free Air Correction—that is, the correction for distance from the centre of gravity of the earth. Careful topographic surveys are necessary if a better accuracy than this is to be attained. Another point is that the density of the superficial layers of the earth's surface is not known with sufficient accuracy to enable the effect of adjacent land masses to be calculated well enough. The density may be in error by as much as 20 per cent; this causes an error of 20 per cent in the topographic correction.

For the case of a sloping surface

$$\text{Error in correction} = 2kzad$$

where k = gravitational constant
z = total rise of slope
a = angle of slope
d = error in density.

If $z = 300$ ft or, say, $100m$, $a = 5\frac{1}{2}°$ or 0.1 radian, and $d = \frac{1}{5}$.

$$\text{Correction} = 2 \times \tfrac{200}{3} \times 10^{-9} \times \tfrac{2}{10} \times 100 \times 10^2 \times \tfrac{1}{10} \times 10^3 \text{ milligals.}$$
$$= \tfrac{8}{3} \times 10^{-2}$$
$$= \tfrac{3}{100} \text{ milligal.}$$

That is to say, the possible error in density of 20 per cent on a $5\frac{1}{2}°$ slope 300 ft high gives an error equal to the reading accuracy of the instrument.

In early gravity meters the effect of creep of the spring material was considerable, and in the course of a day the datum of the instrument might vary as much as three or four milligals. The movement, moreover, was rather erratic, and elaborate arrangements had to be made to keep a close watch on the drift of each instrument. This sometimes entailed the use of two instruments simultaneously to check on each other during the survey. Improved knowledge of materials has led to a great improvement in this respect, and, while drift is still present, it is fairly uniform, and therefore corrections can easily be made.

Temperature changes also affect the datum level of the instrument, and most makers endeavour to get around this difficulty by using thermostatic control of temperature.

In addition to the improvement in the accuracy of gravity meters there has been a great improvement in their general handiness and ease of operation. The early torsion balances needed 5 hours to observe one station, or to make one complete reading, and at least three heavily-loaded men were needed to carry the instrument. Gravity meters can be read in under 1 minute, and they can be carried easily by one man. The North American gravity meter weighs 28 lb for the instrument alone, and with pack frame and accumulators for operating the thermostat the weight is 45 lb. A 12-lb motor-cycle battery is used. The Norgaard instrument, which has no thermostat, but which is very heavily insulated, has a weight of 25 lb. The Thyssen instrument without extra insulation weighs 50 kg (110 lb).

Weight of large torsion balance $= 57 \cdot 7$ kg $+$ packing $38 \cdot 6$ kg
$\qquad\qquad\qquad\qquad\qquad\quad = $ total $96 \cdot 3$ kg $= $ *212 lb*

,,   ,, small   ,,   ,, $= 47 \cdot 4$ kg $+ 34 \cdot 8$ kg
$\qquad\qquad\qquad\qquad\qquad\quad = $ total $82 \cdot 2$ kg $= $ *182 lb*

,,   ,,   ,,   ,, $= 37 \cdot 5$ kg $+ 41 \cdot 2$ kg
$\qquad\qquad\qquad\qquad\qquad\quad = $ total $78 \cdot 7$ kg $= $ *174 lb*

One final improvement may be mentioned. Some early units were too much influenced by variations in the earth's magnetic field : this has been cured in most modern instruments.

Seismic Methods.

The earliest seismic surveys made use of the refraction method, and it is this method which has shown the most recent development. The new technique is known as " Refraction Correlation."

Study of time–distance graphs of early refraction work shows that sometimes the beginning of the " First Kick " was lost altogether, and that a second loop of the vibration had to be chosen ; it was seen also that in many cases there were strong second arrivals which assisted greatly in the interpretation. Attempts to obtain the true initial impetus led to the use of exceedingly large charges of dynamite (over a ton), but the new technique makes deliberate use of the second arrivals to determine the relative depths of successive points. The method can be used only where the energy frequency spectrum is fairly constant from the point of view of the generation of energy at the shot point, the absorption in the ground up to the receiving point and the receptive characteristics of the instrument. The method is particularly adapted to shallow investigations and to those cases where the existence of a shallow high-speed layer makes the reflection method of no avail, because of excessive reflection of the energy and insufficient penetration.

Because of the rapid variation of the energy content of the record from beginning to end some form of amplitude control has been found to be necessary. This first took the form of an arbitrary increase in amplification by either mechanical or electrical means, or a combination of them. Later designs, however, have favoured the use of automatic volume control with a delayed action to avoid excessive uniformity of appearance and consequent difficulty in the picking of bursts of reflected energy.

Automatic volume control has a great additional advantage, in that it enables the operator to get a good record from his first shot, instead of having to fire at least three shots for adjustment of instrument amplitude before he shoots the one which has to be used for interpretation. It sometimes happens, too, that the shot-holes have to be drilled in very sandy ground which would cave in a very short time after the hole had been drilled. This trouble used to be surmounted by casing the hole, and this is still frequently done, but with automatic volume control on the recording unit it is possible for the driller to load the hole as soon as it has been drilled, and to leave the charge in the hole for the shooter to fire the following day, or even later. This practice is obviously not recommended in populated areas where small boys or other inquisitive individuals may cause damage by playing with the blasting cap leads.

This question in turn leads to that of improvements in the quality of explosives. In the above case the charge of explosive may have to remain submerged in water for anything from 12 to 36 hours, or even more, under a hydrostatic pressure of up to 100 p.s.i. Great credit is due to the explosive manufacturers who have made a product of the required standard, largely by virtue of development of better packing methods.

A further critical feature of explosives is their speed of detonation. In order that a proper comparison may be made between records with different filter settings at any one set-up, and between records of consecutive set-ups with the same filter settings, it is essential that the whole operation of detonation of the explosive should take place in a time which varies less than the accuracy of measurement of the instrument. The instrument is accurate to one thousandth of a second, and it is expected that the depth calculations will in general be carried out to this accuracy also. Now the time lag in the detonation of a blasting cap is of the order of half a thousandth of a second with a firing current of 5 amperes or more for a first-grade cap; for lower grades the variation from one cap to another may be much greater than this total lag. It is therefore essential that only first-grade caps be used. The length of a normal charge of 20 lb is about 3 metres, and the length of charge may vary from zero to this value. Therefore the detonation must take place over the whole charge in less than half a thousandth of a second, assuming the cap to be at one end, and then the velocity of detonation of the dynamite must be 6000 m/sec. This is close to the highest speed of detonation of dynamite, and so it is essential also that the dynamite should retain its high-speed characteristics even under adverse conditions of humidity and high pressure. This difficulty has not been entirely overcome, and so the average seismic man is apt to be extremely critical of claims made by explosive manufacturers, even although he gives them all praise for the good work which they have already done in developing special products for seismic uses. The automatic volume control compensates to some extent for any irregularities in the quality of the explosive, but this is not its true function, and it is a mistake to use it so.

Seismic drilling equipment is also undergoing continuous improvement, and truck-mounted drills have reached a high state of efficiency. There is still, however, much room for improvement in that type of drilling outfit which has to be sufficiently portable to be carried through tropical jungle and swamps. The greatest need is for a light-weight pump capable of delivering dirty water or light mud at 70 p.s.i. to an amount of about 70 gal/minute.

EXTENSION OF ESTABLISHED METHODS TO NOVEL CONDITIONS.

We may turn now to the extension of established methods to novel conditions.

Aerial Magnetometer Surveying.

Possibly the most spectacular innovation is that magnetometer surveys have taken to the air.

During the war a modified type of magnetometer was used in aircraft to detect the presence of submarines submerged at sea. The device had a fair measure of success in this direction, but it bids fair to revolutionize magnetic prospecting.

For anyone who is interested in a detailed description of the instrument, there is an excellent paper describing it in *Geophysics*, July 1946.

The area which can be surveyed magnetically with the required standard of accuracy has been immensely widened. With the Schmidt-type magnetometer the areas surveyed were subjected to the restrictions of adequate transport and a stable foundation for the instrument. The airborne magnetometer removes these restrictions at once, and permits the carrying out of magnetometer surveys virtually anywhere.

A magnetic survey carried out on the surface of the earth is subject to the effect of many small local magnetic disturbances due to, say, a little magnetic sand or some pieces of metal, but the airborne instrument measures the magnetic field at a sufficient distance from these local influences to make their effect negligible. Another point is that surveys may be made at several different elevations, and then increasing height of observation will give an increasing proportion of the effect to the more deep-seated influences, and thus permit the separation of shallow and deep anomalies.

It is a pity that the magnetic methods of prospecting are not of greater utility in the search for oil. It has been found, however, that the lateral variations in magnetism of the several geological bodies in which we are interested is sufficient to mask the effect of their configuration, and this is what is of greatest interest to us.

Submarine Gravity Meter Surveying.

It is not expected that the gravity meter will ever become airborne like the magnetometer, because the atmosphere is so unstable and subject to acceleration in all directions that the exceedingly small accelerations which we have to measure would be quite lost in the general disturbances and external influences.

Gravity methods have already been used at sea, notably in the pendulum observations made in submarines by Prof. Vening Meinesz. His observations, however, were probably only accurate to about a milligal, whereas for the purpose of prospecting for oil an accuracy of at least a tenth of a milligal is necessary.

The technique of gravity measurements at sea using gravity meters has developed along four lines.

1. Tripods of various heights are used in different depths of water. The chief difficulty here is to make the tripod sufficiently rigid. It frequently happens that additional legs have to be fastened to the original tripod to give the necessary stability.

2. Spud barges or pontoons have been used. These consist of a barge, or a pair of pontoons having a common deck, to which are fixed three long vertical legs or spuds. When the barge arrives at the desired location the legs are lowered until they touch the bottom, and then the barge itself is lifted up the legs until it is quite clear of the water and the crests of the waves. The action of the waves on the legs of the platform has been found

to have a very slight effect on the stability of the platform, and most disturbance has been found to be due to vibration set up by wind action. The method is suitable for depths of water varying between the limits of the length of the spuds and the draught of the barge.

3. Diving-bell methods. A series of practical tests have been made using diving bells proper with an open bottom, within which the instrument operator sat and read the instrument on the bottom of the sea. This has the advantage that the gravity meter may be set firmly on the bottom while the reading is being made. It is open to the serious objection, however, that the instrument operator has to work under high air pressure. This entails considerable discomfort, and the raising and lowering of the bell has to be undertaken very slowly, in order to avoid injury to the operator. Another difficulty is that in shallow water, where the pressure question is not so significant, wave action affects the bell, and this transmits vibrations to the ground, thus upsetting the instrument readings.

The open-bell method has now been abandoned in favour of the bathysphere or closed diving chamber, which is operated at atmospheric pressure, thus making possible the attainment of much greater depths without personal discomfort. The problem now becomes that of settling the chamber steadily on the bottom. Early designs had a flat or rounded bottom, but later ones have three short, rigid legs, which should increase the stability considerably.

4. The fourth method is that of an instrument either operated by remote control or fitted with automatic levelling and a self-recording device. This was one of the earliest lines of endeavour, and it seems to be the most logical, but so far the results achieved have not been satisfactory. It still remains the most useful line of research because it is the least dangerous, and it will be least subject to limitations of depth.

Under-water Seismic Surveying.

As in the case of gravity measurements, it seems that seismic methods will never take to the air, but they are being applied more and more to water-covered areas.

In shallow water it is usually adequate to set the seismographs on the bottom, to let the seismograph cables trail along the bottom, and to use a shot hole which is cased from above the level of high tide to below the bottom of the " Weathered layer." The technique is the same as for land shooting, except that extra care has to be taken of the hazard of cable leakage, with consequent coupling between the traces and the creation of fake reflections.

In deeper water the problem becomes more serious for many reasons.

In the first place, there is the difficulty of locating the shot point and the instrument spread in the proper place several miles out at sea. In the past this has been done by directing the floating craft from two towers on shore from which surveyors with theodolites set out the exact angles to provide an intersection at the required spots. Having been directed and anchored in the proper place, the surveyors then check the position of the craft whenever a shot is fired to find out whether there has been any drift. In most recent work the modern navigational aids using ultra short-wave radio are being used. The advantage of these is that the various floating

craft are able to locate themselves exactly. The precise separation of the shot point and the instrument spread is then checked by means of the sound-wave which travels through the water.

Then there is the question of the anchoring of the seismographs in deep water in which there may be considerable currents. One system is to float all the seismographs at a predetermined depth below the surface so as to be free from wave action, and to let them stream out in the direction of the current from the mother ship, which is securely anchored. Another method is to string the seismographs between two large buoys which are securely anchored. This method is open to the objection that a cross-current will cause vibration of the rope between the buoys, and thereby disturb the readings.

The shot may be lowered to the bottom by means of weights, or it may be fired at any depth which is found to give the best practical results.

Each new area which is being surveyed may present new problems. Double or repeated impeti through the water are sometimes troublesome. Some writers associate these with collapse or oscillation of the gas bubble which is formed after the explosion, but it is difficult to see how these would cause sharp impeti at long intervals rather than a damped vibration of relatively low frequency.

The extended area opened for exploration by the spread of geophysical exploration out to the edge of the continental shelf (or the 100 fathom line) opens a new area of tremendous extent to investigation, and our researches are being pressed forward to solve the many problems as soon as possible.

DISCUSSION.

THE CHAIRMAN (Professor A. O. Rankine) : Mr Van Weelden has made a very comprehensive statement on this important matter. I find myself so much in agreement with what he has said that I have no comments to offer, at any rate at this stage. I therefore invite remarks from others present.

Dr W. L. F. NUTTALL : In connexion with the use of the magnetic survey method from the air, Mr Van Weelden has mentioned that by flying at different altitudes different results are obtained from those that are obtained on the ground. It has been found possible also, by flying at different altitudes, to make an interpretation of the depth of a basin. Perhaps he could give us some further observations on that matter and could tell us whether in any particular area it has been possible to check up the results of an aerial magnetometer survey where the depth of the basin is known.

In connexion with the seismic work from the water, objections have been raised in certain countries in the past to its effect on marine life, i.e., that it results in killing fish. Perhaps he can say what has actually occurred in that respect as the result of this type of survey.

MR VAN WEELDEN : With regard to surveying from the air at different heights, if we have certain layers with different magnetic susceptibilities, and if we have a very complete—and it must be very complete and very

accurate—magnetic or gravitational picture for one level, we can compute it for the other levels. But that is very academic and hypothetical. It is much better to establish a different level and thereby get a reversible gradient. But that is still theoretical, and I personally do not know of any place where a check has been made, except that illustrated in a paper advertising the method. Certainly the method has been used to show that confirmation can be obtained; but the matter is still largely in the hands of the contractors, and we shall have to wait. I know of two surveys which are being made, or will be started very soon, and I am very anxious to see the results. Until I have seen them I am rather reluctant to recommend anybody to do very much more work on those lines.

The problem of the effect of explosives on animal life seems to be largely a matter of propaganda and of care. It is true that a charge of explosives under water will kill fish, and has been used for that very purpose, but the very small amount of dynamite used for the sensitive instruments makes the actual amount of damage done to animal life extremely small provided proper care is taken. Extensive tests made under the supervision of the Louisiana Department of Wild Life and Fisheries has led to that State approving the use of the seismograph methods in their waters. I refer to articles in the *Oil Weekly* of February 19 and October 22, 1945, page 34. Nevertheless, the crews are never very popular with the local fishermen and the matter is one which needs very careful handling.

Mr Percy Evans : I should like to express my appreciation of Mr Van Weelden's very excellent and interesting review of modern developments. Mr Van Weelden has referred to the lack of success of electrical methods as a direct indication of the presence of petroleum. I wonder whether he could give us any indication whether there have been any recent improvements in electrical methods for water surveys down to a depth of a few hundred feet. In the Geological Society a year or two ago we heard of some attempts which did not appear to have been entirely successful, and it would be interesting to know whether there have been any modern developments in water survey methods, either electrically or otherwise, although I have in mind electrical methods particularly.

Mr Van Weelden : I do not believe that anything really new has come out. Electrical methods for shallow work have been fairly successful; I know they have been used, for instance, to determine the depths of bed rock, and so on, in the United States, and also for finding water. But I do not know of anything which puts a new angle on the use of those methods, or which has rendered those methods better than they were formerly. The old resistivity method is still about as good as any, for all practical purposes. There are all sorts of theoretical reasons why some people claim that their particular systems will do better than any other, but I do not know that there is any reason to believe that.

Mr G. Morris (I.C.I. Ltd, Explosives Division) : I should like to express my appreciation of Mr Van Weelden's very interesting and illuminating summary of geophysical methods of prospecting.

In the paper he mentioned the difficulty that rock deformation limits the effectiveness of explosives, and expressed the desire for higher velocities of detonation. As a result of researches carried out during the war, the hydrodynamic theory of detonation can now be considered to be fully established. According to this theory conventional types of explosives, *i.e.*, those which depend for their action on chemical changes, are unlikely to have velocities of detonation appreciably greater than 8000 metres per second, so that the velocities obtained from modern geophysical explosives are unlikely to be greatly exceeded. A paper summarizing the present position of this theory was recently published by one of my colleagues, Mr Paterson, in *Engineering*.

Mr Van Weelden mentions the limitation of the weight of explosives by the fact that the length of charge is limited to 3 metres. Of course, the size of charge can be increased by incurring the added inconvenience and expense of drilling a larger shot-hole ; a larger cartridge has certain advantages in respect of the velocity achieved.

I should like to ask whether Mr Van Weelden has any views on some work that we published in *Geophysics* last July, work carried out in conjunction with Anglo-Iranian Oil Co. in which it was shown that for medium distances, from 6000 to 19,000 ft, the experts were not able to distinguish any appreciable differences either in the amplitude or in the frequency distribution when using charges consisting of high explosives detonating at high velocities, or explosives which were deflagrating and not detonating at all. That led us to consider that the impulses which are characteristic of refraction shooting are due largely to elastic deformation of the ground in the vicinity of the bore-hole, and that a good part of the energy of very high-power explosives is wasted in local shattering.

With regard to electric detonators, I think I may safely say that recent developments now enable us to provide detonators of at least as good performance as any to be obtained elsewhere. In that connexion I would put forward the plea that, since there are small but significant differences in the time sequences of electric detonators depending on the actual firing current they receive due to the actual firing arrangements used by different companies, perhaps a little more information on the subject of exploder " hook-ups " might be given to us when we are asked to specify the time characteristics of our electric detonators.

Mr Van Weelden : With regard to the last point, I am supposed to know my company's instruments but not the instruments of the various contracting firms working for us ; therefore I could not possibly give you more information on that score.

There are representatives here of the Anglo-Iranian Oil Company and they may care to say what they have discovered. But I think I mentioned at the beginning, that, for refraction shooting we used all sorts of dynamite and it did not seem to matter so much as long as we had a sufficiently large charge. It is certainly true that a good deal of the energy is used up as the result of deformation around the shot-hole.

The requirement of reflection shooting in tropical swamp areas are quite different, however, from those for refraction shooting in a desert. Moreover, we must comply with local law and therefore are not always free to

build storage warehouses of the type we like, but must often store our supplies in Government bodegas, which do not always come up to our specifications.

Mr R. Davis : Whilst I agree with Mr Morris that it has been demonstrated that changes in velocities of detonation in the range of 7500 to 1000 metres/second have no significant effect on the amplitude of refracted waves recorded at distances over 6000 ft from her shot-point, in other words the " shock wave " is unimportant, it does not follow that this will be the case for reflected waves. It is possible that the mechanism of the reflected wave is dependent on the higher frequencies and they in turn we would expect to be more closely related to the shock wave and speed of detonation.

Mr J. N. Adamson (I.C.I. Ltd., Explosives Division) : As we have heard from Mr Van Weelden, a velocity of 6000 metres/second is desirable for seismic explosives. Generally speaking, the present seismic explosives give this up to depths of 100 ft with ordinary detonator initiation, but for depths in excess of this, or where the explosives have to withstand adverse storage conditions, it is advisable to initiate the explosive by means of a suitable primer. These primers can be made of compressed Pentolite, Tetryl, or C.T.M.T.N. (i.e., the R.D.X. of the war period), and are available for this work.

Even when high velocity is not essential, for the reason indicated by Mr Van Weelden, the use of a primer is advantageous in that it ensures complete propagation of the explosive column under heavy water pressure, and thus makes absolutely certain that no undetonated cartridges are ejected from the shot-hole.

Mr Van Weelden : The use of primers in seismic prospecting is not uncommon ; it depends on the type of explosive used.

Vote of Thanks

The Chairman : I wish to propose a very hearty vote of thanks to Mr Van Weelden. We have had a very useful meeting this evening, and it is all because Mr Van Weelden has taken so much trouble to prepare a paper of this comprehensive kind, thus bringing to our notice many things we did not know concerning recent practical developments in geophysics. I ask you to join with me in expressing to him our appreciation.

(The vote of thanks was carried with acclamation.)

On the motion of Mr T. Dewhurst, the warm thanks of the meeting were also extended to Professor Rankine for having presided.

THE APPLICATION OF A NEW NOTATION TO PETROLEUM HYDROCARBONS.

By G. Malcolm Dyson, M.A., Ph.D., F.R.I.C. (Fellow).

The need for a new method of delineating organic compounds has been felt for some considerable time; Richards [1] pointed out the necessity and set out a list of abbreviations which had been used in his laboratory for the designation of petroleum hydrocarbons. As the present author pointed out at the time [2] the proposed abbreviations were not generally applicable to organic compounds as a whole, and did not provide more than a very restricted temporary solution of a single aspect of the problem. In a monograph [3] the reasons for adopting a cipher system as the basis of a new notation are set out in detail, and in this communication the particular impact of the new system on the nomenclature of petroleum hydrocarbons is set out.

Acyclic and alicyclic hydrocarbons are all delineated in terms of the six symbols :—

C = Carbon.
E = The double bond.
E1 = *Cis*-arrangement at double bond.
E2 = *Trans*-arrangement at double bond.
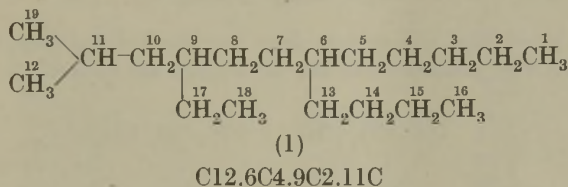E3 = Triple-bond.
A = Bridge or ring.

Before proceeding to illustrate the use of these symbols, some explanation of the terms used in the notation is desirable; the purpose of the notation is to delineate exactly all features of the structure in a linear form—this form is referred to as a " cipher." Thus, a typical hydrocarbon cipher is :—

$$C7.2,2,3,5,6C.3E$$

It will be noted that the cipher is divided into sections by stops : each section is referred to as an operation, and in the cipher set out above, there are three operations, " C7 " being the first, and " 3E " the last. Where a letter is followed by a figure as in " C7 " the figure is termed a *modulant*; where the figure precedes the letter it is termed a *locant*, as its function is to delineate the position of what follows it.

The principle of ciphering a saturated acyclic hydrocarbon is to locate the longest carbon chain. This is always, without exception, the starting point of the cipher. Thus, in the case of a straight chain hydrocarbon of 3, 7, or 16 atoms the cipher would be C3, C7, or C16. In arborescent hydrocarbon structures the longest chain still commences the cipher, and

is followed by a series of operations, stating the branches in order of decreasing magnitude. Thus, 'in the example (1) below, the cipher is C12.6C4.9C2.11C,
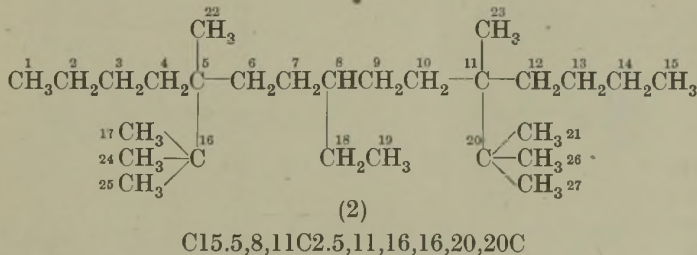
$$\underset{\underset{CH_3}{\overset{12}{}}}{\overset{\overset{19}{CH_3}}{}}\!\!\!\!\!\!\!\!\!\!>\overset{11}{C}H\!-\!\overset{10}{C}H_2\overset{9}{C}H\overset{8}{C}H_2\overset{7}{C}H_2\overset{6}{C}H\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_3$$

$$\underset{\overset{17}{C}H_2\overset{18}{C}H_3}{\big|}\qquad\underset{\overset{13}{C}H_2\overset{14}{C}H_2\overset{15}{C}H_2\overset{16}{C}H_3}{\big|}$$

(1)

C12.6C4.9C2.11C

implying the existence of portions of structure as set out below :—

>   C12.   A main atom of twelve carbon atoms.
>   6C4.   A butyl branch at position " 6."
>   9C2.   An ethyl branch at position " 9."
>   11C.   A methyl branch at position " 11."

It will be noted that all carbon atoms are numbered in order of citation in the cipher : in this way " dashed " numerals, and those with super-scripts are avoided, and there is only one possible enumeration for any given structure, *i.e.*, that imposed on it by the rules of the new notation. In this way all ambiguities of enumeration are eliminated. In choosing the direction of enumeration of the parent dodecyl stem for example (1) the right-hand side was chosen so that the locant of the second operation (6C4) is as low as possible (*i.e.*, " 6 " and not " 7 ").

An example of the use of the notation for the delineation of sample structures is given in Table I (on p. 359). The structures are those of the table given in *J. Inst. Petrol.*, 1946, **32**, 689 :—
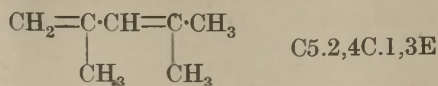
Where there is considerable arborescence, as in example (2), several groups of the same size have to be specified ; these are indicated by multiple locants, as in 5,8,11C2 and in 5,11,16,16,20,20C

$$\overset{\overset{22}{CH_3}}{\underset{1}{C}H_3\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}\!-\!\overset{6}{C}H_2\overset{7}{C}H_2\overset{8}{C}H\overset{9}{C}H_2\overset{10}{C}H_2\!-\!\overset{11}{C}\!-\!\overset{12}{C}H_2\overset{13}{C}H_2\overset{14}{C}H_2\overset{15}{C}H_3}$$

(structure with branches)

(2)

C15.5,8,11C2.5,11,16,16,20,20C

Where unsaturation is present it is specified after the delineation of the carbon structure as in the following examples : [4]—

ter-Butylallene

$$CH_2\!\!=\!\!C\!\!=\!\!CH\cdot C\!\!<\!\!\begin{array}{c}CH_3\\CH_3\\CH_3\end{array}$$

C5.2,2C.3,4E
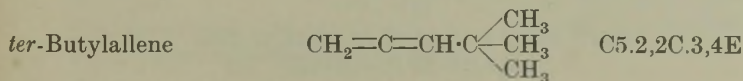
2 : 4-Dimethylpentadiene-1 : 3

$$CH_2=C \cdot CH=C \cdot CH_3$$

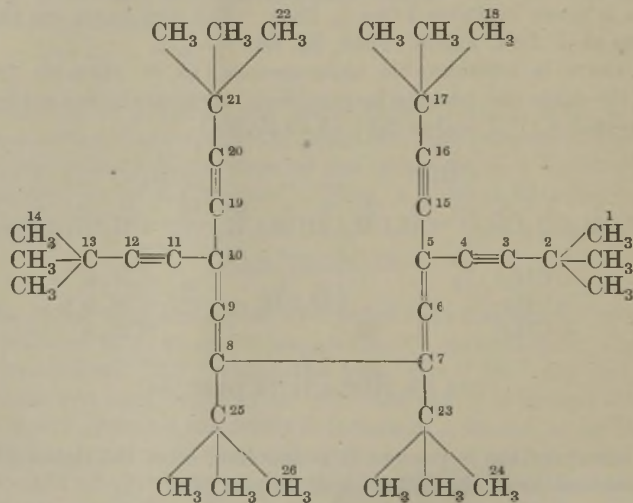$$\underset{CH_3}{|} \qquad \underset{CH_3}{|}$$

C5.2,4C.1,3E

Whilst to prove that the system does not break down even under stress of complexity, two samples from the same page are quoted :—
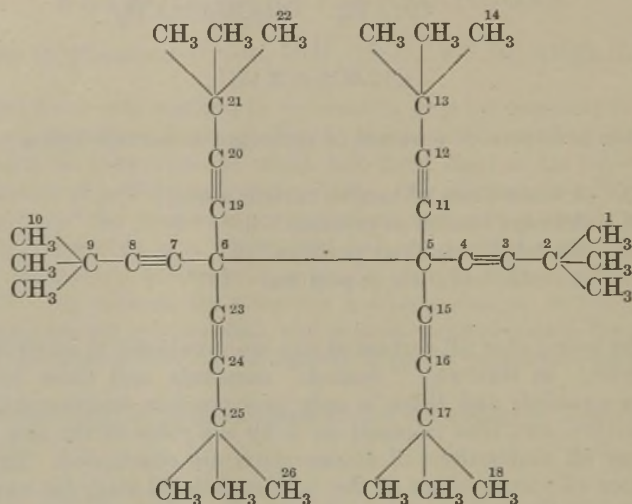
(3)

C10.5,5,6,6C4.2,2,9(4)25,9(4)25C.3(4)23E

(4)

C14.5,6C4.2,2,13,13,17,17,21,21,23,23C.
5,6,8,9E.3,11,15,19E3.

TABLE I.

Structure.						CFR.MM.NO.
C8 .	.	.	.	.	.	—17
C7.3C	.	.	.	.	.	26·8
C6.2,5C	.	.	.	.	.	55·8
C6.2,3C	.	.	.	.	.	78·9
C6.3,4C	.	.	.	.	.	81·7
C5.2,3,3C	.	.	.	.	.	99·4
C5.3C2.2C	.	.	.	.	.	88·1
C5.2,3,4C	.	.	.	.	.	95·9
C5.2,2,4C	.	.	.	.	.	100
C5.2,2,3C	.	.	.	.	.	99·9
C4.2,2,3,3C	.	.	.	.	.	103

It will be noted that in the cipher for example (3) the C locant has been written " 2,2,9(4)25,9(4)25 "; this is equivalent to " 2,2,9,9,13,13,17,17, 21,21,25,25," but whenever the numbers of a multiple locant form an arithmetical series of more than three terms they are expressed as, *e.g.*, 9(4)25—the " 9 " and " 25 " defining the limits of the series and the figure in parentheses—(4)—the constant difference.

The general effect of this notation on linear saturated and unsaturated hydrocarbons is shown in Table II.

TABLE II.

Name.[5]					Cipher.
2 : 3-Dimethylhexane	.	.	.	.	C6.2,3C
2 : 4-Dimethylhexane	.	.	.	.	C6.2,4C
n-Octane	.	.	.	.	C8
3-Methylheptane	.	.	.	.	C7.3C
2 : 2-Dimethylhexane	.	.	.	.	C6.2,2C
2 : 2 : 4-Trimethylpentane	.	.	.	.	C5.2,2,4C
2 : 3 : 4-Trimethylpentane	.	.	.	.	C5.2,3,4C
iso-Butane	.	.	.	.	C3.2C.E
1 : 3-Butadiene	.	.	.	.	C4.1,3E
Isoprene	.	.	.	.	C4.2C.1,3E
1 : 3-Pentadiene	.	.	.	.	C5.1,3E
2 : 3-Dimethylbutadiene-1 : 3	.	.	.	.	C4.2,3C.1,3E
$(CH_3)_2CH.CH(CH_3)CH=C$ ⟨CH₃ CH₃ / C⟨CH₃ CH₃				.	C7.2,2,3,5,6C.3E

A further example is from *Organic Chemistry* (Whitmore) wherein the following statements appear :—

    ". . . as follows : Di-*iso*-butylenes (Whitmore, 1932), 2,4,4-tri-methyl-pentene-1 ; 2,4,4-trimethylpentene-3 ; these are formed in the ratio 4 : 1. Tri-*iso*butylenes, 2,2,4,6,6-pentamethylheptene-2,2-*neo*pentyl-4, 4,Ml₂-pentene-1 (*unsym*-di-neopentyl-ethylene), 2,4,4,6,6-pentamethylheptene-2 &-1. . . ."
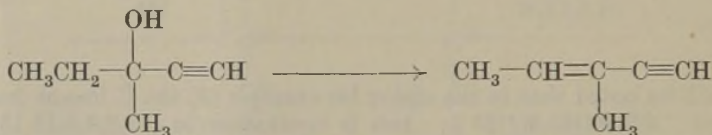
C C

This may be interpreted as :—

    " the following substances are formed (Whitmore, 1932) :—
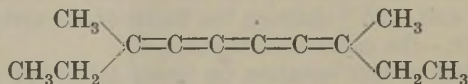
        C5.2,2,4C.4E
        C5.2,2,4C.3E
        C7.2,2,4,6,6C.2E
        C7.2,2,4,6,6C.4–10E
        C7.2,2,4,4,6C.5E
        C7.2,2,4,4,6C.6E . . ."

Again, an important decomposition of an unsaturated alcohol has been written thus [6] :—

$$CH_3CH_2-\overset{\overset{\textstyle OH}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-C\equiv CH \longrightarrow CH_3-CH=\overset{}{\underset{\underset{\textstyle CH_3}{|}}{C}}-C\equiv CH$$

Methylethylethynyl carbinol   +

$$\overset{\textstyle CH_3}{\underset{\textstyle CH_3CH_2}{}}{>}C=C=C=C=C=C{<}\overset{\textstyle CH_3}{\underset{\textstyle CH_2CH_3}{}}$$

This, in the new notation becomes :—

   C5.3C.E3.3Q $\longrightarrow$ C5.3C.2E.4E3 + C10.3,8C.3 ⋯ 7E

(Note the use of " Q " for the hydroxyl group, and of the sign of a series in, " 3 ⋯ 7 " to indicate " 3,4,5,6,7.")

Cyclic compounds (when not aromatic) are ciphered in terms of A; two well-known examples are thujane and adamantane which are illustrated below; the simple cyclic saturated structures AC4, AC5, and AC6 represent *cyclo*-butane, *cyclo*-pentane, and *cyclo*-hexane respectively.
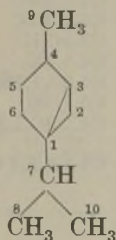
Thujane
1-*Iso*propyl-4-methylbicyclo[3.1.0]hexane
AC6.1–3A.C2.4,7C
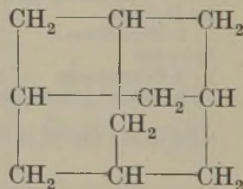
Adamantane
Tricyclo[3.3.1.1[3,7]]decane
AC8.1–5,3–7AC

This convention enables the naphthenes to be referred to a simple systematic code. In Table III is shown a series of naphthenes and the corresponding ciphers in the new notation. Attention is drawn to the fact that the average number of symbols used in the full names is twenty-six; whilst the corresponding average for the ciphers is ten.
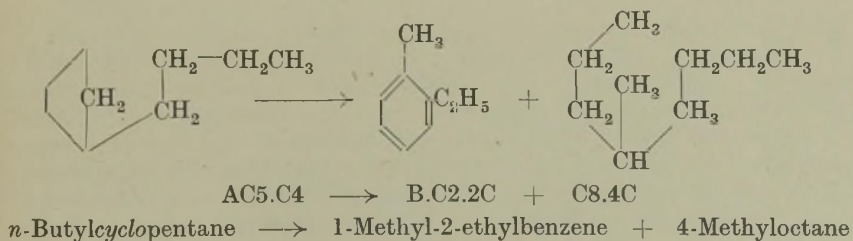
TABLE III.

Some Naphthenes.

Full name.	Cipher.
1 : 1-Dimethyl*cyclo*butane	AC4.1,1C
1 : 2-Dimethyl*cyclo*butane	AC4.1,2C
1 : 1 : 2-Trimethyl*cyclo*butane	AC4.1,1,2C
1-Ethyl-2-*iso*propyl*cyclo*butane	AC4.1,2C2.5C
1-Ethyl*cyclo*pentane	AC5.C2
1 : 2-Dimethyl*cyclo*pentane	AC5.1,2C
1 : 2-Dimethyl-4-ethyl*cyclo*pentane	AC5.C2.3,4C
1 : 3-Diethyl*cyclo*hexane	AC6.1,3C2
1 : 2-Dimethyl-4-ethyl*cyclo*hexane	AC6.C2.3,4C
1 : 3 : 5-Trimethyl-2-ethyl*cyclo*hexane	AC6.C2.2,4,6C
1-Methyl-4-butyl*cyclo*hexane	AC6.C4.4C
1 : 1-Dimethyl-3-*iso*propyl*cyclo*heptane	AC7.C2.3,3,8C

The aromatic hydrocarbons are all referred to one or more of the conventional structures.

*cyclo*pentadiene   VI   Naphthalene   K

Benzene   B   Phenanthrene   J
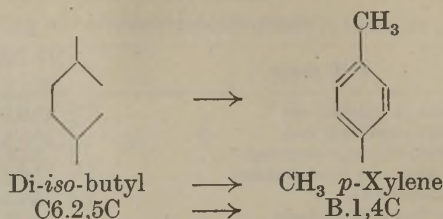
Indene   WI   Anthracene   T
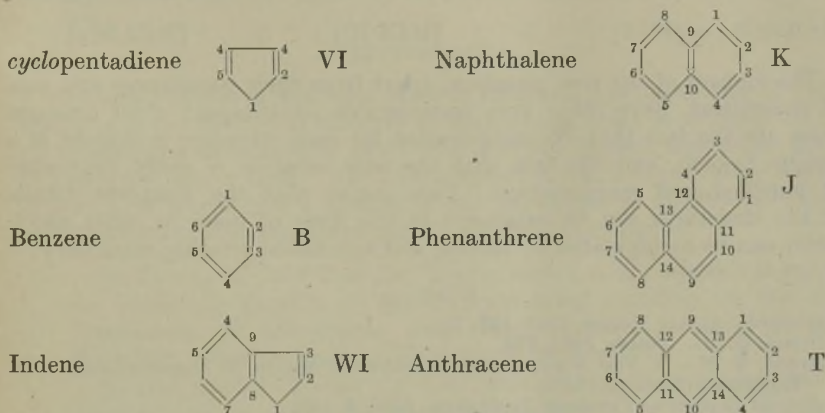
These six structures are arranged in order of seniority and it is obligatory to choose as the basis of notation the most senior ring-system where two or more are potentially present in the same compound. More complex rings are built up in the new notation by the process of adduction, but for details of this procedure, reference must be made to the original monograph. Three examples, taken from reactions familiar to petroleum chemists, are shown below as examples of the methods set out above.
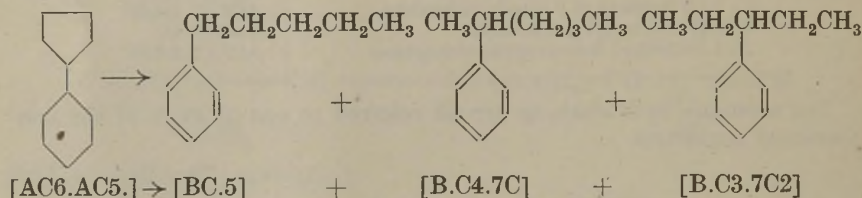
Example 1.

AC5.C4 $\longrightarrow$ B.C2.2C   +   C8.4C

n-Butyl*cyclo*pentane $\longrightarrow$ 1-Methyl-2-ethylbenzene   +   4-Methyloctane

Example 2.

Di-*iso*-butyl   ⟶ CH_3 *p*-Xylene
C6.2,5C   ⟶   B.1,4C
        ⟶

Example 3.

$CH_2CH_2CH_2CH_2CH_3$ $CH_3CH(CH_2)_3CH_3$ $CH_3CH_2CHCH_2CH_3$

[AC6.AC5.] → [BC.5]   +   [B.C4.7C]   +   [B.C3.7C2]

The ciphers of the new notation, apart from their conciseness and ease of recognition, have other very considerable advantages; chief amongst these are the fact that the enumeration for each structure is defined in a unique fashion, and the fact that the new notation is easily applicable to punched-card manipulation. This means that the complete details of the structures can be expressed in the form of holes in cards which latter can be manipulated by sorting and automatic printing machinery.

References.

[1] Richards, A. R.   *Nature*, 1944, **153**, 715.
[2] Dyson, G. M.   *Nature*, 1944, **153**.
[3] Dyson, G. M.   *A New Notation and Enumeration System for Organic Compounds.* Longmans (London, 1947).
[4] *Annual Reviews of Petroleum Technology*, 1938, **3**, 132.
[5] *Annual Reviews of Petroleum Technology*, 1938, 3, 181–183.
[6] *Annual Reviews of Petroleum Technology*, 1938; **3**, 147.

THE CHEMICAL ASPECTS OF THE PETROLEUM ACTS.

By S. G. Burgess, Ph.D., B.Sc., F.R.I.C. (Fellow).

Summary.

The author maintains that the Petroleum (Consolidation) Act, 1928, is an important contribution towards public safety and traces the development of the present legislation from the first Act of 1862. The definitions and chemical aspects of the current Act are discussed together with the problems that arise from different interpretations. The general types and possible compositions of statutory samples are enumerated and methods suggested for the separation of the petroleum, if any, from other substances that may be present. These methods are critically examined and attention is drawn to the difficulties of the interpretation of analytical data obtained in connexion with the examination and certification of samples taken under the Act.

INTRODUCTION.

The first Petroleum Act was passed in 1862 and it is interesting to recall the state of the petroleum industry at that time in order to appreciate fully its tremendous development since then and the present legislation which this progress has evoked. The following are a few comparatively disconnected facts which give a picture of the conditions at about that period and illustrate the limited use of petroleum and its products :

(a) It was in 1850 that Dr. Young took out his celebrated patent for obtaining paraffin oil (or oil containing paraffin) by the slow combustion of bituminous coals, and founded Young's Paraffin Company which started the Scottish oil industry ;

(b) Not until 1865 was the first successful pipeline constructed in America, and in that year the total amount of petroleum products exported by the U.S.A. was only about 25 million gal of which nearly 13 million gal was for illuminating purposes ;

(c) The Brayton Engine patented in U.S.A. in 1872, was the first to use kerosine as the motive fuel, and the first patented gasoline machine, the Hock engine, was patented in Vienna in 1873 ;

(d) The use of mineral oil for illuminating purposes had only been general in Great Britain for a comparatively few years. The exact date of its introduction is not known, but authorities consider it to be about 1859.

One of the purposes of the early legislation was to protect the public from the " deadly " low-flash oils which were sold occasionally for illuminating purposes. The fatalities that occurred were popularly attributed to this cause and there was a great outcry in the Press at that time. It is quite understandable that low-flash oils were then sold occasionally for use in lamps, because if the lower fractions were removed by distillation to raise the flash-point it was also necessary to remove some of the heaviest fractions, otherwise the kerosine would not burn satis-

factorily in the wick lamps then in use. The removal of these two fractions naturally reduced the yield and gave by-products which at that time had not a ready sale. The question of the safety of oils to be used in lamps was considered by the Petroleum Conference at Baku, 1886, and the recommendation made for Russian kerosine of specific gravity 0·830 was as follows :

Safe oil	.	.	Flash-point not less than 77° F;
Unsafe oil	.	.	Flash-point below 77° F

The subject of lamp accidents was first investigated by Dr. Chandler of New York in 1871, and later, in 1890, Sir Frederick Abel and Sir Boverton Redwood made their comprehensive report to Her Majesty's Chief Inspector of Explosives. They gave explanations and causes of lamp explosions, but did not consider that they were mostly caused by low-flash oil. In fact, the words used in the report were : "the substitution of mineral spirit for mineral oil has in some cases probably caused the accident." As the result of this work the Metropolitan Board of Works published in 1885 suggestions as to the construction and management of mineral oil lamps, and in 1893 the London County Council made recommendations on this subject in view of the numerous fatal and other accidents caused by petroleum lamps.

As the need for legislation was appreciated in 1862, it would not be an exaggeration to say that the position to-day would be chaotic without some measure of supervision and control, for it is common knowledge that the uses of petroleum, its products, and its mixtures are so wide that they affect practically every industry. Not only the obvious manufacture and storage of motor spirit, fuel oil, lubricating oil, kerosine, etc, but multifarious solvents, cellulose paints and varnishes, synthetic resins, plastics and paints, insecticides, and fine chemicals are either products of petroleum or contain petroleum. The efficient administration of the Petroleum Acts in view of such general use becomes, therefore, a matter of supreme importance for the protection and general safety of the public. The rôle that the scientist plays in industry naturally assists to a considerable extent the work of the responsible authority, because such trained personnel realize the dangers of the materials employed and regulate their precautions accordingly. At the same time there are some firms without such professional guidance which, either through ignorance or unwillingness to spend sufficient money on suitable precautions, will take serious risks and expose their staff and their neighbours (who may be on a higher floor of the same building) to a constant danger of fire and/or explosion. It is difficult for anyone unconnected with the administration of this Act to appreciate fully the great contribution that it makes to public safety and how important it is that all entrusted with this duty shall rightly interpret and apply the spirit of the law. Indeed, it is to be hoped that as knowledge on all aspects of the subject becomes more general all people opening businesses employing inflammable materials will initially ensure that they are conversant with the Acts, Orders, and Regulations that apply and, if necessary, seek guidance from the licensing authorities to obviate the legal enforcement of compliance with laws designed for safety purposes.

Before discussing the chemical aspects of the definitions and the general methods of examination it will be of interest to review briefly the earlier Acts and the reasons for their repeal or modification so that the significance of the present legislation can be better appreciated.

HISTORICAL.

In Great Britain, as mentioned above, the first Act relating to petroleum was passed in 1862 (25 & 26 Vict., Ch. 66) and was entitled " An Act for the Safe-keeping of Petroleum." The preamble was as follows :

" Whereas it is expedient to provide for the safe keeping of petroleum and certain products thereof that are dangerous to life and property, from their properties of giving off inflammable vapours at low temperatures," etc.

The Act defined petroleum as including " any product thereof that gives off an inflammable vapour at a temperature of less than 100° of Fahrenheit's thermometer," but as no method of testing was prescribed the Act remained practically inoperative. After the subject of flash-point had been experimentally investigated by Sir Frederick Abel and his co-workers, an Amending Act was passed in 1868 (31 & 32 Vict., Ch. 56) giving details of the apparatus and the manner of testing and amplifying the definition of petroleum. It read as follows :

" Petroleum for the purpose of the two Acts includes all such rock oil, Rangoon oil, Burmah oil, any product of them, and any oil made from petroleum, coal, schist, shale, peat, or other bituminous substance, and any product of them as gives off an inflammable vapour at a temperature of less than 100° of Fahrenheit's thermometer."

Considering the scientific knowledge then available it would hardly seem possible that such a comprehensive definition could fail to include any kind of petroleum which the administering authority chose to consider as petroleum. The labelling then required on a " bottle " or " vessel " which contained petroleum to which the Act applied was as follows :

" Great care must be taken in bringing any light near to the contents of this vessel as they give off an inflammable vapour at a temperature of less than 100° of Fahrenheit's thermometer."

The method of test was given in detail, but for the present purpose it may be stated briefly as an open flash-test in which the sample was placed in a conical cup heated by a water-bath under which was placed a *small* flame. Across the cup was fixed a wire and a *very small* flame was passed along the wire after every rise of temperature of two or three degrees. The test was then repeated and the test flame applied after every rise of two degrees. On applying this test to imported petroleum from the U.S.A., which had a fire test of 120° F before shipment, it was found that the flash-point obtained was several degrees above the legal limit of 100° F. When this Act was generally adopted it was soon found that the directions for testing were not sufficiently precise and the words " small flame " and " very small flame " were differently interpreted by various operators. As the result

vendors of petroleum were frequently proceeded against and sometimes convicted for selling kerosine which had a flash-point below the legal limit, although the oil had been passed by independent experts. Moreover, it became clear that the open flash-test was unreliable, especially when made by comparatively unskilled and inexperienced persons.

In 1871 another Act (34 & 35 Vict., Ch. 105) was passed which repealed the previous Acts of 1862 and 1868, but the first schedule was a reproduction of the directions for testing given in the schedule of the 1868 Petroleum Act. The definition of petroleum was slightly but not significantly altered. Petroleum to which the Act applied was required to be labelled as " highly inflammable." Owing to continued criticism and complaints as to the method of test the Government in 1875, with the concurrence of the Metropolitan Board of Works and of the Petroleum Association, requested Sir Frederick Abel to investigate the matter experimentally, and after exhaustive enquiries he submitted a report in 1876 that the test was not of a nature " uniformly to ensure reliable and satisfactory results." His work led to the introduction of the closed flash-point apparatus and test which to-day bears his name, and the figure of 73° F in this apparatus was found by an exhaustive series of trials to be equivalent to the 100° F open flash-point test. A short amending Act was passed in 1879 to legalize this closed method of test and to substitute a test standard of 73° F. A model of the apparatus was deposited at the Weights and Measures Department of the Board of Trade and provisions were made to standardize the apparatus used by appointed inspectors.

After this Act was passed it was decided by the Court of Queen's Bench that a cart could not be licensed as a " place " for keeping petroleum to which the Act applied, and in 1881 the Petroleum (Hawkers) Act was introduced to regulate the " hawking of petroleum and other substance of a like nature."

The Act of 1879 gave no directions applicable to the testing of such material as india-rubber solution, and to meet this the first schedule of the Inflammable Liquids Bill of 1891 contained the instruction to " place a tablespoonful in the cup, place the cover on and add $1\frac{1}{2}$ inches of water to the air chamber and maintain the water-bath at 76° F, etc."

In material of this type the absence of convection currents resulted in an unfairly low flash-point being recorded and it became apparent that a stirrer was required to ensure reproducible results with viscous materials.

In 1899 the London County Council appealed against a magistrate's decision that a composition containing 20 per cent of petroleum did not come withing the meaning of the Acts and the High Court remitted the case to the magistrate for him to convict. The Privy Council, in 1907, acting on section 14 of the Act of 1871 which stated that the Act or any part thereof may be applied to any substance, endorsed this view of the law, and strengthened it by an Order " that certain parts of the Acts of 1871–1881 should apply to any mixture of petroleum with any other substance or substances which . . . gives off inflammable vapour at a temperature of less than 73 degrees of Fahrenheit's thermometer, whether such mixture be liquid, viscous, or solid in the same manner as if such mixture were petroleum, to which the said Acts apply." Such mixtures

were to be labelled " Petroleum mixture giving off an inflammable heavy vapour "—" Not to be exposed near a flame."   A stirrer was now incorporated in the Abel apparatus specified in the Act of 1879 and directions for its use, as well as instructions for testing solid mixtures.   This order (S.R. & O. 1907, No. 483) contained the statement that " mixtures of petroleum with other substances present dangers similar to those presented by petroleum without admixture."   This paragraph has been omitted from all subsequent orders on this subject, probably because although applicable to the mixtures then envisaged it would not in 1927 (when the next order was made) be correct within the ordinary meaning of the words " dangers similar."

In 1926 a Petroleum Act was passed which amended and supplemented the Acts of 1871 and 1879 and repealed the Act of 1881.   The meaning assigned to petroleum was as follows :

> " Petroleum includes crude petroleum, oil made from petroleum, or from coal, shale, peat or other bituminous substances, and other products of petroleum."

Petroleum to which the Act applies was for the first time called petroleum spirit and defined as " such petroleum as when tested in the manner set forth in the First Schedule to this Act gives off an inflammable vapour at a temperature of less than seventy-three degrees Fahrenheit."   Clearer instructions with regard to testing were given but without altering the test. A complete specification of the testing apparatus was drawn up without making any alteration in the apparatus itself and important new regulations as to verifying and stamping of the apparatus by the Board of Trade were made.   Two important requirements in connexion with certification are that :

(a) The apparatus has been stamped within ten years; and
(b) No part of the apparatus has been materially altered, repaired, or replaced since the apparatus was last stamped.

In 1927 an Order in Council was made to apply the provisions of the Petroleum Act, 1926, to mixtures of petroleum defined by the Order in like manner as they apply to petroleum spirit.   The apparatus specified and the manner of test were similar to those detailed in the 1907 Order and the labelling of such mixtures was " Petroleum mixture giving off an inflammable heavy vapour " instead of " Petroleum spirit—Highly inflammable," which was the wording required for the petroleum spirit defined by the Act.

In 1928 a Petroleum (Amendment) Act was passed and at the same time the whole of the petroleum legislation (including the Amendment Act) was consolidated in the Petroleum (Consolidation) Act, 1928, and all previous Acts were repealed.   No alteration of the apparatus, method of test, or certification of apparatus by the Board of Trade was made.   In 1929 an Order in Council to apply this Act to certain mixtures of petroleum was approved (S.R. & O. 1929, No. 993).   The previous Orders of 1907 and 1927 were revoked, but no change in definition or method of test was made. Since this date various other substances, e.g., calcium carbide, carbon disulphide, and some compressed gases (including methane) have been

included under certain sections only of the Act by virtue of the power obtained under Section 19, " Power to apply Act to other substances."

CHEMICAL ASPECTS OF THE DEFINITIONS.

Before an analyst can select suitable methods for ascertaining whether a material is :

    (*a*) A petroleum spirit ; or
    (*b*) A petroleum mixture to which the provisions of the Act apply ; or
    (*c*) A substance or mixture to which the provisions do not apply ;

he must first have clear ideas as to which types of chemical compounds or mixtures fall into the respective categories. In order to give some guidance for thought in this matter the author will endeavour to consider the definitions in the present British petroleum legislation and to deduce from the meanings of the words used possible interpretations in the light of modern knowledge of petroleum chemistry. The accepted definitions of the words used are those given in the *Oxford Dictionary*. For the benefit of those unfamiliar with legal phrasing and terminology it must be stated that the following is only a layman's interpretation and the meaning in law cannot be established until some case has been heard and a ruling obtained on its legal significance. To the author's knowledge no case law exists on these definitions and their interpretations, and the Interpretation Act of 1889 which applies to all statutes gives no help on such matters as these. If a difficult point arises the official opinion of the appropriate licensing authority can always be sought and an agreed policy acted on pending legal decision.

The definition of petroleum in the Petroleum (Consolidation) Act, 1928 (called hereafter the Act), is as follows :

    " Petroleum " includes crude petroleum, oil made from petroleum, or from coal, shale, peat or other bituminous substance, and other products of petroleum.
    " Petroleum spirit " means such petroleum as when tested in the manner set forth in Part II of the Second Schedule to this Act gives off an inflammable vapour at a temperature of less than seventy-three degrees Fahrenheit.

" Crude petroleum " is quite specific. " Oil made from petroleum " would include the products of distillation, cracking, hydrogenation, alkylation, polymerization, isomerization, etc, provided these products could be included in the definition of " oil ! " which is " a substance having the following characters (or most of them) : viz. those of being a liquid at ordinary temperatures, of a viscid consistence and characteristic unctuous feel, lighter than water and insoluble in it, soluble in alcohol and ether, inflammable, chemically neutral " (*Oxford Dictionary*). The expression " oil made from petroleum " coupled with the words " or from coal, shale, peat," could in view of the wide range of conditions attainable in modern processes, be held to include almost the complete range of possible hydrocarbons of all types. " Bituminous substances " include a wide range of materials when defined as " of the nature of, consisting of, or containing

bitumen." Included among such substances are natural bitumens, pyrobitumens (asphaltic and non-asphaltic), pyrogenous distillates (pyrogenous waxes and tars), pyrogenous residues (pyrogenous asphalts and pitches). Each member of the bituminous family is a homogeneous or heterogeneous mixture of a multitude of chemical substances and consequently the oil thereform will have a very variable composition. The next phrase " and other products of petroleum " presents considerable difficulty which is in no small measure due to the rapid advances of the petroleum industry in the manufacture of industrial organic chemicals from what is without doubt petroleum as defined. Accepting the definition of " product " as " that produced by any action, operation or work, the result " it would follow that alcohol, acetone, ether, etc, are petroleum spirit as defined by the Act, since these substances are produced commercially from the paraffins and olefins formed by the cracking of petroleum oil. These hydrocarbons are without doubt products of petroleum as also are aniline, nitrobenzene, etc. In fact, in a text-book published in 1914, both aniline and nitrobenzene were declared to be petroleum as defined. This interpretation leads us to the position that alcohol produced from petroleum is petroleum spirit as defined, but if produced by fermentation it is not. Similar remarks apply to acetone and consequently before such substances could be certified as being petroleum spirit (both flash below 73° F) their source would have to be ascertained. Such an interpretation would make administration impossible and is, moreover, at variance with the spirit of the legislation as shown by section 19 of the Act. This section is most important, as it allows the Act to be extended to any substance should necessity arise. It reads :

Section 19 : *Power to apply Act to other substances.*

(1) His Majesty may by Order in Council apply to any substances any of the provisions of this Act specified in the Order, with such modifications, if any, as may seem to his Majesty to be desirable having regard to the nature of the substance to which the Order relates

(2) While any Order in Council relating to any substance is in force under this section the provisions of the Act thereby applied shall have the effect as if the substance were included in the definition of petroleum spirit, but subject to such modification, if any, as may be provided by the Order

(3) Any Order in Council made under this section may be varied or revoked by any subsequent order.

Under this section certain provisions of the Act have been applied to mixtures of petroleum and to calcium carbide, carbon disulphide, specified liquid gases (including methane), etc. Considering the wide powers under this section it does not seem right to apply the Act to substances which have been derived from petroleum by the addition of a foreign grouping not originally present in this petroleum. When the Act was framed such an interpretation as alcohol being petroleum spirit was not possible; it only became so as a result of fairly recent technical advances. Considering this fact together with the knowledge that had it been desirable for the provisions of the Act to apply to alcohol a specific Order in Council would have been made long since, it does not seem reasonable to drag in such

substances by a back door which has only just been opened. Similar argument applies to acetone, ether, acetaldehyde, etc. By considering only those compounds which contain the elements originally present in the crude petroleum, etc, we are left with the hydrocarbons if the small amounts of nitrogen, sulphur, oxygen, etc, are disregarded. Compounds produced on distillation containing these last-mentioned elements are omitted from consideration. It seems more in the spirit of the legislation, bearing in mind its history to consider petroleum as hydrocarbons produced from the sources defined and leave all other compounds to be dealt with under Section 19, rather than to endeavour to embrace all the products of petroleum under this phrase and be faced with a constantly expanding number of substances. It is, of course, possible to manufacture petroleum spirit from sources not defined, *e.g.*, octane from ethylene obtained from alcohol produced by fermentation; but as this process would not at the present time be a commercial proposition consideration of the matter need not be pursued.

For the purposes of the Petroleum (Mixtures) Order, 1929, the expression " mixtures of petroleum " means " all mixtures (whether liquid, viscous, or solid) of petroleum with any other substance except mixtures which, when tested in a manner set forth in Part II of this schedule, do not give off an inflammable vapour at a temperature below seventy-three degrees Fahrenheit." This definition contains a somewhat delicate point because two substances, such as paraffin oil and acetone, which are not considered as coming within the provisions of the Act, will, if mixed together, become a petroleum mixture to which the Act applies. Another example is mineralized methylated spirit. The low flash-point of these mixtures is due to the presence of the acetone and alcohol respectively. It may be considered that to apply the provisions of the Act to such mixtures is tantamount to assuming the existence of an Order in Council, made under the statutory powers of Section 19, applying the provisions of the Act to these compounds. In such cases it is well to consider the danger of the petroleum constituent, for in those samples where the petroleum content is of such a nature that by itself it would be classed as petroleum spirit, it is a straightforward case of the intention of applying the provisions of the Act to such a mixture. In cases where the provisions of the Act would not apply to the petroleum fraction without admixture, it would hardly seem right that it should be included under the category of petroleum spirit by virtue of admixture with a substance which is not petroleum (to which the Act applies) and almost assume the existence of a Statutory Rule and Order for the inclusion of this substance. However, the definition is clearly worded and if strictly construed implies that any mixture which flashes below 73° F and contains petroleum is a petroleum mixture. As it is a matter of considerable importance to manufacturers the opinion of the licensing authority should be asked in doubtful cases.

Petroleum mixtures to which the Act applies must be labelled " Petroleum mixture giving off an inflammable heavy vapour " and, in view of the definition, cases can be considered of some selected motor fuels which are taken as examples of the difficulty in deciding when a petroleum spirit becomes a petroleum mixture. Benzole motor fuel

normally contains a small amount of dissolved water which is in no way an essential part of the preparation. Its presence is purely adventitious and when completely in solution not objectionable. This product can hardly be considered a mixture as the result of the presence of a foreign substance which may be described as an impurity. A reasonable assumption in this matter is that the mixture should be intentional and the added products should form an essential part of the whole. In a lead-doped motor spirit lead tetra-ethyl and ethylene dibromide, *inter alia*, are intentionally added to promote anti-knock qualities, but are only present in small quantity. An alcohol blended fuel, however, contains alcohol in very appreciable amount (a pre-war branded petrol contained about 16 per cent) and such a product must be considered a mixture. From the analytical viewpoint this is a difficult matter to decide, especially when a sample is received for analysis with no information regarding its source or uses. The added constituent may be any liquid or dissolved solid and qualitative indication of the presence of the unknown may be difficult to obtain (even if its nature were known) in the presence of petroleum of very varied composition. This matter will be discussed more fully in the next section when methods of analysis are reviewed.

General Considerations.

Nature of the Sample.

The official sample may be any product suspected by the inspector of being petroleum spirit or a petroleum mixture. The materials most likely to be used or stored without a licence or in greater quantity than that stated in the licence generally fall into one of the following categories :

(1) Paints, lacquers, varnishes intended for spraying, and their respective thinners;
(2) Petroleum spirit and petroleum oils;
(3) Paint removers, strip washes, and miscellaneous solvents;
(4) Rubber solutions, adhesives, and thinners.

The problem confronting the analyst is to prove that :

(*a*) the sample is petroleum spirit to which the Act applies; or
(*b*) the sample is petroleum mixture to which the Act applies; or
(*c*) the provisions of the Act do not apply to the sample.

For the issue of a certificate of test it is sufficient to prove qualitatively the presence of petroleum spirit or petroleum when the sample has a flash-point below 73° F, but in practice it is advisable to obtain an approximately quantitative estimate of the amount present. It must be borne in mind that, in the event of a prosecution, evidence may be required from the analyst and such information may be called for together with the scientific proof that the material isolated is petroleum or petroleum spirit and that it was present in the original sample. The analyst must, therefore, obtain the physical and chemical properties of the petroleum fraction, if any, to prove its identity in order to meet possible cross-examination on this point.

Flash-point.

General and Variations with Atmospheric Pressure.—The first procedure is, of course, to determine the flash-point with the apparatus specified in Part I of the second schedule of the Petroleum (Consolidation) Act, 1928, strictly in accordance with the statutory manner prescribed in Part II of that schedule. No details of the instructions need be given here because they are clearly defined in this Act and in the Petroleum (Mixtures) Order, 1929, S.R. & O. No. 993 and cover all possible contingencies, liquid, viscous, and solid mixtures.

On perusing the stated method it will be noticed that the Act does not permit any adjustment of the flash-point for variation in atmospheric pressure. Alteration in barometric pressure produces quite an appreciable effect on the flash-point obtained as shown by the correction given in the Institute of Petroleum " Standard Methods of Testing Petroleum and its Products " that, for each 25 mm above or below 760 mm, the observed flash-point shall be reduced or increased by 1·6° F.

Hence, for example, a sample of xylol having a flash-point of 74° F one day and to which the provisions of the Act therefore do not apply may flash at 72° F another day, owing to ordinary atmospheric pressure fluctuation, and then have to be certified as petroleum as defined. Official samples taken by an officer authorized by a local authority have a date and time fixed for their testing and " the dealer or other person or any other person appointed by him may be present at the testing " Petroleum (Consolidation) Act, 1928, Section 17 (2). According to the Act, therefore, the flash-point of the sample is that obtained by the method specified at the appointed time on the day fixed for testing. Although fluctuation of atmospheric pressure has no legal significance, it is recommended that the analyst should record the height of the barometer, because it may explain divergencies in the result of a test on a sample in the event of a dispute.

When considering the flash-point of the very complicated mixtures that are present in samples of the cellulose paint type it is well for the analyst to remember that the flash-point of a liquid is not a specific property, but varies not only with the pressure as mentioned above, but with the rate of heating, source of ignition, design of apparatus used, and general procedure of test, etc. It is, in reality, the temperature at which the minimum explosive mixture is formed under the conditions obtaining in the apparatus.

A mixture of two or more liquids may have a flash-point below that of the lowest flashing constituent if an azeotropic mixture with a boiling point lower than any of the original constituents present is formed. Amongst the solvents that must be considered in connexion with possible samples a very large number of azeotropic mixtures have been recorded ; aromatic and aliphatic hydrocarbon mixtures ; hydrocarbons with esters ; alcohols and ketones ; ketones and alcohols ; esters, etc.

Variation of Flash-point with Dissolved Solid Content.—The solution of a solid substance, having no appreciable vapour pressure will, according to Raoult's law, raise the flash-point of a solvent by reducing its vapour pressure. This effect is only significant in the present case when the flash-point of the solvent is near the upper limit of the prescribed range, 66° F to 72° F for petroleum spirit. In general, a hydrocarbon will flash

at a temperature approximating to that at which its vapour pressure is 12 mm, and by making this assumption and employing the formula :

$$\frac{P_0 - p}{P_0} = \frac{\dfrac{a}{m}}{\dfrac{b}{M} + \dfrac{a}{m}}.$$

where ;

P_0 is the vapour pressure of the pure solvent,
p is the vapour pressure of the solution at the same temperature,
a is the weight of dissolved substance in the solution,
b is the weight of solvent in the solution,
m is the molecular weight of the dissolved substance,
M is the molecular weight of the solvent (in gaseous state),

it can be calculated that by dissolving 10 grams of a substance (of molecular weight 131) in 90 grams of xylole the vapour pressure is reduced 1 mm. This depression is inversely proportional to the molecular weight of the solute for a given gram concentration in a particular solvent.   By employing the following equation derived from the Clausuis–Clapeyron formula,

$$\frac{d(\log_e p)}{dT} = \frac{L}{RT^2}$$

where :

p is the vapour pressure of the liquid at the absolute temperature T,
L is the molecular heat of evaporation of the liquid,
R is the gas constant,

it can be shown, using the previous assumption, that a decrease of vapour pressure of 1 mm will increase the flash-point approximately 3° F.

Decrease of Flash-point of High-flash Petroleum.—As petroleum spirit is by definition petroleum which has a flash-point below 73° F it follows that a high-flash petroleum fraction to which a small amount of very volatile petroleum has been accidentally or intentionally added will become, according to the definition, wholly petroleum spirit if its flash-point is below 73° F.   Table I shows the amounts of various low-flash petroleum liquids which when added to relatively high boiling-point petroleum fractions reduce the flash-point to 72° F and thereby make the whole bulk into petroleum spirit.

TABLE I.

Mixtures Having a Flash-Point of 72° F.

	Flash-point, °F.	Petroleum 40–60° C.	Petrol.	Benzene.
Kerosine .	111	1·1% v/v	2·3% v/v	3·1% v/v
Lubricating oil .	435	3·2 ,,	3·9 ,,	4·6 ,,

The graph in Fig 1 shows the decrease of the flash-point of a kerosine by increasing additions of various low flash-point petroleums.
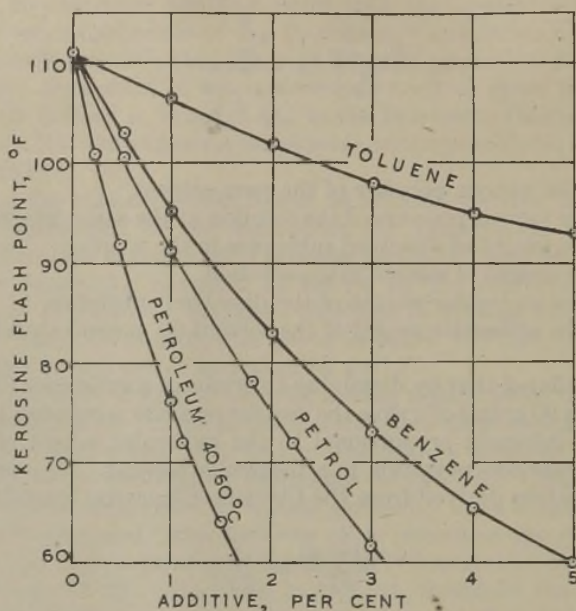

FIG. 1.

EFFECT OF ADDITION OF LOW FLASH-POINT MATERIALS ON THE FLASH-POINT OF A KEROSINE.

Raising of Flash-point by Addition of Organic Halides.—The flash-point of a petroleum spirit may be raised to a considerable extent by the addition of a highly volatile non-inflammable liquid, such as, for example, methylene chloride, chloroform, carbon tetrachloride, trichlorethylene, etc. Such mixtures are sold for paint removers, home dry cleaning, etc, and the examples in Table II show the order of the concentration required to raise the flash-point of benzene and a special boiling-point spirit (70/95).

It is often a matter of difficulty to determine the flash-point of some chlorinated hydrocarbon–petroleum mixtures because, above the flash point, the volatile organic halide may extinguish the test flame : then as the petroleum content increases the mixture burns round the test flame, but will not support its own combustion : then over a narrow range a flame just detaches itself from the test flame and on further increase in petroleum content the mixture burns with the test flame and will support its own combustion. The flash-point is taken as the lowest temperature at which a flame detaches itself from the test flame and moves towards the surface of the liquid. The figures given above for S.B.P. (70/95) and trichlorethylene show the very narrow range of the actual flash. With very volatile halides, *e.g.*, methylene chloride, chloroform, etc, a true flash is almost impossible to obtain owing to the high vapour pressure of the mixture and consequent lack of oxygen to form the lower explosive

TABLE II.

Mixture.		Flash-point, ° F.	Mixture.		Flash-point, ° F.
Benzene, % by vol.	Carbon tetra-chloride, % by vol.		S.B.P. (70/95), % by vol.	Carbon tetra-chloride, % by vol.	
38	62	74	25	75	above 80
40	60	69	26	74	72
43	57	68	27	73	69
45	55	67	28	72	67
47	53	below 66	29	71	67
			30	70	66
Benzene, % by vol.	Trichlor-ethylene, % by vol.		S.B.P. (70/95), % by vol.	Trichlor-ethylene.	
12	88	75	5	95	above 75
13	87	73	5·5	94·5	below 66
14	86	72			
15	85	69			
16	84	66			

limit.   In such cases only a limiting value can be obtained depending on when the mixture will just not support its own combustion, although this figure is a fire-point rather than a flash-point.   A feature of these mixtures is that the rate of the evaporation of the petroleum and the organic halide are not proportional to their initial concentrations.   No mixture of these constituents has been recorded that will evaporate at ordinary temperatures and will remain constant in composition during the evaporation.   In general, constant evaporating mixtures are formed by compounds which give azeotropic mixtures.   Two such examples are :—

Carbon tetrachloride 82·6 per cent and ethyl alcohol 17·4 per cent;
Carbon tetrachloride 70·0 per cent and methyl-ethyl-ketone 30·0 per cent

Other examples are recorded by Hofmann.[1]   The composition of these mixtures is always different from that of the constant boiling mixture, because the rate of change of vapour pressure with temperature is almost invariably different for the various components.   In a binary mixture both solvents evaporate simultaneously at different rates and have no effect upon each other.   When the faster evaporating compound has gone the remainder of the other component evaporates at a constant rate.   Also the evaporating characteristics cannot be predicted from distillation data. Hofmann has recorded the evaporation rates of many solvents and referred them to normal butyl acetate to which he gave the value of 100.   He concluded that :

(a) evaporation rates of organic liquids are not proportional to their boiling points;

D D

(*b*) the rate of evaporation of a liquid may be approximately predicted by means of the following formula :—

$$\frac{\text{Vapour pressure} \times \text{Molecular weight}}{11}$$

(referred to *N*-butyl acetate 100)

If these conclusions are applied to a mixture containing 62 per cent by vol carbon tetrachloride and 38 per cent by vol benzene (flash-point 74° F), and their respective vapour pressures calculated from the formula

$$100\ P_{ab} = M_a P_a + (100 - M_a)\ P_b$$

where

M_a = molecular percentage of liquid A

P_a, P_b = the respective vapour pressure of liquids A and B at the given temperature.

(assuming that A and B do not react chemically or associate),

it is found, assuming rate of evaporation equals K (vapour pressure $\times$ molecular weight), that the ratio of the loss of carbon tetrachloride to benzene for this mixture at 20° C is in the proportion of 3·6 to 1, whereas the weight to weight proportion is 3·0 to 1. Practical experiments with mixtures of these components showed that, for proportions that would not flash below 73 F, a preferential loss of carbon tetrachloride with a consequent lowering of flash-point occurred. This is, however, a complicated matter, and the conditions of evaporation are considered to have a bearing on the composition of the liquid remaining, especially in circumstances where the vapour densities of the constituents vary greatly. This possible change in composition implies that a mixture may be sold with a flash-point just above 73° F but, when used in such a manner that evaporation occurs, the flash-point may be reduced by the process and the mixture then becomes a petroleum mixture within the meaning of the Order. This point shows that chlorinated hydrocarbon–petroleum mixtures are not necessarily so free from danger of possible ignition as is commonly supposed and, furthermore, an infringement of the Act could occur as the result of loss of organic halide.

ANALYTICAL CONSIDERATIONS.

Possible Composition of the Sample.

Considering that samples taken under the Act may vary so vastly in chemical composition no detailed scheme can be given for their examination. A few guiding principles may, however, be stated with the applicability of varying procedures, but the analyst must examine the sample according to its probable composition. Some substances that may be found in the various categories of samples referred to above may be briefly summarized :

(*a*) A *cellulose lacquer* usually consists of :
cellulose ester,
resin,
solvent of high vapour pressure,

solvent of medium vapour pressure,
diluent.
plasticizer.
pigment or dye.

Typical of the mixed solvents added are benzole, toluole, V.M.P. naphtha, ethyl and butyl acetates and alcohols, butyl propionate, amyl esters and alcohols, etc.

(b) *Petroleum spirit*, petroleum oils, and miscellaneous solvents need no further amplification.

(c) *Paint removers* may contain aromatic hydrocarbons, acetone, alcohols, methylene chloride, various esters with or without wax, cellulose acetate, etc, to retard evaporation. The strip wash may be benzole or mixed solvents.

(d) *Rubber solutions and adhesives* contain a variety of solvents possibly including aromatic hydrocarbons, chlorinated hydrocarbons, special boiling point petroleum distillates. Generally, the thinners have the same type of volatile constituents as the primary material.

Separation of Mixed Solvents.

For the purpose of this examination the petroleum solvents must be obtained free from dissolved or suspended solids, which may be accomplished by distillation with or without steam, but both procedures have disadvantages in certain circumstances. For example, a paint remover containing wax, benzene, and acetone may be distilled to remove the solvents from the wax, but if a cellulose lacquer is distilled a considerable amount of solvent would be trapped in the precipitated solids and it would be very difficult to avoid thermal decomposition, which may materially alter the composition of the distillate. In cases where, for example, poly-*iso*-butylene or polyvinyl resins are present it is conceivable that by such thermal decomposition liquid petroleum could be produced ; such a possibility would be difficult to refute in court if put to a professional witness by the opposing learned counsel. If the sample is of such a nature that ordinary distillation is possible it is important that all the solvents should be collected, otherwise possibly important alterations of flash-point may occur. This is particularly true for petroleum solvents or mixtures of solvents that have a wide distillation range. In order to show the extent of such alteration of flash-point, mixtures (Table III) were distilled and 75 per cent of the original volume collected. Practically this would be

TABLE III.

Solvent.	Original flash-point, ° F.	75% Distillate flash-point, ° F.
Kerosine	113	103
Kerosine +3% benzene	73	66
Kerosine + 1% 40–60° C petroleum . .	76	66
S.B.P. 140/160	80	77
Xylene	79	78
Xylole (A)	69	67
Xylole (B)	74	73

regarded as an unsatisfactory yield, but it serves to illustrate the point. When the nature of the sample is such that the decomposition difficulty is likely to be encountered steam distillation is the only means available. It has the advantage that fairly volatile solvents can be practically recovered and also the process assists in removing water-soluble constituents which are not considered as petroleum.   The procedure adopted is to pass steam at atmospheric pressure through 100 ml of the sample and to collect 1 litre of distillate in 2 hours.   All-glass apparatus is recommended with a standard " Inland Revenue Pattern " condenser, which is not only very efficient for the purpose, but is of a design which enables the analyst to observe when all the volatile petroleum has been distilled.   Solvents and mixtures were distilled in this manner and the flash-points determined before and after to ascertain what alteration had occurred (Table IV).

TABLE IV.

Solvent or mixture.	Petroleum Content.			
	Original flash-point, ° F.	Original flash-point, ° F.	Final flash-point, ° F.	Percentage recovery, ± 1.
1. S.B.P. 140/160 .	78	78	78	99
2. Xylene	79	79	79	99
3. Xylole	69	69	69	99
4. Xylole + 25% acetone	below 66	69	69	99
5. S.B.P. 140/160 + 25% acetone	,, ,,	78	78	99
6. Kerosine	113	113	102	71
7. Kerosine + 25% acetone	below 66	113	102	72
8. Kerosine + 3% benzene	73	73	66	71
9. Kerosine + 3% benzene + 25% acetone	below 66	73	67	71

These results are to be expected from theoretical considerations, but calculations indicate that normal burning kerosine would distil more completely with ten times its volume of water.   Consequently, when this method of separation is employed the possibility of incomplete recovery of the petroleum content must be borne in mind resulting in a decrease in flash-point.   As already explained it is desirable to ascertain whether a mixture contains petroleum or petroleum spirit if its flash-point is below 73° F and the unwary worker could report mixture 8 and 9 in Table IV as containing petroleum spirit, whereas the original petroleum was not petroleum to which the Act applied.   The disadvantage of possible cutting of the petroleum fraction hardly ever arises with cellulose paints, lacquers, etc, because such relatively high-boiling petroleum would generally be unsuitable for incorporation in a preparation where controlled volatility is essential.   It is, however, liable to occur with a mixture of unknown composition, especially when the purpose for which it has been manufactured is unknown.

When the solvent is free from cellulose, resins, pigments, etc, those solvents not considered as petroleum should be removed in such a manner as not to alter the petroleum fraction, produce petroleum from products

not considered as such, or lose by solubility the petroleum present. Solvents that are completely miscible with water, for example, methyl, ethyl, propyl, *iso*propyl, tertiary butyl, and diacetone alcohols, acetone and di-ethyl ether can be removed by repeated shaking with water and the petroleum content be recovered without appreciable loss and with its original flash-point.   But even with acetone, six washings with an equal volume of water at 20° C are required to remove it completely from a mixture of xylene, 75 per cent by vol plus acetone, 25 per cent by vol, and the method becomes very laborious for the commonly occurring solvents given in Table V.

TABLE V.

Solvent.	Solubility in water, per cent.
N-Butyl alcohol	8·9
iso-butyl alcohol	10·0
Pri.-*N*-amyl alcohol	2·6 ⎫ values for all the eight isomeric amyl
Tertiary amyl alcohol	20·5 ⎭ alcohols lie between these limits.
Methyl ethyl ketone	23·0
Methyl acetate	24·4
Ethyl acetate	8·6
Higher esters	Solubility progressively decreases.

It is clear that a selective solvent is required to remove these alcohols, esters, ketones, etc, and a very satisfactory one in spite of its disadvantages is sulphuric acid.   Before, however, describing the recommended method of application it is of interest to consider briefly the action of cold concentrated sulphuric acid on organic compounds generally, because all classes of solvents may be encountered in these samples.

Action of Sulphuric Acid on Organic Compounds.

Sulphuric acid dissolves most oxygenated organic compounds through the formation of oxonium salts.   These are readily hydrolyzed by water, but this reagent suffers from the disadvantage, if these compounds are required to be identified, that it often produces much more fundamental changes.   Aldehydes and ketones may be polymerized;   phenols, sulphonated;   primary and secondary alcohols generally esterified;   and tertiary alcohols may be dehydrated with the formation of olefins which may polymerize and appear as acid insoluble petroleum.   If it is required to identify these non-petroleum solvents a more satisfactory reagent is 85 per cent syrupy phosphoric acid.   With few exceptions this latter solvent dissolves alcohols, aldehydes, methyl ketones, cyclic ketones, and esters of less than nine carbon atoms.   For ethers the solubility limits appear to be somewhat lower than this.   Thus di-ethyl ether dissolves readily whereas di-*n*-butyl ether and anisole do not.   Some olefins, such as amylene, are soluble;   ethyl benzoate is not and certain compounds, such as aceto-phenone and ethyl oxalate, form solid compounds with phosphoric acid.   The particular advantage of this solvent (phosphoric acid) is its ability to dissolve these compounds without the generation of appreciable heat and the absence of charring.   In addition to oxygenated compounds sulphuric acid also dissolves unsaturated hydrocarbons and polyalkylated

aromatic hydrocarbons, such as mesitylene.   Most unsaturated compounds dissolve through the formation of the alkyl hydrogen sulphates which are soluble in excess of sulphuric acid :

$$RCH{=}CHR + HOSO_2OH \longrightarrow RCH_2 - \underset{\underset{OSO_2OH}{|}}{CHR}$$
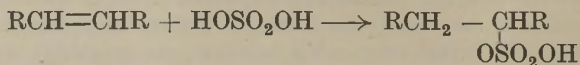
The rate of reaction of these unsaturated compounds is determined by the nature of the groups adjacent to the double bond.   An accumulation of negative groups retards the effect as, for example, in dichlorethylene which is comparatively inert to sulphuric acid.   Butylene and the higher homologues dissolve readily in cold concentrated sulphuric acid and undergo extensive polymerization, but the diluted acid forms an alcohol and alkyl sulphate.   This tendency to form an alcohol and alkyl sulphate reaches a maximum with amylene and hexene, and higher members show an increasing tendency to polymerize.   Sulphuric acid also causes, for example, the interaction of toluene, xylene, and pseudo-cumene with styrene to give di-arylethanes, and benzene with hexene to form hexyl-benzene.

The action of *cold* concentrated sulphuric acid may be summarized :

Soluble

    (1) Acyclic and cyclic olefins,
    (2) Di-olefins,
    (3) Acetylenes,
    (4) Certain polyalkylated aromatic hydrocarbons,
    (5) Esters, alcohols, ketones, and similar oxygenated compounds.

Insoluble *

    (1) Acyclic and cyclic paraffins,
    (2) Aromatic hydrocarbons,
    (3) Halogen derivatives of (1) and (2) above,
    (4) Di-aryl ethers,
    (5) Carbon disulphide.

Recommended Procedure.

General.—In order to avoid as far as possible some of the undesirable effects of concentrated sulphuric acid it has been found advantageous to extract initially with dilute acid, because this procedure reduces the dehydration of tertiary alcohols and to a large extent obviates violent polymerization and charring.   This method was recommended by Armstrong[2] for the examination of turpentine.   He extracted with (one-quarter to one-third of the volume) 2 : 1 sulphuric acid and water mixture followed by 4 : 1 sulphuric acid and water mixture and found a residue of 4 to 5 per cent cymene and paraffin hydrocarbon.   The residue increased with increase of acid strength and temperature.   Coste[3, 4] adapted this

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* Insoluble is used in the sense of the substance not going readily into solution : long shaking with a large excess of acid will effect solution of the aromatics.

method to the analysis of turpentine substitutes and mixtures of turpentine with aliphatic and aromatic hydrocarbons and recommended :—

(a) Removal of terpenes and some olefins by polymerization with dilute sulphuric acid ;

(b) Removal of the remaining olefins with concentrated sulphuric acid.

This method was also further discussed by Coste, Shelbourne, and Andrews.[5]

Many misleading abstracts appear in the literature regarding the solubility of aromatics in sulphuric acid because the conditions are not specified. It must be realized that the loss of aromatics from a petroleum containing either mixed aliphatics and aromatics or aromatics alone depends on :

(a) acid strength ;

(b) temperature ;

(c) relative volume of acid employed ;

(d) method of mixing ;

(e) time of contact.

In the following experiments the acid strengths used were :

(1) dilute sulphuric acid (2 volumes of acid to 1 volume of water),

(2) dilute sulphuric acid (4 volumes of acid to 1 volume of water),

(3) strong sulphuric acid (99 $\pm$ 0·5 per cent).

The method employed was to add slowly to the sample about one-quarter of its volume of the appropriate acid solution, shake in a separating funnel for 30 seconds with constant cooling and not permitting the temperature to rise, then allow the layers to separate whilst being kept cold with running water. If a considerable volume of the sample is removed by the more dilute acid, as will be the case when esters, alcohols, etc, are present in quantity, the extraction should be repeated one or more times with this solvent before proceeding to a stronger acid. Care as regards temperature and time are very necessary when the strong acid is added otherwise considerable loss, especially of the higher aromatic hydrocarbons, will result. Table VI shows the flash-points of various petroleum samples and synthetic mixtures together with the figures obtained on the petroleum content of the mixture before and after treatment.

It was observed that the larger the proportion of non-petroleum solvent the greater the loss of petroleum. This was shown to be due to solution of the petroleum in the non-petroleum solvents dissolved in the sulphuric acid, and was demonstrated by extracting an aromatic free petroleum with dilute sulphuric acid (2 acid : 1 water) to which an equal volume of acetone and ethyl acetate had been added and then extracting with dilute acid to constant volume. The loss of petroleum was found to be some 5 to 6 per cent which would be expected to vary with the type of solvent in the sulphuric acid solution.

In order to test the efficiencies of the steam distillation separation 4 g of cellulose nitrate were dissolved in mixed solvents A and B (Table VI). The solution was steam distilled and treated with the various strengths of sulphuric acid already stated. The recovery of the petroleum content as a

TABLE VI.

Sample.	Flash point ° F.			Percentage yield of original petroleum, ± 1%.
	Original.	Petroleum content before treatment.	Petroleum content after treatment.	
Benzene	below 66	below 66	below 66	98
Toluene	,,	,,	,,	98
Xylene	78	78	78	97
Xylole	69	69	69	97
S.B.P. 140/160	77	77	77	99
Kerosine	112	112	113	98
Kerosine + 3% benzene	73	73	74	98
Kerosine + 1% (40–60) petroleum	76	76	77	98
Kerosine + 3% benzene + 25% acetone	below 66	73	73	97
Xylole + 25% acetone	,,	69	69	96
Xylole + 25% ethyl acetate	,,	69	69	95
S.B.P. (140–160) + 25% acetone	,,	77	77	97
S.B.P. (140–160) + 25% ethyl acetate	,,	77	77	97
Mixed solvents A	,,	69	70	90
,, ,, B	,,	77	77	88
,, ,, C	,,	78	78	94

Mixed solvent A = 50% xylole, 12·5% acetone, 12·5% amyl acetate, 12·5% ethyl acetate, 6·25% ethyl alcohol, 6·25% butyl alcohol.

Mixed solvent B = 43·5% xylene, 17·4% acetone, 17·4% amyl acetate, 8·7% amyl alcohol, 8·7% butyl acetate, 4·3% butyl alcohol.

Mixed solvent C = S.B.P. (140–160° C) instead of xylene in B above.

percentage of that added was 93 per cent from A and 91 per cent from B. This is a slightly higher yield than when the mixed solvents alone were treated with acid which is due to about 31 per cent of the non-petroleum solvents being removed by the steam distillation process.

After the sulphuric acid treatment the solution may now contain :

(a) Petroleum,
(b) Aryl and alkyl halides,
(c) Di-aryl ethers,
(d) Carbon disulphide.

The presence of organic halides or carbon disulphide can be observed when the initial flash-point is determined by the formation of hydrogen halide or sulphur dioxide if they are present to the extent of a few per cent. Carbon disulphide may be removed by treatment with alcoholic potash to form the xanthate and removed in the aqueous layer on dilution with water. However, experience with thousands of samples taken under the Act shows that this solvent rarely occurs mixed with other solvents. Similarly, di-aryl ethers are so infrequently encountered in the type of product usually suspected that they need not be further considered. Organic halides as the chloro-hydrocarbons are very common and should be tested for by means of the Beilstein lamp. They present a difficulty

because in some cases they cannot be quantitatively removed from the petroleum fraction without the possibility of changing the nature of the hydrocarbons. Also some chlorinated hydrocarbons which are very resistant to sulphuric acid have a flash-point below 73° F, e.g. :

1 : 1 dichloroethylene	57° F flash-point
1 : 2 ,,	43° F ,,
1 : 2 dichlorethane	63° F ,,

Identification of Organic Halides.—Identification with alcoholic potash does not provide a solution of the problem because although the normal alkyl halides are fairly readily attacked unsaturated hydrocarbons and ethers may be formed. For example, n-propyl bromide gives about 20 per cent of the theoretical yield of propylene and 60 per cent of n-propyl-ethyl-ether. Carbon tetrachloride is slowly hydrolysed to potassium carbonate and chloride, and trichlorethylene becomes ββ-dichloroethyl-ether and chloracetylene. An indication of the boiling point of the halide may be obtained by fractionation since few halides form azeotropic mixtures with petroleum ; chloroform 72 per cent by weight and n-hexane 28 per cent by weight is an exception. The halides may be classified into two classes by (a) action with n-alcoholic potassium hydroxide ; (b) alcoholic saturated solution of silver nitrate. A few examples are given in Table VII, but for further information the original paper of Agruss, Ayers, and Schindler [6] on a the detection, determination, and identification of organic halogen compounds in mineral oils should be consulted.

TABLE VII.

Reaction with N-alcoholic Potassium Hydroxide.

Positive reaction.		Negative reaction.
Positive reaction to Alc. AgNO$_3$.	Negative reaction to Alc. AgNO$_3$.	
Carbon tetrachloride Chloroform * Ethylene dichloride * Methylene chloride * Amyl chloride	Trichlorethylene Tetrachlorethane Tetrachlorethylene Acetylene tetrachloride	Chlorobenzene o-Dichlorobenzene p-Dichlorobenzene Trichlorobenzene

* Positive reaction, but only slightly so.

In many cases the halogen compound may be extracted as the thiuronium salt and identified as the picrate. A fairly comprehensive list of melting points of these compounds is given by Levy and Campbell.[7] There are many special tests for individual common chloro-compounds, such as the characteristic compound of mercuric cyanide and trichlorethylene, m.p. 83° C, that can be used for identification and selective nitration and sulphonation of aryl halides to effect a separation from the parent hydro-carbons.

Confirmation of Petroleum.—If these or other methods serve to identify the halide, physical properties, e.g., specific gravity, refractive index,

viscosity, and flash-point combined with the chemical behaviour of the residue with nitric acid will enable the presence of petroleum to be definitely established, and the approximate relative proportions ascertained. Although the residue after the sulphuric acid treatment can only be petroleum, in the absence of halides, carbon disulphide, and diaryl ethers, the physical and chemical properties should always be ascertained in order to prove beyond doubt that this is a fact in every particular case. If this residue has a flash-point below 73° F the presence of petroleum spirit can be reported subject to this confirmatory evidence. It may happen that the volume of the residue is insufficient to determine the flash-point strictly according to the statutory method in which case a few ml may be floated on water and the required conditions observed in other respects. The flash-point so obtained will be a maximum figure and, if it had been possible to fill the cup to the mark with the test liquid only, this temperature would be reduced perhaps 2 to 3 degrees. If the petroleum residue is not petroleum spirit careful consideration must be given to the original mixture to ascertain that no compound, such as turpentine, is present which would produce, under the conditions described, a small amount of cymene. Some hydrocarbons of this type can be isolated from petroleum as defined by the Act and also from liquids not of this origin, and it is in this respect that serious difficulties could in some theoretical cases be encountered in certifying a low-flash mixture as being a petroleum mixture by virtue of a petroleum content as distinct from a petroleum spirit content.

Detection of Unsaturated Petroleum.—Many solvent mixtures on the market are completely soluble in the sulphuric acid mixtures employed and the analyst must be prepared to encounter wholly unsaturated petroleum compounds, many of which are petroleum spirit as defined. Also, as previously mentioned, the presence of a considerable proportion of olefins may cause a complete loss of low-flash aromatics and produce high-boiling petroleum hydrocarbons. Due to polymerization of low-flash unsaturateds, such as trimethylethylene, boiling point 30° C, which produces a mixture of di-amylenes boiling point 150–160° C, or the isomeric hexenes which produce di-polymers boiling between 190–200° C, it may be thought that some non-petroleum solvent had been removed from the mixture and that the original was a petroleum mixture containing petroleum instead of petroleum spirit. There is no short method of analysis for such solvents. The distillation range must be ascertained and the various constituent classes identified. A qualitative test, apart from the usual reagents, for unsaturated hydrocarbons which may be useful is the mercuric acetate–olefin complex. Hugel and Hibou [8] recommended treating the petroleum with mercuric acetate in glacial acetic acid when the unsaturateds dissolve by forming a complex with this salt. The loss of volume would not necessarily be of any value because of the solution of esters, alcohols, etc, if present; but by steam distilling the solution the complexes are retained in the water and the olefines may be regenerated with hydrochloric acid and examined. For full details of procedure the original paper should be consulted and also the work of Brame and Hunter,[9] but the method is not suitable for quantitative work because the reaction is rather uncertain, oxidation to a varying degree depending on the hydrocarbon may take place and some unsaturated hydrocarbons do not react.

It may be necessary in some prosecutions under the Act to prove that two samples of volatile petroleum are from the same bulk.   One possible procedure is to separate into fractions as described by Thomas, Block, and Hoekstra,[10] as shown in Table VIII :

TABLE VIII.

Fraction.	Boiling point.	Constituents.
1. C_5	10–40° C.	C_5 paraffins, olefins
2. C_6	40–70° C.	C_5, C_6 naphthenes C_6 paraffins, olefins
3. C_7	70–100° C.	C_6 naphthenes, aromatics C_7 paraffins, olefins
4. C_8	100–125° C.	C_7 naphthenes, aromatics C_8 paraffins, olefins, naphthenes
5. C_9	125–150° C.	C_8 naphthenes, aromatics C_9 paraffins, olefins, naphthenes
6. C_{10}	150–175° C.	C_9 aromatics C_{10} paraffins, olefins, naphthenes
7. C_{11}	175–190° C.	C_{10} aromatics C_{11} paraffins, olefins, naphthenes

and to estimate the olefin content in each fraction by bromine absorption, aromatics and olefins by solution in fuming sulphuric acid, and the naphthene and paraffin content by refractive index.   For experimental details the original paper should be consulted.   This method may also be applied to those cases where no residue is obtained after the prescribed sulphuric acid treatment and yet unsaturated hydrocarbons are suspected owing to the absence of other classes of solvents.

DIFFERENTIATION OF PETROLEUM SPIRIT AND PETROLEUM MIXTURES.

When the presence of petroleum spirit is proved it is necessary to ascertain whether the original substance is petroleum spirit or a petroleum mixture. In many cases, *e.g.*, paints, it is obvious, but with colourless or even yellowish-brown solvents it can be a matter of considerable difficulty. Theoretical mixtures can be envisaged where it would be impossible to arrive at a decision based on analytical methods.   However, in the author's experience of thousands of samples extending over twenty years, very few really difficult cases of this nature have been encountered.   It must be stressed on this matter that a practical viewpoint must be taken otherwise administration would become very difficult.   As already stated, a trace of water in a benzole should not cause a petroleum to become a petroleum mixture ; also for the sake of uniformity in labelling motor spirit the licensing authority may prefer to consider alcohol blends and doped fuels as petroleum spirit although they are actually petroleum mixtures as defined.   If a manufacturer has any doubt about labelling in this respect the licensing authority should be consulted.   The decision is not usually difficult since the maker knows the constituents.   The analyst, however, who has not this information, should test for the various classes of possible organic solvents in the original mixture.   Generally, extraction with calcium chloride solution for alcohols, saponification for esters and

extraction with sodium bisulphite for some ketones and aldehydes will prove sufficient for most samples having no dissolved or suspended solids content. As regards the bisulphite reagent it must be remembered that some unsaturated hydrocarbons, *e.g.* amylene, *cyclo*hexene, pinene, combine with the elements of sulphurous acid on shaking with solutions of bisulphite to give as the principal product the corresponding sulphonic acid. Also some unsaturated acids, aldehydes and ketones containing the grouping $> C : C-CO$ react similarly to give sulphonic acids and with the aldehydes and many ketones the product is the sulphonate of the bisulphite compound. The methods given may not lead to a decision as to whether the sample is a petroleum spirit or a mixture. It must again be stated, however, that this paper does not attempt to formulate a solution of the almost impossible task of separating petroleum as *defined in the Act* from any other substance or mixture of substances, but rather describes a method which is suitable for most samples taken under the Act and points out the difficulties of interpretation of analytical information obtained on examining these samples. Furthermore, the tests given for substances or classes of compounds are not claimed to be exhaustive, but are considered useful for the purpose, and further information is readily obtainable from the references quoted and from standard works on organic analysis.

CONCLUSION.

Whilst as already stated it is impossible to give a general method for the examination of all possible samples which may be taken under the Act, it is considered that it would be an advantage to give complete details of the method recommended for the certification of a typical sample containing saturated petroleum, namely, a cellulose spraying lacquer (Petroleum Mixture), so that the details which are of necessity spread over this paper are readily accessible in a concise form.

Method.

(1) Determine the flash-point strictly according to the method laid down in the Act or (as in this case) the Petroleum (Mixtures) Order.

(2) Transfer the contents of the pot (noting the volume or the weight taken) to a 1 litre flask having a ground neck ; add about 50 ml of water so that the steam passes through the water (otherwise blockage of the inlet tube will occur) and attach to an all glass apparatus fitted with an " Inland Revenue Pattern " condenser; distil in steam at atmospheric pressure and collect about ten times the volume of the sample in 2 hours.

(3) Separate the water insoluble layer (which may have a specific gravity greater than one), and measure.

(4) Add about one quarter the volume of dilute sulphuric acid (2 vol acid : 1 vol water) slowly with constant cooling to prevent rise of temperature. Shake for 30 seconds with constant cooling; allow to separate and run off the acid. Repeat with this strength of acid if appreciable absorption takes place; repeat with dilute sulphuric acid

(4 vol acid : 1 vol water); repeat with strong sulphuric acid (99 $\pm$ 0·5 per cent).

    (5) Wash with an equal volume of water until acid freed.

    (6) Dry with anhydrous sodium sulphate and measure.

    (7) Ascertain the absence of organic halides and carbon disulphide.

    (8) Determine :

        (*a*) Flash-point ;
        (*b*) Refractive index ;
        (*c*) Specific gravity ;
        (*d*) Effect of nitrating mixture ;
        (*e*) Effect of fuming sulphuric acid.

Table IX gives approximate values for the refractive indices, specific gravities, and boiling ranges of typical petroleum fractions.

TABLE IX.

Petroleum.	Boiling range ° C.	Flash-point, ° F.	Specific gravity.	Refractive index.
Petroleum ether	40–60	below 66° F.	0·67	1·37–1·39
S.B.P. spirit	70–95	,,	0·71	1·40
S.B.P. spirit	140–160	74	0·77	1·43
White spirit	150–190	90 ca	0·76–0·80	1·43–1·44
Petrol	50–180	below 66	0·72–0·75	1·41–1·44
Kerosine	160–275	110 ca	0·80 ca	1·45
Benzene	80	below 66	0·879	1·501
British Standard pure benzole	79·5–80·5	,,	0·874–0·879	1·499–1·501
Industrial benzole	80–145	,,	0·864–0·879	1·496–1·500
Toluene	111	,,	0·871	1·499
British Standard 90's toluole	up to 101, 5% max. below 120, 90% min.	,,	0·855–0·870	1·495–1·499
British Standard 2° xylole	138–142	75 min.	0·860–0·865	1·49
British Standard 5° xylole	135–145	75 min.	0·853–0·865	1·49
Coal tar solvent naphtha (light)	96% up to 160	73 ca	0·854 min.	1·495
Coal tar solvent naphtha (heavy)	90% up to 190	90 min.	0·860 min.	1·495

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OBITUARY.

LEWIS BOSWELL INMAN HAMILTON.

THE death of Lewis Hamilton on January 20, 1947, at the goodly age of eighty-nine will be lamented by many of his old associates and admirers. He was one of the few surviving British pioneers in oilfield enterprise, and he leaves a creditable record of achievement in a branch of enterprise that showed so little promise of greatness in its infancy, when many refinery products were a drug on the market and were often destroyed as a nuisance and danger.

The younger son of Thomas Hamilton, of Sundrum, Ayrshire, he trained as a Mining Enigneer and pursued the course of so many Scots by travel abroad. It was during some of his early investigations of mining prospects in Central Europe that he became associated with Messrs. Bergheim and MacGarvey, then engaged in developing oilfields on Galicia, at that time part of the Austrian Empire. From MacGarvey, one of those Canadians who had practiced pole tool drilling in the Ontario oilfields, he not only learnt much about oilfield practice but became inspired with the desire to follow a profession concerning which so few had, at that time, any practical knowledge. The lure of a coal-mine in Roumania for a time distracted his attention from oil, but realizing the opportunities of oilfield development in that country he eventually drifted into oil and applied himself to the study of oilfield prospects. Hamilton's geological studies of the Sub-Carpathian regions convinced him that amidst the many folds associated with the development of saliferous cores in the foot-hills there were favourable prospects of oil concentration.

The success that attended his various prognostications led to numerous calls on his professional services, and this in turn led to travel in many countries outside Roumania where British interests were entertaining oil prospecting or acquiring oil properties. The writer's first acquaintance with Hamilton was in Baku, Russia, in 1902, and from then onwards it was his privilege and pleasure to be associated with him in many ventures and evaluations of oil properties. His successive visits to Russia were largely connected with certain British oil interests in Cheleken, that mysterious and little-known Island in the Caspian Sea, off the mainland of Trans-Caspia.

Being an accomplished linguist and a man of striking personality and charm he made innumerable friends of all nationalities, and few distinguished visitors to Roumania failed to experience the hospitality of Hamilton and his charming and talented wife. No one who has been a guest in their delightful house at Campina could fail to recall, with pleasure, the warmth of the reception accorded and the arrangements made for their comfort.

Hamilton had the distinction of being one of the only two British nationals honoured by election to membership of the very exclusive Jockey Club of Bucharest; a surprising tribute to the regard in which he was held by Roumanians.

When the Germans embarked on oil enterprise in Roumania it was upon Hamilton that the Disconto Gesellschaft and the Deutsche Bank depended for the selection of lands and sites for development and for a time he was entrusted with management of their oil affairs in Roumania. To Hamilton main credit is due for the proving of the famous Moreni oilfield, the first of that group of oilfields developed of the flanks of the intrusive salt masses. He never faltered in his insistence that payable oil would be found in this belt, and he alone was responsible for drilling the first production well in the Bana sector of Moreni, where enormous outputs of unusually light density oil were subsequently obtained.

The writer can vividly recall the many happy field-days spent with Hamilton and Professor Mrazak foot-slogging over the numerous propective oilfields in the Carpathians at a time when the chief producing field was Bushtenari, and speculation was rife regarding the potentialities of other areas.

Two major wars in which Roumania became involved deprived Hamilton of the well-deserved rewards of years of hard work and energy, for he had staked his faith in the country where he and his wife had become such familiar and popular personages. No one of importance in Roumania was unaware of his efforts to advance and foster the industry upon which he had devoted so much time and energy.

No higher tribute of the respect in which he was held and his popularity could be paid than the large number of letters received by Mrs. Hamilton from all parts of the world.

A. BEEBY THOMPSON.