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CONTENTS

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THE CLEMENT-PIGNEGUY KNOCK INDICATOR.*

By D. M. Clement and P. G. Pigneguy.†

Synopsis.

A long-felt need in engine-fuel testing has been an indicator of knock intensity which is unaffected by combustion pressure and one also in which the accurate functioning does not rely on the interdependent setting of its component parts.

The indicator described in this paper is shown to possess the desired qualities, which enables testing to be carried out over the entire octane scale without alteration of the original setting. While the construction may appear to be on similar lines to the A.S.T.M./C.F.R. bouncing-pin indicator, the change in principle involved is fundamental.

The new indicator has so far only been used in the standard C.F.R. engine and also a high-speed C.F.R. engine, but it is felt that the principle can be successfully adapted for full-scale car and aero-engine testing.

In the anti-knock rating of fuels it is well known that the C.F.R. engine is in considerable use and has shown itself reasonably reliable. If criticism can be made against any particular part of it, that part is the bouncing-pin, which is a source of direct error in the rating of fuels. This apparatus is the medium by which the knock intensity in the engine is registered quantitatively as a knock-meter reading. As is known, the method of fuel rating is by comparing two known fuels against the unknown sample, the comparison being effected by the use of the knock-meter readings. Should these knock-meter readings not be truly representative of the knock intensity occurring in the engine on the various fuels, then an immediate error in rating is made.

Investigation has been carried out for some time past on the actual physical phenomena which take place in the Standard A.S.T.M./C.F.R. bouncing-pin. The knock indicator described in this article has been designed to overcome certain faults inherent in the operation of the standard apparatus.

A brief outline of the standard C.F.R. bouncing-pin apparatus is as follows :—

A steel pin about 7 in. in length and ¼ in. diameter rests in a vertical position on a diaphragm, the diaphragm and pin being supported in the main body, which is screwed into the engine cylinder. On top of the main body is an assembly of two leaf-spring contacts and a bumper spring mounted one above the other. The lower leaf-spring contact rests on the pin-top and exerts sufficient pressure on it, to hold the pin against the diaphragm during normal combustion of the engine. Above this lower leaf-spring contact separated by about a 0·003-in. gap is the upper leaf-spring contact arranged in a buffer system with a plunger and spring sliding in a guide. This upper leaf-spring and plunger may be adjusted to vary the gap between the two contacts, and they arrest the motion of the lower contact without shock, when it is driven up by detonation, so that an impulse of current flows in the circuit through the contacts. The

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time of contact is registered on the knock-meter as a mean value of current flowing.

Under detonating conditions the steel bouncing-pin is driven off the diaphragm by the impact of detonation and is brought to rest by the retarding forces of the lower leaf-spring and the action of closing the contacts. The pin has thus partly stored its energy of upward movement in the resilience of the lower leaf-spring, and this member returns the pin to the diaphragm with such a velocity that it rebounds and the process is repeated. Thus for one knock impact in the engine cylinder, the pin is set into a state of oscillation. The frequency of this oscillation is dependent on the pressure on the pin downward and the mass of the pin itself. With the normal setting of the standard pin the frequency is of approximately 800 cycles per second. With a very light lower leaf-spring pressure this vibration may continue throughout the engine cycle until the next detonation occurs. Under normal leaf-spring pressure the vibration dies away well before the commencement of the next engine cycle.

It is important to note now what is occurring to the diaphragm while this vibration of the pin upon it is taking place. Its vertical deflection is altering according to the pressure in the cylinder. Thus, as the knock impact is being recorded by the vertical travel of the lower contact under the action of the vibrating pin, it may well be that the time of closure of the contacts is due more to the combustion pressure in the cylinder than to the rapid vibration of the pin set up by detonation. The effect of combustion pressure being recorded as detonation is more troublesome at the higher compression ratios where the deflection of the diaphragm due to higher combustion pressures is much greater. For example :—

In recent experiments it was determined that when an engine was not detonating, a considerable deflection of the diaphragm took place, due to combustion pressure : this was found to be 0·0015 in. at 4 : 1 compression ratio, 0·0025 in. at 8 : 1 compression ratio, and the diaphragm deflection plotted against compression ratio was almost exactly a straight line. With this evidence it is clear that, when the engine is being run on any non-detonating fuel, if this diaphragm deflection curve rises above the leaf-spring contact clearance, a reading on the knock-meter is recorded due to combustion pressure. (A detailed account of this experimental work and fundamental theory underlying it is given later in this paper (Appendix A).)

It was also determined that with a normal pressure downwards on the pin by the lower leaf-spring, the pin remained in contact with the diaphragm when no detonation was present.

Fig. 1 shows the displacement of the diaphragm, on which is superimposed the movement of the lower leaf-spring contact, under the action of the vibrating pin. It was evident that when a standard bouncing-pin was set with a contact gap of 0·003 in., part of the closure of the gap was due to combustion pressure, and the rest due to the oscillation of the pin and lower leaf-spring caused by detonation. As expected, it was determined that the bouncing-pin contacts closed three to four times per engine cycle (see Fig. 2).

Owing to the smaller deflection of the diaphragm shortly after combustion when the gases begin to expand, the recording of the oscillation on the standard bouncing-pin is masked after the first three or four vibrations.

Thus the standard bouncing-pin records only a portion of the vibration or oscillation due to detonation, and in the case of a heavier detonation

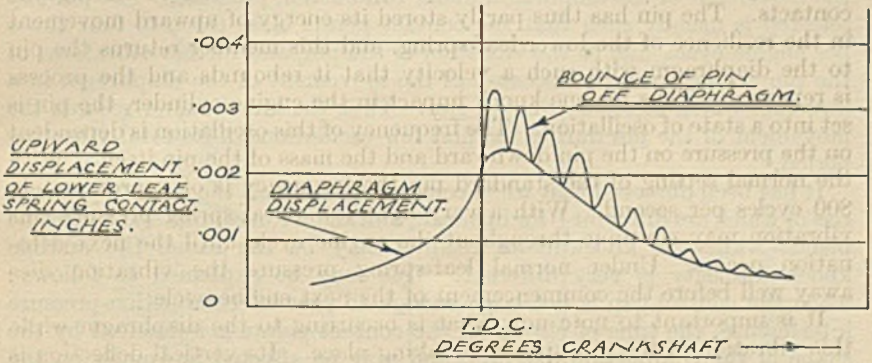


Fig. 1.

the pin relies on a wave of larger amplitude to increase the time of contact and thus increase the knock-meter readings.

If the standard pin could be relied upon to record the same number of vibrations on all fuels—*e.g.*, the first three—without any influence due to combustion pressure, then the knock-meter readings would be comparative for the degree of detonation in the engine.

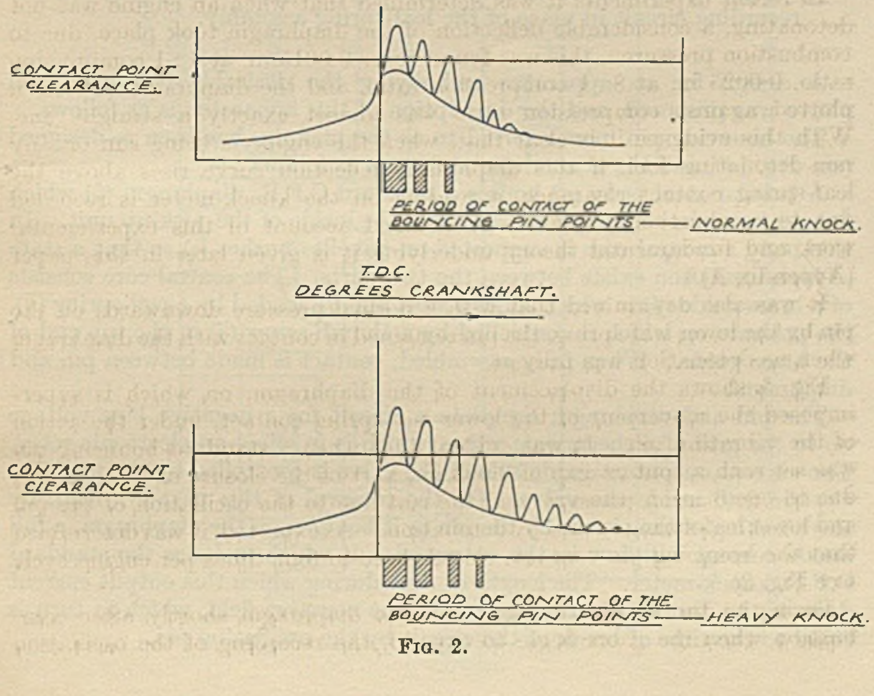


Fig. 2.

The foregoing criticism of the standard C.F.R. bouncing-pin may be summarized as follows :—

The knock-meter readings being proportional to the duration of contact of the points, activated by the pin movement, are always influenced by the movement of the diaphragm under combustion pressure. The pin-gap selected is usually such that the contact points close three to four times per engine cycle, due to the vibration of the pin, and further vibrations of the pin are not recorded because of the movement of the diaphragm in a direction which increases the pin-gap. Thus the knock-meter records the movement of the pin during the first few oscillations of its total vibrating period.

It has been observed that when comparing two fuels the rates of pressure rise of which are different—for instance, a straight-run sample and a benzene blend—while the knock-meter reading may be the same, the audible knock intensity is very different. This may be explained as follows: when the control gap is not large enough to prevent combustion-pressure interference, the time of closure of the contact points is influenced by the shape of the combustion diagram, and may be affected unequally on the two fuels by combustion, depending on the broadness of the peak of the diagram, quite apart from the detonation wave accompanying it.

From the foregoing analysis, advantageous changes in the design of the pin and recording circuit were made, and are as follows :—

1. Recording all pin movement *relative* to the diaphragm.
2. Measuring by an extremely small current the time of bounce of the pin *off* the diaphragm, by including the pin and diaphragm in the recording circuit in place of the leaf-spring assembly.

A design for an apparatus embodying the desirable features given above was proposed, and the description of this apparatus is as follows.

The bouncing-pin, now referred to as the pick-up, has been re-designed (see Fig. 14), and the general description is as follows :—

A tubular steel body (*a*) houses a standard C.F.R. diaphragm (*b*) which is held by a sleeve (*c*) and nut (*d*) from the inside of the pick-up unit. In this body a central core is supported on bakelite bushes (*e*) so that a state of high insulation exists between the two parts. The central core consists of a brass guide (*f*) in which slides a steel pin (*g*), loaded by a coil-spring (*h*), the pressure on which is controlled by a thumb-screw (*j*) in the top end of the brass guide. When fully assembled, contact is made between pin and diaphragm.

The pin and diaphragm complete a circuit for a negative bias voltage on to the grid of a thermionic valve, which is in effect an electronic relay. The current output or anode side of the valve is controlled by the negative electric field inside the valve. On the removal of this negative field, by the breaking of the circuit by the pin as it bounces on the diaphragm, a full anode current will flow in the output circuit which includes the standard C.F.R. knock-meter. The length of time during which this output current flows is the duration of the absence of the negative field, which in turn is equal to the time of break of the circuit by the oscillating pin.

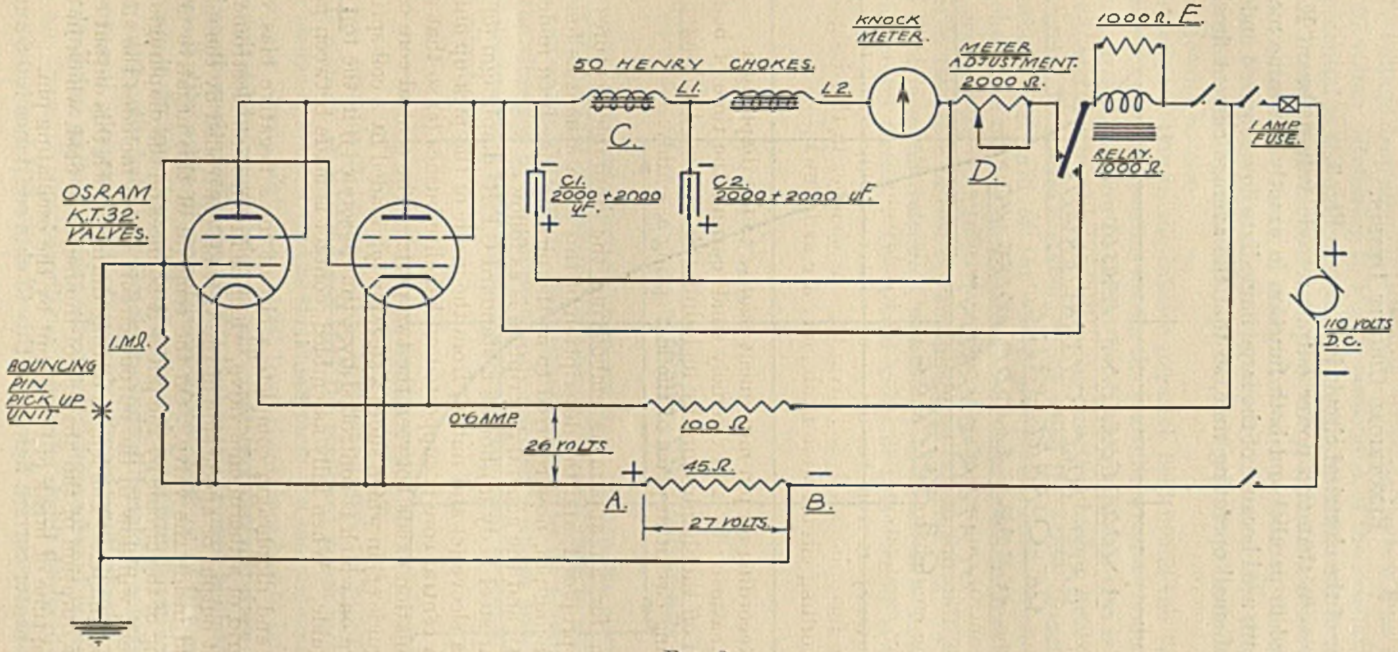


FIG. 3.

CLEMENT–PIGNEGUY KNOCK INDICATOR. CIRCUIT DIAGRAM—SUITABLE FOR USE WITH COIL OR MAGNETO IGNITION C.F.R. ENGINE.

Electrical Circuit Design.

A diagram of the electrical circuit is shown in Fig. 3.

It will be seen that two power output tetrode valves Osram K.T. 32 are connected in parallel and both function in exactly the same manner. Two valves are used because of the large immediate flow required under the conditions of small operating time, so that the average current flowing is sufficient to work the knock-meter. The supply of current for the valve-heaters is obtained from the standard C.F.R. generator, the voltage being reduced from 110 V. to 26 V. by two resistances in series with the valve-heaters. One resistance is of 100 ohms and the other of 45 ohms. The 45-ohm resistance is placed in the outgoing or negative side of the valve-heaters. Besides its function of reducing the 110-V. supply, it serves as a source of negative bias for application to the grid via the pin and diaphragm. The manner in which this is effected is as follows :—

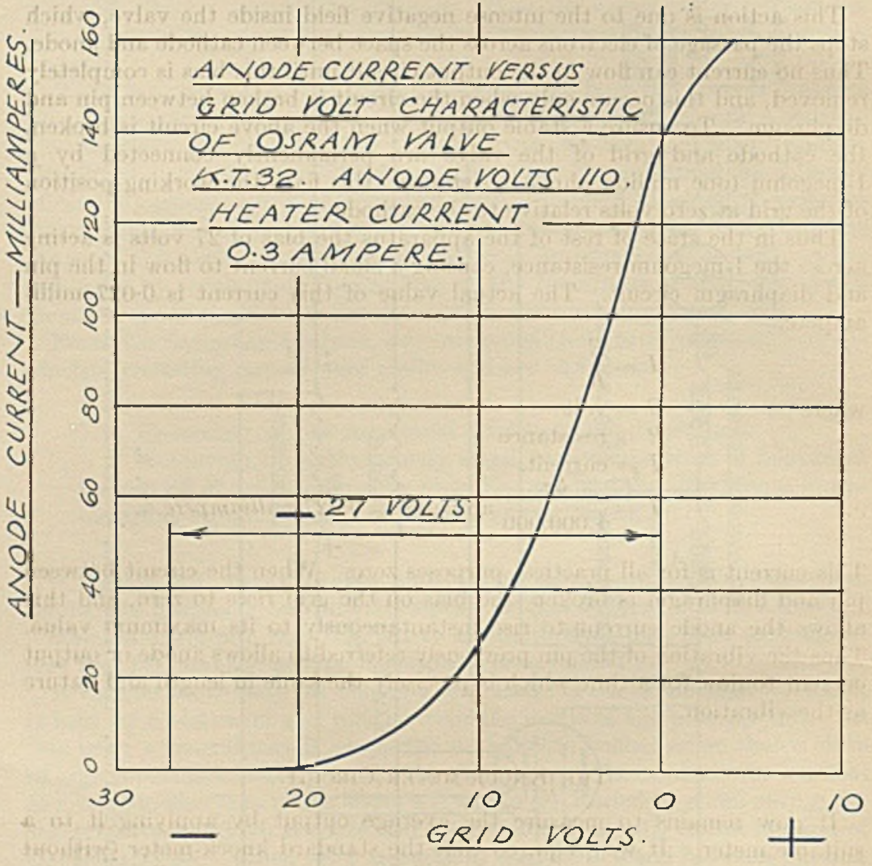


Fig. 4.

The valve-heater current flowing in this 45-ohm resistance is 0·6 ampere, thus the voltage drop along it is 27 volts. (From the law $E = RI = 45 \times 0{\cdot}6 = 27$ volts.) Referring to Fig. 3, position A of the resistance is at the same potential as the cathodes of the valves, and thus, as there is a voltage drop of 27 volts along the resistance to B, the position B is of lower potential than A, or, in other words, it is negative with respect to the cathodes by 27 volts. From the grid volt/anode current characteristic (Fig. 4) it can be seen that this 27 volts when applied to the grid will reduce the anode current flowing to zero.

This action is due to the intense negative field inside the valve, which stops the passage of electrons across the space between cathode and anode. Thus no current can flow in the output circuit until this bias is completely removed, and this occurs only when the circuit is broken between pin and diaphragm. To ensure a stable output when the above circuit is broken, the cathode and grid of the valve are permanently connected by a 1-megohm (one million ohms) resistance; this fixes the working position of the grid at zero volts relative to the cathode.

Thus in the state of rest of the apparatus the bias of 27 volts is acting across the 1-megohm resistance, causing a small current to flow in the pin and diaphragm circuit. The actual value of this current is 0·027 milliampere.

$$I = \frac{E}{R}$$

where E = volt
R = resistance
I = current.

$$\therefore \quad I = \frac{27}{1{,}000{,}000} \text{ amperes} = 0{\cdot}027 \textit{ milliampere.}$$

This current is for all practical purposes zero. When the circuit between pin and diaphragm is broken, the bias on the grid rises to zero, and this allows the anode current to rise instantaneously to its maximum value. Thus the vibration of the pin previously referred to allows anode or output current to flow for a time which is precisely the same in length and nature as the vibration.

THE KNOCK-METER CIRCUIT.

It now remains to measure the average output by applying it to a suitable meter. It was required that the standard knock-meter (without heater element) be used, and as this instrument is a moving-coil meter with no damping of any sort, the output from the valves has to be electrically damped to deliver a steady D.C. current to the meter.

With reference to the circuit Fig. 3c, it will be seen that this damping consists of a network of capacity and inductance.

The effect of inductance is to oppose any change in the value of current flowing; capacity has the effect of storing current. Thus in the arrangement shown, assuming the current to be rising, inductance L1 offers a large resistance to the current; C1, which is a capacity of 2000 or 4000 uF, offers an alternative path, and the current flows into it and is stored. The inductance L1, however, will not resist all the rapidly changing current, and, whatever current passes, it meets a similar inductance and capacity L2 and C2 with the meter in series. Capacity C2 is charged, and the meter registers a reading. Now, if the current is cut off at the source, C1 and C2, being charged with a definite amount of current, now discharge through the meter—*i.e.*, in the same direction as the original current—and thus the constancy of the reading is maintained.

In the case of the output from the valve, which is a rapidly pulsating supply (when detonation is being measured), the condensers at each interval between pulsations discharge the correct amount to maintain a constant reading on the meter.

The surges of current in the meter circuit are illustrated graphically, with an accompanying explanation, in Appendix B.

The current passing through the meter to the anodes of the valves is also passed through a variable resistance *D* of 2000 ohms and a relay *E*.

Resistance *D* allows of adjustment to the anode supply voltage so as to vary the meter reading as required.

Relay *E* is a magnetic relay with one break and one make contacts. The reason for its inclusion in the circuit may be explained as follows :—

The output of the set through the meter and relay is controlled by the time of absence of the negative grid bias. Should the wires connecting the set to the pin on the engine be accidentally parted, the meter would be damaged by the high current which would flow. With the relay in circuit, when the current flowing rises to a value slightly in excess of that required for full-scale meter reading—*i.e.*, 2 milliamperes—the relay operates and opens the circuit through the meter and by-passes the current straight through to the valves. The relay locks itself in this position, thus safeguarding the meter, until it is released by the action of again completing the negative bias circuit.

The set has been found to give sufficient output at a supply voltage of 110 volts from the D.C. generator, which is part of C.F.R. equipment. The total power required is 0·6 ampere at 110 volts = 66 watts. The set operates satisfactorily on either coil or magneto ignition engines; there are several minor checks to the wiring, however, when first fitting the apparatus to the engine. These are as follows :—

Engine with magneto ignition.

Check that there is no earth on the positive pole of the generator.

Engine with coil ignition.

1. The end of the 500-ohm resistance in the coil ignition circuit must be transferred from the negative pole of the generator to the positive.

2. The earth on the positive pole of the generator must be removed and the earth placed on the negative pole.

The essential point in both cases is to ensure that no earth exists on the positive pole of the generator, because the negative pole is earthed when the set is operating correctly, and thus a direct short circuit on the generator must be avoided.

The following performance is claimed for this apparatus :—

(*a*) The apparatus measures the true knock intensity over the entire testing range of octane numbers without any change of original setting.

(*b*) Combustion pressure effects are not recorded. If the engine is run on 100-octane fuel at the compression ratio giving standard knock intensity, with the knock-meter reading at mid-scale, and the fuel is then changed over to pure benzene, the knock-meter reading will fall away to zero even though the fuel is " bumping " quite heavily.

(*c*) The operation of the apparatus is more simple than that of the standard pin.

(*d*) The sensitivity per octane number is controllable. 10 knock-meter divisions per octane number is practicable.

(*e*) The current, 0·027 milliampere, is so small that there can be no trouble due to arcing at the point of contact between pin and diaphragm.

(*f*) The apparatus can be fitted in a quarter of an hour to operate satisfactorily from the D.C. generator on either coil or magneto ignition C.F.R. engines.

(*g*) Maintenance of the set should be negligible. New valves may be required at intervals of two years. Cleaning of the pick-up unit should be carried out at the same time as decarbonizing the engine—*i.e.*, approximately every 100 hours running time.

The authors wish to thank the Asiatic Petroleum Co., Ltd., and Shell Refining and Marketing Co., Ltd., for permission to publish the results of the experimental work described, which was carried out in the Company's research laboratory in London.

APPENDIX A.

DETAILED EXPERIMENTAL INVESTIGATION ON MOTION OF STANDARD BOUNCING-PIN.

An apparatus called the Weidenhoff distribuscope which was designed to measure the time of make and break of the contact points of automobile ignition distributors was used to study the movement of the contact points of the standard bouncing-pin. The duration of contact of the points is indicated on a circular scale of degrees by the flashing of a neon lamp which is incorporated in the rotating arm of the distribuscope. By rotating the arm at a speed synchronous with the engine speed, the duration and number of contacts of the bouncing-pin points during one engine cycle can be readily estimated.

The shaded diagrams on the drawing Fig. 5 A and B represent the periods of contact, on crankshaft degree scale, for various bouncing-pin contact point clearances at 5·3 : 1 and 8·0 : 1 compression ratio respectively. Diagram *X* represents contact time on the detonating fuel, and diagram *Y* non-detonating fuel, the latter therefore showing interference due to combustion pressure. For standard knock intensity at 5·3 to 1 compression ratio (C.R.) on a 65-octane-number fuel, the contact points usually close three times. On reducing the gap from 0·004 in. to 0·0025 in. the closure of the contact points is due to the sum of the deflection of the diaphragm

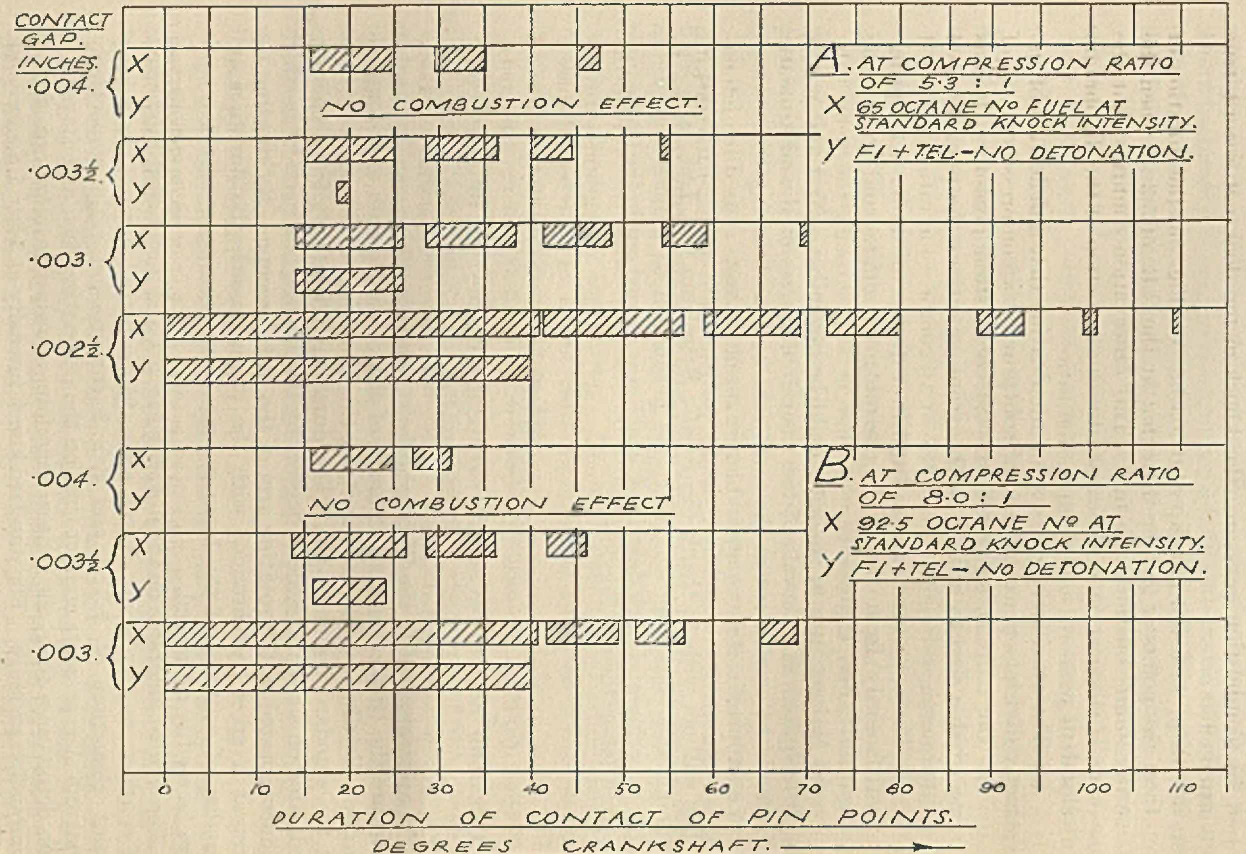

CONTACT GAP. INCHES.
·004.
·003½.
·003.
·002½.
·004.
·003½.
·003.
X
Y
NO COMBUSTION EFFECT.
NO COMBUSTION EFFECT
A. AT COMPRESSION RATIO OF 5·3 : 1
X 65 OCTANE No FUEL AT STANDARD KNOCK INTENSITY.
Y F1 + TEL.—NO DETONATION.
B. AT COMPRESSION RATIO OF 8·0 : 1
X 92·5 OCTANE No AT STANDARD KNOCK INTENSITY.
Y F1 + TEL—NO DETONATION.
0
10
20
30
40
50
60
70
80
90
100
110
DURATION OF CONTACT OF PIN POINTS.
DEGREES CRANKSHAFT.

Fig. 5.

caused by combustion pressure and the induced vibrations of the pin caused by detonation. When the gap is less than the deflection of the diaphragm caused by combustion pressure, the knock-meter does not record true detonation effect.

At a C.R. of 8 : 1 and pin-gap of 0·003 in. (see Fig. 5B) the duration of contact of the points is greater than that at the C.R. of 5·3 : 1 when the engine is running on the same fuel. This observation confirms that the movement of the lower contact caused by the deflection of the diaphragm increases with an increase in compression ratio.

It was found when an engine was not detonating that a deflection of the diaphragm took place amounting to 0·0015 in. at a compression ratio of 4 : 1 and 0·0025 in. at 8 : 1 C.R. due to combustion pressure. It was determined that under these non-detonating conditions the pin remained on the diaphragm throughout the cycle at all compression ratios, provided that there was a normal pressure downwards by the lower leaf-spring. This was carried out by insulating the pin in its guides and completing the circuit through the pin and diaphragm and through the neon tube referred to above. If the spring pressure was insufficient there was a bounce of the pin due to combustion when toluene, benzene, and aromatic fuels were used, although there was no detonation.

The total period of make of the bouncing-pin contacts caused by detonation has a duration of about 15° crankshaft when the gap is set to 0·004 in. Frictional losses and other damping cause the pin eventually to come to rest before the end of the engine cycle.

Diagrams of pin movement were also observed with the aid of the Standard–Sunbury cathode-ray oscillograph. These diagrams are reproduced in Fig. 6. The vertical and horizontal axes represent displacement and time respectively. Although they carry no scale, they are all relative in size to one another. These were obtained by placing a magnetic pick-up above a steel lower-leaf spring resting on the pin-top. Thus movement of the spring was recorded.

Fig. 6B shows the leaf-spring contact movement at standard knock intensity on 65 O.N.–5·3 : 1 C.R.

Fig. 6A—leaf-spring contact movement at 5·3 : 1 C.R. when running on non-detonating fuel—*i.e.*, no vibration of pin.

Fig. 6F standard knock intensity at approximately 8 : 1 C.R. on 92·5 octane fuel.

Fig. 6E leaf-spring contact movement at 8 : 1 C.R. when running on non-detonating fuel. Note the relative position of diaphragm or leaf-spring deflection at 65 O.N. setting Fig. 6A (non-detonating).

Thus, while it can be seen that the vibration of the pin when detonation is occurring is approximately of the same nature and amplitude at both 5·3 : 1 and 8 : 1 C. Ratios; in the case of Fig. 6F—that is, when at standard knock intensity on 92·5 octane fuel—the vibration is displaced vertically under the action of the diaphragm deflection.

By increasing the thickness of the diaphragm from the standard 0·015 in. to 0·025 in. the deflection by combustion pressure is greatly reduced. At the same time the vibrations of the pin due to detonation have approximately the same amplitude. Diagrams 6 D, C, H and G are the corresponding diagrams with the thicker diaphragm.

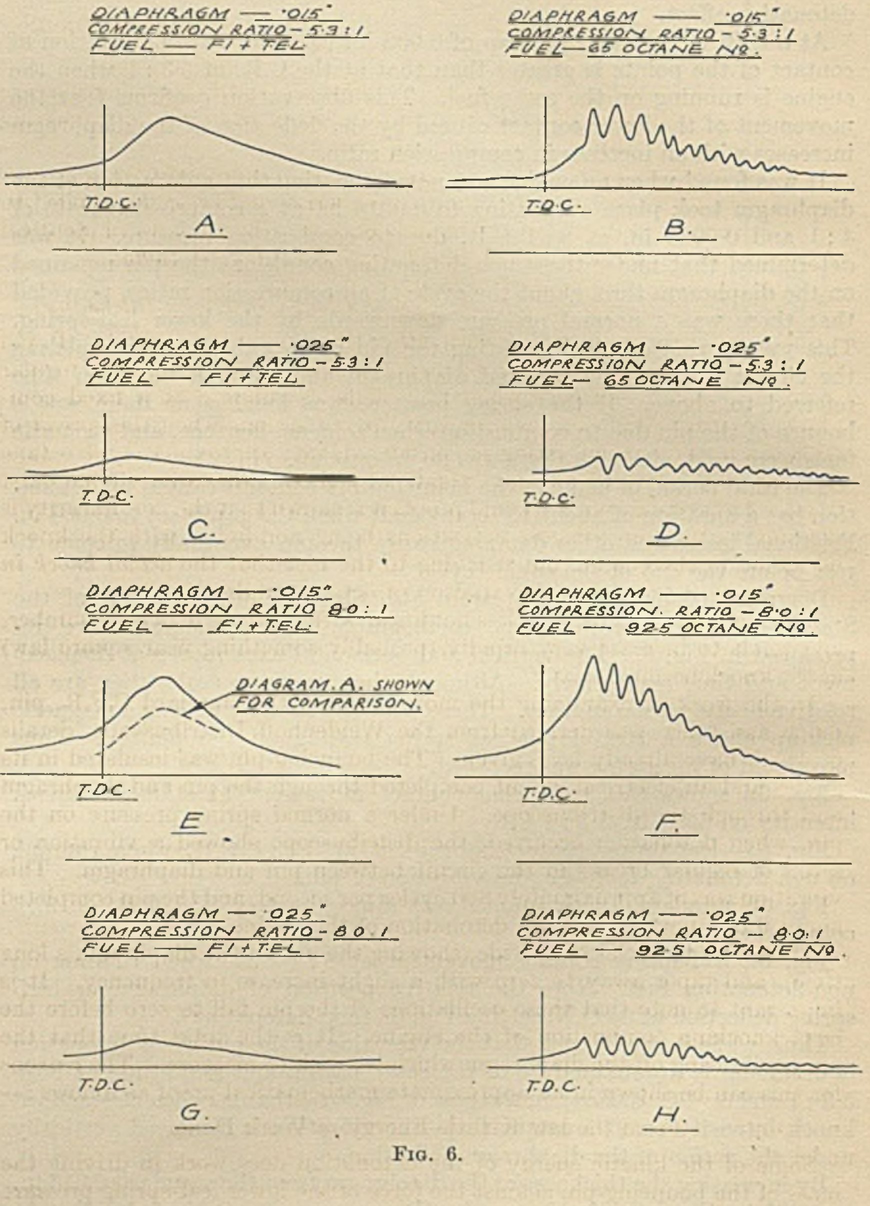

DIAPHRAGM — ·015"
COMPRESSION RATIO – 5·3 : 1
FUEL — F1 + T.E.L.
T.D.C.
A.
DIAPHRAGM — ·015"
COMPRESSION RATIO – 5·3 : 1
FUEL — 65 OCTANE No.
T.D.C.
B.
DIAPHRAGM — ·025"
COMPRESSION RATIO – 5·3 : 1
FUEL — F1 + T.E.L.
T.D.C.
C.
DIAPHRAGM — ·025"
COMPRESSION RATIO – 5·3 : 1
FUEL — 65 OCTANE No.
T.D.C.
D.
DIAPHRAGM — ·015"
COMPRESSION RATIO 8·0 : 1
FUEL — F1 + T.E.L.
DIAGRAM. A. SHOWN FOR COMPARISON.
T.D.C.
E.
DIAPHRAGM — ·015"
COMPRESSION RATIO – 8·0 : 1
FUEL — 92·5 OCTANE No.
T.D.C.
F.
DIAPHRAGM — ·025"
COMPRESSION RATIO – 8·0 : 1
FUEL — F1 + T.E.L.
T.D.C.
G.
DIAPHRAGM — ·025"
COMPRESSION RATIO – 8·0 : 1
FUEL — 92·5 OCTANE No.
T.D.C.
H.

Fig. 6.

Thus, although the diaphragm is much thicker, the energy transmitted to the mass of the pin has not been materially reduced. Reference is made to this important and interesting fact in the following discussion.

DISCUSSION ON THE RESPONSE OF THE CLEMENT–PIGNEGUY BOUNCING-PIN TO KNOCK INTENSITY.

It is obvious that the mechanics of the standard bouncing-pin are identical with those of the C.P. pin. The mass of the pin and the spring tension applied to it are closely similar.

Thus any reasoning based on experimental data obtained with the standard apparatus can, within the limits of experimental error, be applied to the C.P. pick-up unit. That this is so is borne out by the several identical characteristics possessed and obtained experimentally by them.

Non-linearity of Knock-meter Readings with Change in Knock Intensity.

It has been determined that with either the standard pin or the C.P. pin the knock-meter readings recorded do not change in proportion with regular changes of octane number when the engine is running at a fixed compression ratio. While the non-linearity is not serious when the spread of octane number during testing is considered, *i.e.*, approximately 4 octane number, it is interesting to investigate why the non-linearity should exist at all. In the following work and proofs it is shown that the non-linearity is not due to the knock-meter indications being non-linear with the knock occurring in the engine, but it is due to the fact that the *actual knock in the engine* is not linear with variation of octane number.

The increase in engine knock is not linear with decrease in octane number, and tends to increase very rapidly (probably something near square law) as the knock becomes heavy.

In the work of examining the movements of the standard C.F.R. pin, much assistance was derived from the Weidenhoff Distribuscope, details of which have already been given. The bouncing-pin was insulated in its guides and an electrical circuit completed through the pin and diaphragm and through the distribuscope. Under a normal spring pressure on the pin, when detonation occurred, the distribuscope showed a vibration or series of regular breaks in the circuit between pin and diaphragm. This vibration was of approximately 800 cycles per second, and the pin completed about 9 or 10 cycles for each detonation of the engine.

These 9 or 10 cycles start wide (showing the pin off the diaphragm a long time), and taper away to zero with a slight increase in frequency. It is important to note that these oscillations of the pin fall to zero before the next knocking combustion of the engine. It is the total time that the pin is vibrating off the diaphragm which we wish to measure. The reasons for this can be shown in an approximate mathematical proof as follows :—

From the law Kinetic Energy = Work Done.

Some of the kinetic energy of the detonation does work in driving the mass of the bouncing-pin against the force of the lower leaf-spring pressure and its own weight :—

thus $$\frac{WV^2}{2g} = FS \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where W = weight of pin, V = velocity of pin, g = gravitational acceleration 32·2 *feet per second, per second,* F = force retarding-pin, S = distance pin moves in coming to rest.

The various figures measured on the standard pin were as follows :—

F = lower leaf-spring pressure (assumed to remain constant although it is deflected slightly) plus pin weight

$$= 210 + 33 \text{ gm.} = \frac{210 + 33}{454} \text{ lb.} = \frac{243}{454} \text{ lb.}$$

W = weight of pin = 33 gm. = $\frac{33}{454}$ lb.

S = the actual distance moved by the pin under detonation measured with the aid of Vernier gap adjustment.

$$= 0{\cdot}0005 \text{ in.} = \frac{0{\cdot}0005}{12} \text{ ft.}$$

therefore from $\frac{WV^2}{2g} = FS$

$$V^2 = 64{\cdot}4 \times \frac{243}{454} \times \frac{0{\cdot}0005}{12} \times \frac{454}{33}$$

$$\therefore \quad V = 0{\cdot}15 \textit{ feet per second.}$$

This is the velocity of the pin immediately after the impact of detonation on the diaphragm.

Now from the law $$Ft = \frac{W}{g} . V \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where F = force retarding-pin, t = time for pin to come to rest, W = weight of pin, g = gravity, V = initial velocity (as obtained).

$$\therefore \quad t = \frac{W}{g} . \frac{V}{F} = \frac{33}{454} \times \frac{0{\cdot}15}{32{\cdot}2} \times \frac{454}{243}$$
$$= 0{\cdot}00064 \textit{ second.}$$

This is the time for the pin to come to rest off the diaphragm, thus total time for one complete oscillation

$$= 2t = 2 \times 0{\cdot}00064$$
$$= 0{\cdot}00128 \textit{ second.}$$

The pin having thus returned to the diaphragm, it has still considerable energy which is stored in the resilience of the diaphragm ; it is thus thrown off again, and oscillates at the natural frequency of the pin system. This frequency can be calculated from our results above :—

$$\text{frequency} = \frac{1}{T} = \frac{1}{2t} = \frac{1}{0{\cdot}00128} = 780 \text{ cycles per second.}$$

This calculated frequency coincides very closely with the frequency of 800 cycles per second measured on the Weidenhoff Distribuscope, proving that our approximate calculations are correct in principle. The following conclusions can be reached from this proof :—

$$\text{Kinetic energy of detonation } K = \frac{WV^2}{2g} \text{ given to pin} \quad . \quad (1)$$

This can be re-written in the form :—

$$K \times \frac{2g}{W} = V^2 \text{ or } V = \sqrt{K \times \frac{2g}{W}}$$

and from equation (2)

$$F.t. = \frac{W}{g} . V$$

inserting in (2) the value for V obtained from (1)

$$\therefore \qquad t = \frac{W}{gF}\sqrt{K \times \frac{2g}{W}}$$

$$\therefore \qquad t = \frac{1}{F} \times \sqrt{\frac{2W}{g}} \times K = \frac{1}{F}\sqrt{\frac{2W}{g}} \times \sqrt{K}$$

but for any particular pin setting F, W, and g are constants and can be expressed as C and therefore t can be written ;—

$$t = C\sqrt{K}$$

or $\qquad$ *t is proportional to* $(K)^{\frac{1}{2}}$

In words, the time the pin is off the diaphragm is proportional to the square root of the kinetic energy of the impact of detonation given to the pin.

A curve to this equation has been drawn (see Fig. 7).

The next important point—does the radio set output current vary in proportion to the time of break of the pin and diaphragm circuit. This point has been accurately checked in the following manner :—

A toothed wheel was obtained and a brush-gear was mounted so as to make good contact with each tooth as the wheel was made to rotate. The wheel was then marked out into 9 parts, and plates were made so that when fixed in position on the wheel they each blanked off a number of the teeth of the wheel. Thus as the wheel rotated a definite number of teeth could be left unblanked, and therefore a definite time of break at the brush could be generated, providing only that the wheel speed was constant. The wheel used has 96 teeth, and 8 of the plates blanked off 10 teeth each. Other plates were provided which made it possible to have open 5 teeth or any multiple of 5 teeth. Thus the contact time could be varied in steps of 5 teeth from 5 up to 90, and finally 96 teeth.

The speed of the wheel was selected at 500 r.p.m. so as to generate a make and break of the circuit similar to the bouncing-pin vibration.
Thus 96 breaks per revolution at 500 r.p.m.

$$= \frac{500 \times 96}{60} \text{ breaks per second.}$$

$$= 800 \textit{ per second.}$$

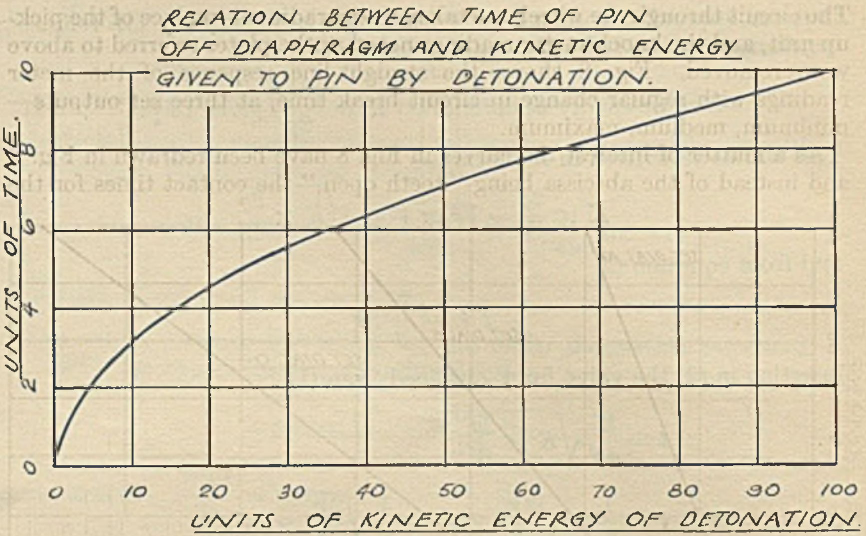

RELATION BETWEEN TIME OF PIN
OFF DIAPHRAGM AND KINETIC ENERGY
GIVEN TO PIN BY DETONATION.
UNITS OF TIME.
0
2
4
6
8
10
0
10
20
30
40
50
60
70
80
90
100
UNITS OF KINETIC ENERGY OF DETONATION.

FIG. 7.

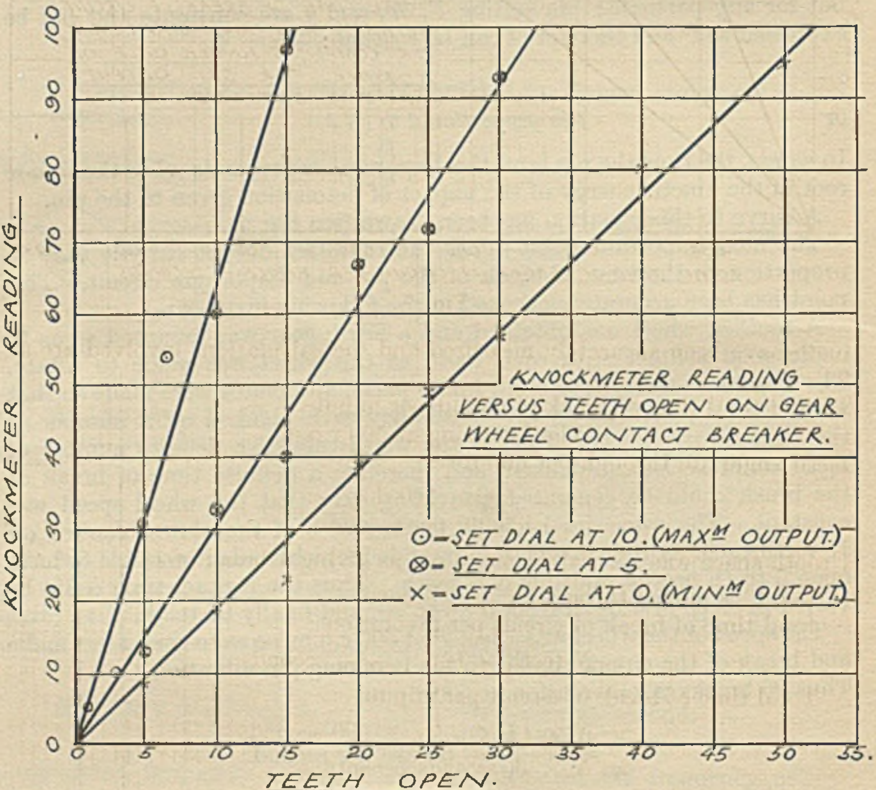

KNOCKMETER READING.
0
10
20
30
40
50
60
70
80
90
100
KNOCKMETER READING
VERSUS TEETH OPEN ON GEAR
WHEEL CONTACT BREAKER.
⊙ - SET DIAL AT 10. (MAX^M OUTPUT.)
⊗ - SET DIAL AT 5.
× - SET DIAL AT 0. (MIN^M OUTPUT.)
0
5
10
15
20
25
30
35
40
45
50
55.
TEETH OPEN.

FIG. 8.

The circuit through the wheel was taken to the radio set in place of the pick-up unit, and the knock-meter readings noted as the plates referred to above were removed. Fig. 8 shows the straight-line response of the meter readings with regular change in circuit break time, at three set outputs—minimum, medium, maximum.

As a matter of interest the curves in Fig. 8 have been redrawn in Fig. 9 and instead of the abscissa being "teeth open," the contact times for the teeth have been accurately measured and the calculations involved are as follows :—

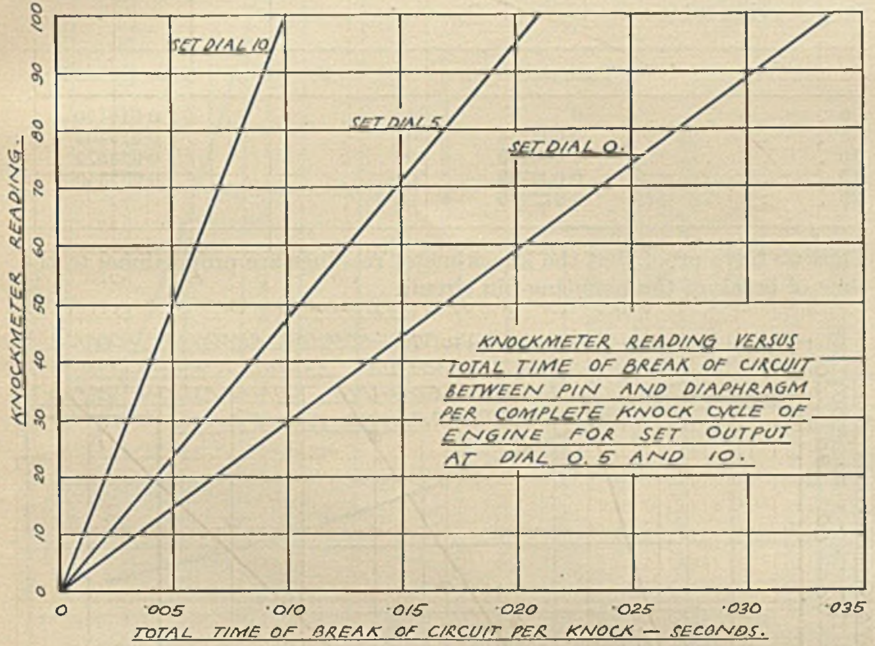


FIG. 9.

To find total time of break of circuit per minute

Wheel running at 500 r.p.m.

Total angle run through per minute

$$= 500 \times 360 \text{ degrees}$$
$$= 3000^\circ \text{ per second}$$

1 tooth-space was accurately measured as giving a break of $1\frac{3}{4}^\circ$.

Now 1° is moved through in $\frac{1}{3000}$ second.

$\therefore$ total time of break of circuit per revolution

$$= N \text{ teeth} \times 1\frac{3}{4}^\circ \times \frac{1}{3000} \text{ seconds.}$$

$\therefore$ Total time of break of circuit per minute

$$= N \times 1\frac{3}{4} \times \frac{1}{3000} \times 500 \text{ seconds}$$
$$= N \times \frac{7}{24} \textit{ seconds per minute}$$

where N is the number of teeth left open on the wheel.

It is convenient to express this time, however, in some term relative to the C.F.R. engine; thus as the speed is 900 r.p.m. of the engine, there are 450 theoretical knock impacts per minute. Thus it is perhaps better to express the break of the circuit as :—

Time of break of circuit per knock of engine

$$= N\,\tfrac{7}{24} \times \tfrac{1}{450} = 0{\cdot}0006468\ N \textit{ seconds.}$$

Using this equation, the values in Fig. 8 have been converted to Fig. 9 from the following table :—

N.	Time (seconds).	*N*.	Time (seconds).
0	0	25 . . .	0·016170
5	0·003234	30 . . .	0·019404
10	0·006468	40 . . .	0·025872
15	0·009702	50 . . .	0·032340
20	0·012936		

Thus we have proof that the knock-meter readings are proportional to the time of break of the bouncing-pin circuit.

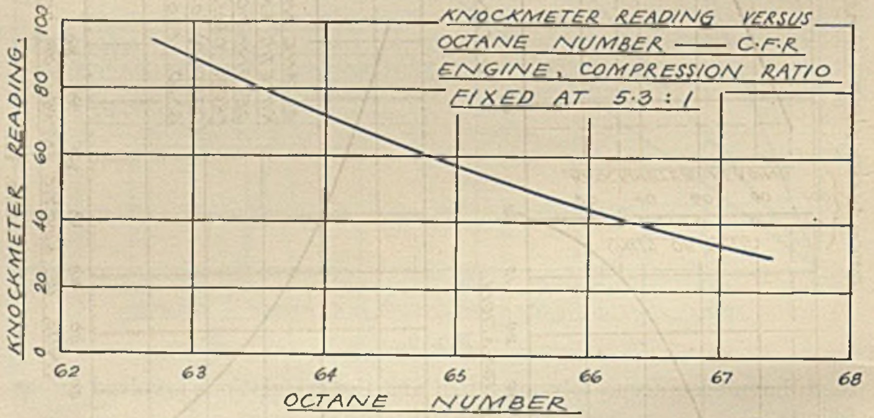


FIG. 10.

As we have already shown, the time the pin is off the diaphragm is a function of the $K^{\frac{1}{2}}$, where K is the kinetic energy of detonation given to the pin; thus Fig. 7 also represents the change in knock-meter reading with change of kinetic energy given to the pin.

Now, the important point is, if the change in kinetic energy of detonation *in the engine* were linear with change in the octane number of the fuel (at a fixed compression ratio), then Fig. 7 would also represent the curve of knock-meter reading versus octane number at the fixed compression ratio.

With the above statement in mind, Fig. 10 was obtained in the following manner :—

The engine was run under standard 65-octane-number conditions and the knock-meter reading set to mid-scale. Then, with no alteration in compression ratio, the engine was run on fuels of various octane number and the knock-meter readings were taken.

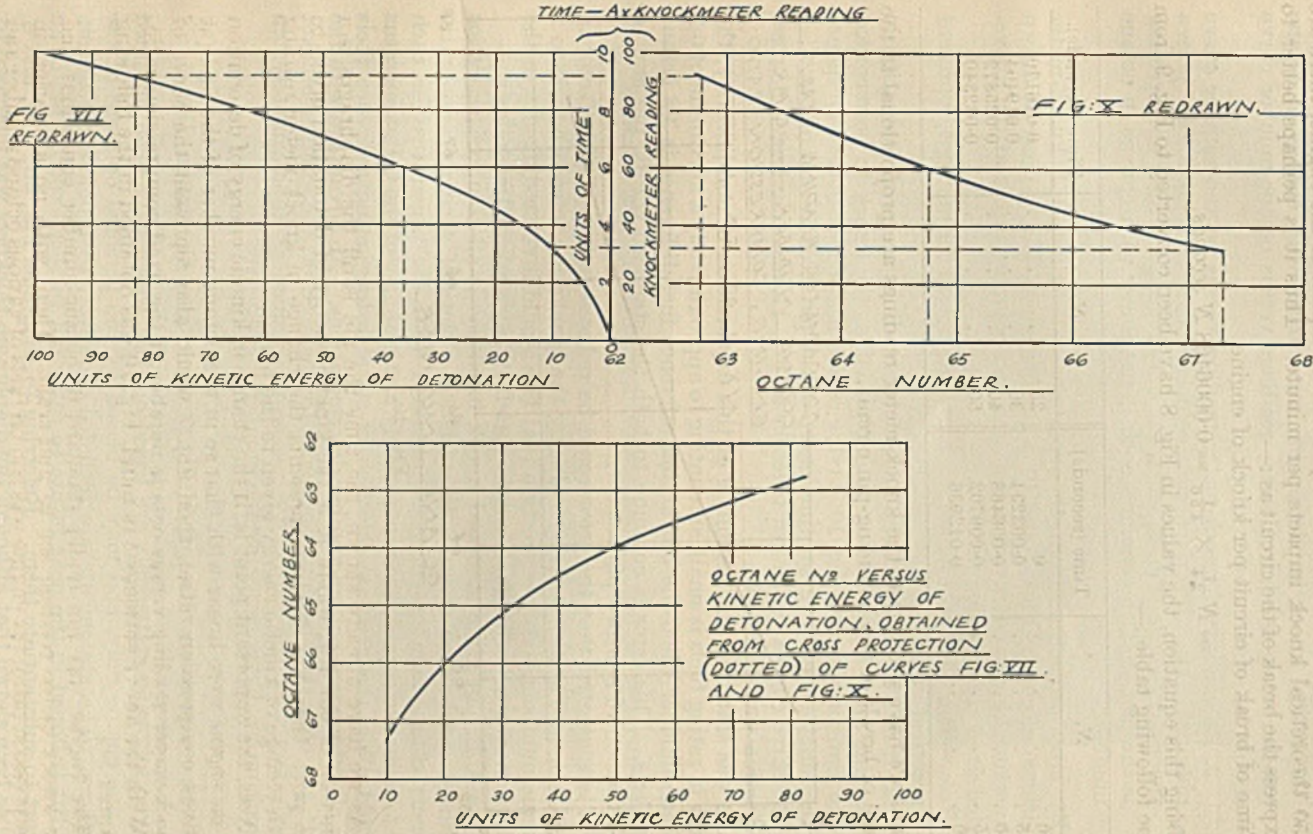

TIME—A×KNOCKMETER READING
FIG VII REDRAWN.
FIG: X REDRAWN.
UNITS OF TIME
KNOCKMETER READING
0
2
4
6
8
10
20
40
60
80
100
100
90
80
70
60
50
40
30
20
10
62
63
64
65
66
67
68
UNITS OF KINETIC ENERGY OF DETONATION
OCTANE NUMBER.
OCTANE NUMBER
62
63
64
65
66
67
68
0
10
20
30
40
50
60
70
80
90
100
UNITS OF KINETIC ENERGY OF DETONATION.
OCTANE No VERSUS KINETIC ENERGY OF DETONATION, OBTAINED FROM CROSS PROTECTION (DOTTED) OF CURVES FIG: VII AND FIG: X.

FIG. 11.

Fig. 10 represents the result of two variables :—

1. If the knock in the engine were linear with change in octane number, then the knock-meter readings versus octane-number curve should be represented by Fig. 7.
2. As the *actual* knock-meter reading versus octane-number curve obtained (Fig. 10) does not coincide with the *previously proven* theoretical curve (Fig. 7), then the only reason for their not agreeing is the fact that the engine knock is not linear with change in octane number.

By cross-projection from the common side (time = A knock-meter divisions) of curves Figs. 7 and 10, a further curve (Fig. 11) can be drawn connecting kinetic energy of detonation and octane number at the above-stated fixed compression ratio.

(*Note.*—The " Units of Kinetic Energy " do not, at the moment, represent any practical value.)

Thus it can be seen that the knock impact or intensity of detonation in the engine must follow the curve of Fig. 11 for the knock to be recorded in the manner of curve, Fig. 10, having regard to the fact that the response of the kinetic energy versus time curve of the pin itself is that of Fig. 7.

The three curves are shown together in Fig. 11, showing how the cross-projection was obtained.

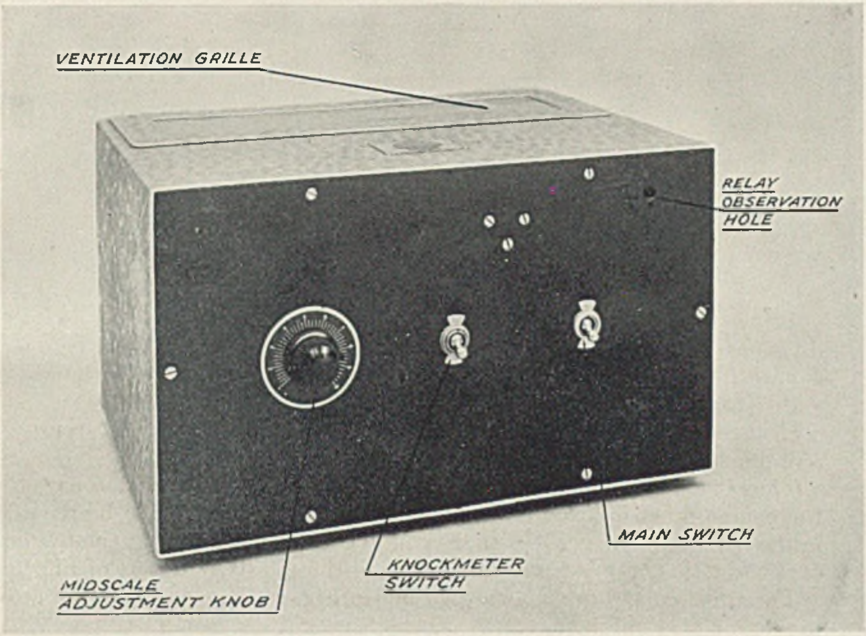
As was stated at the beginning of this explanation of non-linearity, the error in rating fuels is small, amounting to approximately a maximum of 0·2 octane number when the bracketing reference fuel difference is 3·8 octane numbers. This error is common to both the standard C.F.R. pin and to the Clement–Pigneguy pin.

It is suggested that the error could be reduced to a negligible factor in the Clement–Pigneguy pin by reducing the bracketing reference fuels to 2 octane numbers. Any suggestion that this would involve difficulty in the selection of bracketing fuels can be satisfactorily answered as follows :—

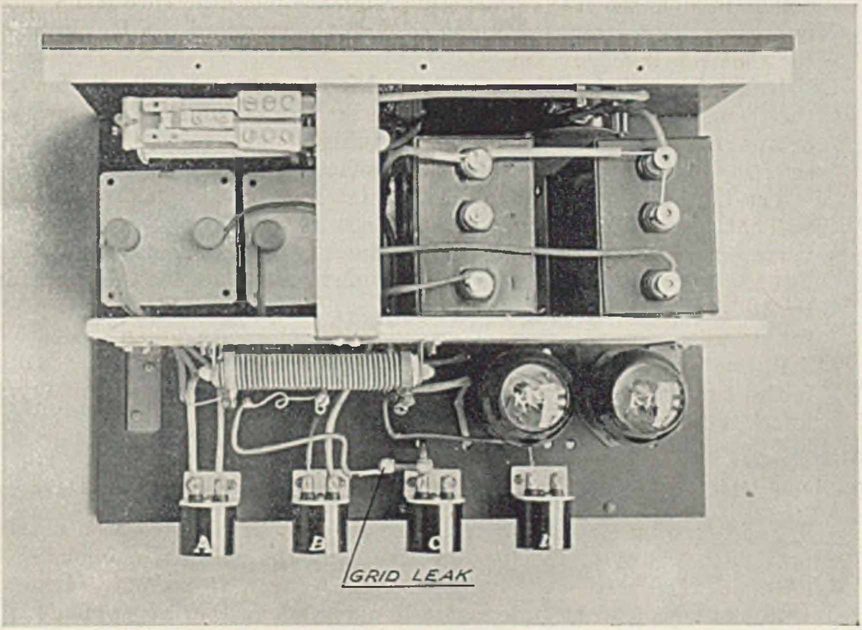
The C.P. pin gives standard knock intensity at all compression ratios without combustion-pressure interference. Thus, if a compression ratio versus octane-number curve be obtained with the apparatus for each test engine concerned, the repeatability and stability of the C.P. apparatus would allow the accurate selection of suitable bracketing reference fuels for all subsequent octane-number determinations. An advantage with the C.P. pin over the standard pin under the reduced octane-number bracket is the fact that the sensitivity can be maintained at approximately ten knock-meter divisions per octane number.

Discussion on Knock Measurement and Observed Data.

The following statements are based on data which have been obtained on one engine only, and may be biased by the personal opinions of the authors. The statements are included, however, to promote discussion, and it is hoped in the near future to carry out further experiments in an effort to substantiate them. Referring to Diagrams Fig. 6D, C, H, and G, it has been shown that although the diaphragm thickness was increased by 0·010 in., the energy of detonation transmitted through the diaphragm to



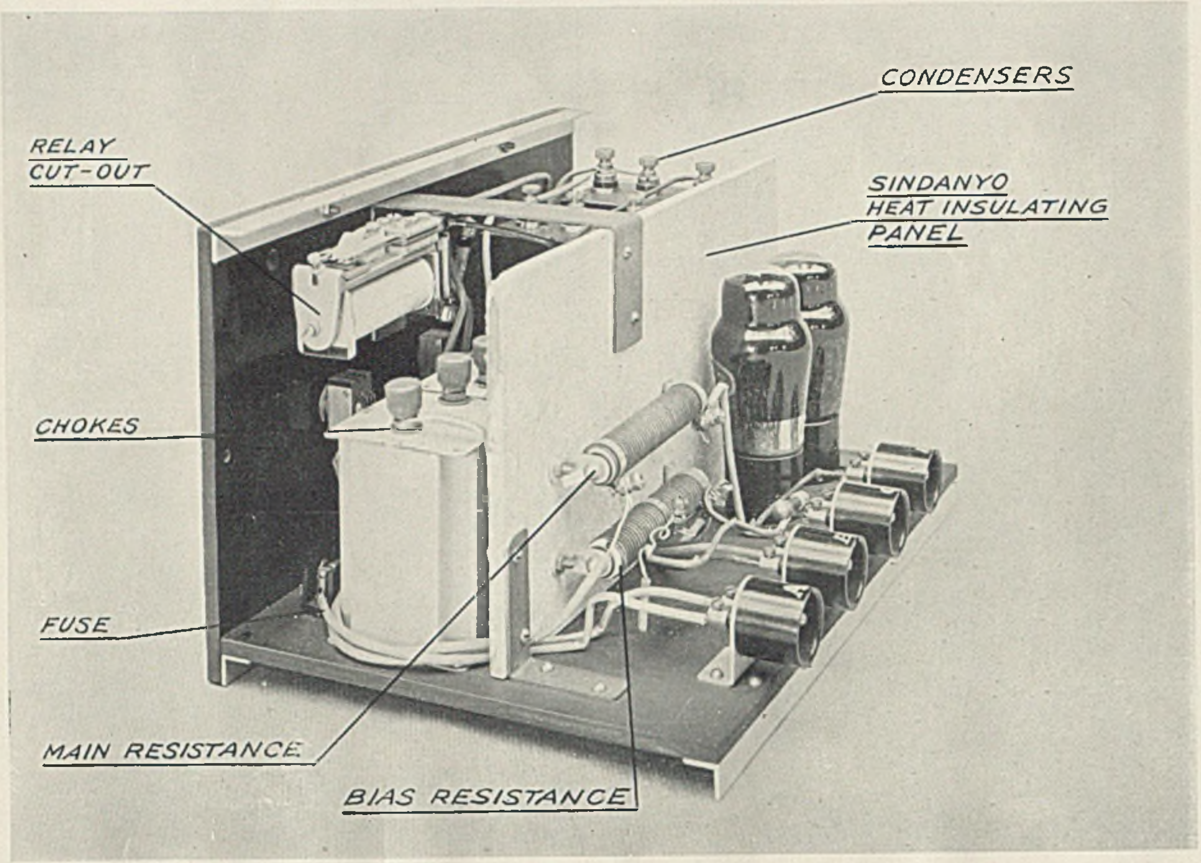
FRONT PANEL.



PLAN.

VIEWS OF "RADIO" SET.

[*To face p.* 508.



GENERAL INTERNAL VIEW OF "RADIO" SET.

the pin was not reduced. This gave rise to the suggestion that the thickness of the diaphragm could be increased without limit—*i.e.*, up to the thickness of the cylinder head. In other words, if a small mass is mounted externally on a solid part of the cylinder head, vibrations are set up in the mass due to the impact of detonation.

Accordingly a small apparatus was made up as follows :—

A $\frac{3}{16}$-in. diameter steel ball loaded with a coil spring was mounted in an insulated frame so that contact was only made by the ball on the cylinder head, which was polished to ensure a smooth contact surface. It was determined that this " pick-up unit " responded in an identical manner with the screwed-in pick-up unit.

An interesting use was made of this " bouncing-ball pick-up unit." As, of course, it is used externally, the bouncing-pin hole in the engine was available for use at the same time. Thus, using the standard C.F.R. pin and the bouncing-ball unit, together with two knock-meters, simultaneous readings on both systems were obtained and compared, and showed close agreement over the range where the standard pin was not recording combustion pressure—*i.e.*, at low compression ratios. This external pick-up shows the possibilities of the use of such an arrangement on engines not equipped for the fitting of screwed-in indicators, such as aircraft engines, etc.

The C.P. pin and the bouncing ball have both been tried out on a C.F.R. engine running under special high-speed conditions. During development of a method of test for rating high-octane fuels the units have shown that they each record detonation satisfactorily and respond to knock intensity described as " frequent slight." The engine speed during the tests was 1800 r.p.m., and jacket temperature using ethylene glycol was approximately 180° C., and the output was 120 B.M.E.P. One or two minor modifications may be necessary to the pick-up units—*e.g.*, greater rigidity and resistance to high temperatures—but, generally speaking, it can be stated that the system of measuring detonation is satisfactory at the high speed, and could be used for the rating of fuels.

At this point in the discussion it is considered appropriate to make reference to some experimental results which are of fundamental importance.

Up to the moment we have considered the effects of detonation on a mass situated on a diaphragm or in any case external to the engine, and have expressed its effects theoretically in " units of kinetic energy."

The following work was carried out on one engine, once only, and therefore the following theory put forward should be accepted with some reserve.

In an attempt to see what relation existed between knock-meter readings and the gas wave inside the cylinder, a " ball unit " referred to above was used simultaneously with a normal cathode-ray oscillograph, the pick-up of which was screwed into the bouncing-pin hole. Then the engine was run at standard knock intensity on 65 O.N. fuel. At this engine setting both apparatus were set to record this knock intensity. In deference to accepted theory that detonation is high rate of change of pressure during the detonation wave, the oscillograph was set to record the rate of change of pressure diagram. The ball unit was adjusted to record a mid-scale reading on the knock-meter.

With the apparatus thus set, the engine was run on fuels of various increasing octane numbers and the compression ratio correspondingly increased to give a mid-scale reading on the knock-meter recorded by the ball unit. At each individual reading so obtained it was noted that the height of the rate of change of pressure of detonation above that of normal combustion (*i.e.*, $Y_1 - Y$ in diagram, Fig. 12A) was constant. Thus it would appear that to measure the height of the rate-of-change diagram at the point of detonation would give a true indication of knock intensity.

In criticism of the Clement–Pigneguy principle, it has been stated that the mass of the pin is activated in its movement by the rate of change of pressure, and thus if the diagram of rate of change of pressure becomes similar to Fig. 12B by virtue of the nature of the fuel or the mixture strength used for the method of test, then the C.P. pin can no longer record detonation, but will respond to the maximum rate of change of pressure Y_2, and not to the detonation rate of change $Y_3 - Y_4$.

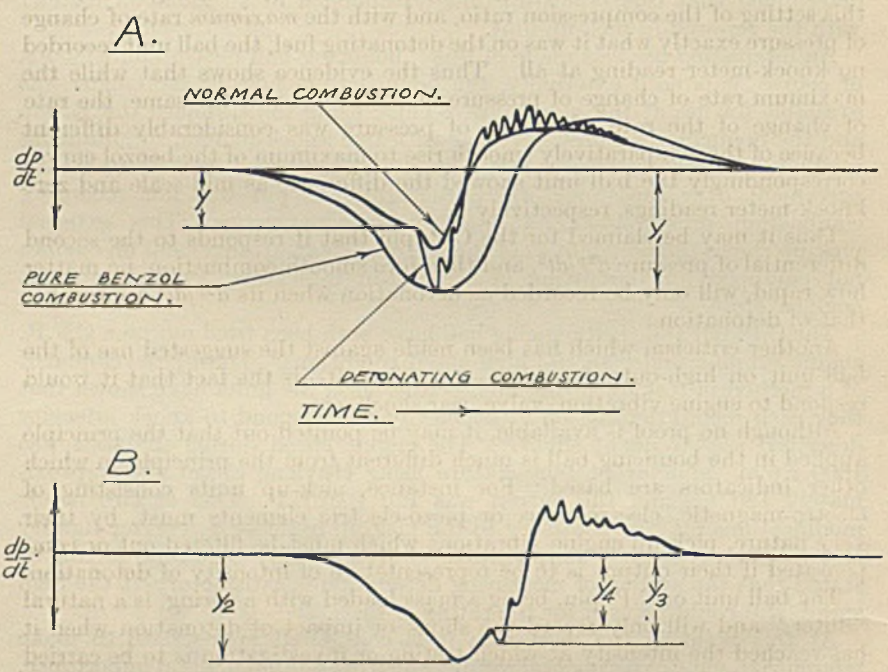


FIG. 12.

The following test results are intended to disprove any statement that the C.P. pin or the ball unit is activated by the rate of change of pressure, and an attempt is made to show that the principle of the apparatus is such that it is only activated by the second rate of change of pressure—*i.e.*, the rate of change of the rate of change of pressure. Furthermore, it is suggested that measuring the height of the rate-of-change diagram is only approximately what is required. That the method is reasonably satisfactory is because in general the height of the rate-of-change diagram is proportional to its *slope*.

Referring again to the simultaneous results obtained with the ball unit and the oscillograph, the following procedure was adopted.

The engine was run on a low-octane reference fuel and the compression ratio adjusted to give mid-scale reading on the knock-meter (standard knock intensity), and the height $Y_1 - Y$ of Fig. 12A noted.

Then the engine was switched over to pure benzol and the compression ratio increased considerably until the height of the rate-of-change-of-pressure diagram was equal to the peak value previously obtained on the low-octane fuel. (The two diagrams are drawn together, Fig. 12A.) At this setting of the compression ratio, and with the *maximum* rate of change of pressure exactly what it was on the detonating fuel, the ball unit recorded no knock-meter reading at all. Thus the evidence shows that while the maximum rate of change of pressure in both cases was the same, the rate of change of the rate of change of pressure was considerably different because of the comparatively smooth rise to maximum of the benzol curve; correspondingly the ball unit showed the difference as mid-scale and zero knock-meter readings, respectively.

Thus it may be claimed for the C.P. pin that it responds to the second differential of pressure d^2p/dt^2, and therefore smooth combustion, no matter how rapid, will only be recorded as detonation when its d^2p/dt^2 approaches that of detonation.

Another criticism which has been made against the suggested use of the ball unit on high-output engines—*e.g.*, aircraft—is the fact that it would respond to engine vibration, valve-gear shock, etc.

Although no proof is available, it may be pointed out that the principle applied in the bouncing ball is much different from the principle on which other indicators are based. For instance, pick-up units consisting of electro-magnetic, electrostatic, or piezo-electric elements must, by their very nature, pick up engine vibrations which must be filtered out or compensated if their output is to be representative of intensity of detonation. The ball unit or C.P. pin, being a mass loaded with a spring, is a natural "filter," and will only record the shock or impact of detonation when it has reached the intensity at which testing or investigation is to be carried out (which intensity is, of course, selected by the adjustment of the spring pressure). It is not expected, however, that the radio set output designed and satisfactory for the C.F.R. engine would be sufficient for direct application to any other engine. This output can easily be increased, however, by the addition of extra power-valves.

APPENDIX B.

THE PERFORMANCE OF THE DAMPING CIRCUIT.

The conditions of this circuit are shown graphically in Fig. 13.

The shaded areas show the time of break of the negative bias circuit at the pin and diaphragm, for one detonation impact in the engine cylinder. A vibration is shown starting off long and gradually shortening, until after about thirteen individual breaks the pin comes to rest.

The curves represent quantities which have been calculated approxi-

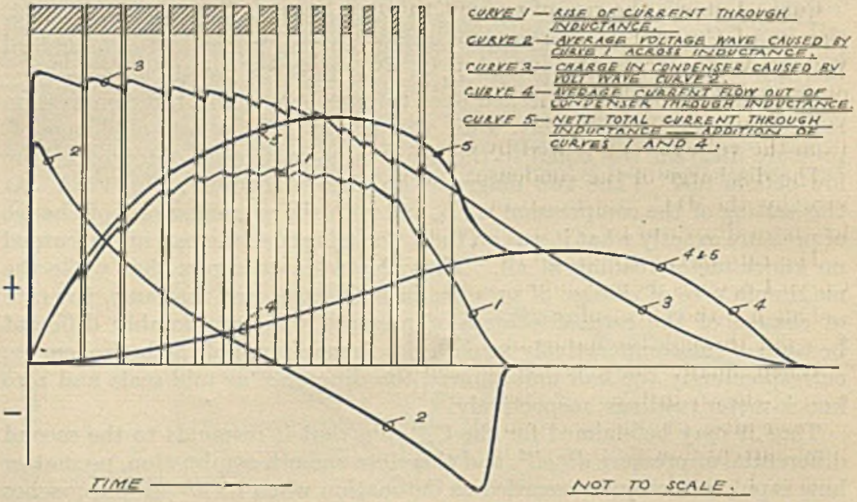

CURVE 1 — RISE OF CURRENT THROUGH INDUCTANCE.
CURVE 2 — AVERAGE VOLTAGE WAVE CAUSED BY CURVE 1 ACROSS INDUCTANCE.
CURVE 3 — CHARGE IN CONDENSER CAUSED BY VOLT WAVE CURVE 2.
CURVE 4 — AVERAGE CURRENT FLOW OUT OF CONDENSER THROUGH INDUCTANCE.
CURVE 5 — NETT TOTAL CURRENT THROUGH INDUCTANCE — ADDITION OF CURVES 1 AND 4.
1
2
3
4
5
4 & 5
+
−
TIME
NOT TO SCALE.

FIG. 13.

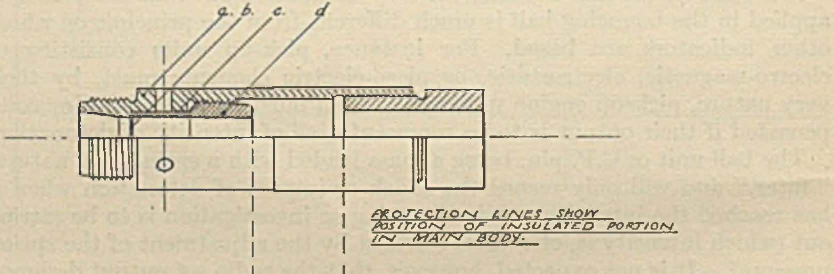

a. b. c. d
PROJECTION LINES SHOW POSITION OF INSULATED PORTION IN MAIN BODY.
g
f
e
h
j
C-P. PICK-UP UNIT—MICROMETER HEAD TYPE.

FIG. 14.

mately from the constants of the circuit, and show the function for one condenser, one inductance, and resistance.

Curve 1 shows the rise of current through the inductance. The rate of change of Curve 1 is represented by Curve 2, and is thus the average voltage wave across the inductance. Now, by the known formula, Q, or quantity of electricity in Coulombs, is given by $Q = VC$, where $V =$ voltage across condenser of capacity C. Thus the condenser charges up from the voltage represented by Curve 2.

The discharge of the condenser through the inductance is limited in its rate by the D.C. resistance of the inductance. An approximate curve has been drawn in to illustrate the action. Curve 3.

The rate of change di/dt of Curve 1 given by Curve 2 falls to zero when Curve 1 reaches its maximum value, and thereafter reverses in sign.

This has the effect of gradually allowing the charge in the condenser to flow out through the inductance represented by Curve 4.

When, finally, the current represented in Curve 1 has fallen to zero, the charge shown in Curve 3 flows out through the inductance in a smooth manner after the knock impulse has finished (Curve 4). To arrive at the total current flowing through the inductance for one knock impulse shown, Curves 1 and 4 can be added together. They are shown so treated in Curve 5.

In the practical case Curve 5 would, of course, be parallel to the time base, showing a steady meter reading.

SYNTHESIS AND PROPERTIES OF MONO-NORMAL-ALKYLBENZENES.*

PART II.—PREPARATION AND PROPERTIES OF THE INTERMEDIATE KETONES AND CORRESPONDING HYDROCARBONS.

By T. Y. Ju, B.Sc., Stud.Inst.Pet., G. Shen, M.Sc., A.M.Inst.Pet., and C. E. Wood, M.Sc., A.I.C., F.Inst.Pet.

Synopsis.

A series of six mono-*n*-alkylbenzenes (alkyl group : C_5, C_6, C_7, C_9, C_{12}, C_{14}) has been prepared from the corresponding ketones by palladium catalytic hydrogenation and Clemmensen's reduction. The palladium catalytic hydrogenation method gives excellent yields and pure products. The ketones were obtained from the corresponding acid chlorides and benzene by Friedel and Crafts' reaction, the reaction medium being carbon disulphide. The yield of ketones decreases on ascent of the series. Optimum conditions for carrying out the hydrogenation and the Friedel and Crafts' reaction were studied. Certain physical properties of the ketone and hydrocarbon series have been determined and are compared with the values given in the literature. The experimentally determined linear relationships between density and temperature and refractive index and temperature are shown for both ketones and hydrocarbons. The effects of increasing chain length, in both instances, on the physical properties are systematically recorded. The phenyl group influences predominantly many of the physical properties of these *n*-alkylated benzenes even when the chain is long. For identification purposes three derivatives (semicarbazone, oxime, 2 : 4-dinitrophenylhydrazone) were prepared for each ketone, and the melting points of the derivations are given.

It is probable that these ketones and hydrocarbons have not been obtained in such large quantities previously. The amounts of ketones synthesized range from 800 to 1500 grams and the corresponding hydrocarbons from 400 to 450 grams. Every precaution has been taken to obtain both compounds in a state of purity, and this is borne out by referring the ketones and hydrocarbons to the criterion for purity of molecular refractivity and of course carbon and hydrogen determination.

From a review of the methods for the preparation of alkylbenzenes it was decided to reduce the *n*-alkyl phenyl ketones, and thus a series of *n*-alkylated benzenes ranging from *n*-amyl- to *n*-tetradecyl was prepared. The ketones were obtained by Friedel–Crafts' reaction from benzene and the corresponding acid chlorides, the reduction being effected by two methods :—

(1) Clemmensen's method.

(2) Catalytic hydrogenation in alcoholic solution in the presence of palladium deposited on animal charcoal.

Experimental.

Synthesis of Ketones.

(a) *Preparation and Preliminary Treatment of the Reagents.*

1. Acid chlorides.

(i) Caproic acid chloride, $CH_3(CH_2)_4COCl$, was redistilled and the fraction of boiling-point range 152–155° C./760 mm. was collected.

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* Paper received 8th May, 1940.

(ii) Heptylic acid chloride, $CH_3(CH_2)_5COCl$, distilled *in vacuo*, had boiling point 65–66° C./15 mm.

(iii) Pelargonic acid chloride, $CH_3(CH_2)_7COCl$, distilled *in vacuo*, had boiling point 98–99° C./15 mm.

(iv) Lauric acid chloride, $CH_3(CH_2)_{10}COCl$, was prepared from lauric acid, $CH_3(CH_2)_{10}CO_2H$, of melting point 42–43° C. Fraction boiling between 134° and 137° C./11 mm. was used.

(v) Myristic acid chloride, $CH_3(CH_2)_{12}COCl$, prepared from myristic acid, $CH_3(CH_2)_{12}CO_2H$ of melting point 52–53° C. had boiling-point range 159–161° C./11 mm.

Method for the Preparation of the Last Two Acid Chlorides.—0·5 mole acid was put into a three-necked flask equipped with a mercury sealed stirrer, reflux condenser, and dropping funnel. The bath was heated until the acid was melted, 0·75 mole thionyl chloride (redistilled) was then introduced by means of a dropping funnel with gentle stirring. The flask was cooled by means of a water-bath to prevent too vigorous a reaction, but the temperature should be kept high enough to maintain the acid in liquid condition. Gentle suction was applied to the top of the condenser to remove the sulphur dioxide and hydrogen chloride evolved. The addition of thionyl chloride was finished in 1–1½ hours. After the thionyl chloride was added, the temperature of the bath was gradually raised to 60–65° C. in order to complete the reaction, and stirring was continued for a further 2 hours. The reaction product was then allowed to stand over-night and the acid chloride was purified by distilling twice *in vacuo*. Yield : 80–84 per cent. theoretical. Product, a colourless liquid.

2. Pure crystallizable benzene was dried over lime for several days and redistilled.
3. Carbon disulphide was dried over anhydrous calcium chloride.
4. Freshly prepared aluminium chloride was used.

(b) *Technique adopted for the Friedel–Crafts' Reaction.*

A 2-litre three-necked flask was fitted with a mercury sealed stirrer, condenser, and 500-c.c. dropping funnel. The flask was immersed in an ice-bath, the temperature not being allowed to rise above 10° C. To 1000 c.c. of carbon disulphide and 2 moles of crushed aluminium chloride a solution of the acid chloride (1·5 moles) in benzene (2·0 moles) was added drop by drop over a period of 1–1½ hours by means of the dropping funnel carrying a calcium chloride drying tube. The reacting mixture gradually darkens with evolution of hydrogen chloride, and suction was applied from the top of the condenser for its removal. Stirring is continued until hydrogen chloride ceased to be evolved. In most cases 30 hours were required. After completion of reaction the mixture is a homogeneous liquid with no solid aluminium chloride. The solution was poured slowly and without stirring into an equal volume of ice-water acidified with hydrochloric acid. The co-ordinated aluminium chloride compound hydrolyses slowly in the course of 1–2 hours. Stirring should be avoided, otherwise the temperature rises with rapid boiling of carbon disulphide and darkening of the product with formation of impurities. The carbon disulphide and aqueous layers were then separated by decantation from aluminium hydroxide, the former being steam distilled to recover the carbon disulphide. Before distillation it is necessary to add 10 c.c. of concentrated hydrochloric acid to prevent foaming. When carbon disulphide ceases to come over the alkyl aryl ketone is left as an oily layer. Generally the crude product is brown and solidifies on cooling at room temperature. After purification the carbon disulphide is utilized in subsequent preparation.

Discussion.—The optimum ratios of carbon disulphide and aluminium chloride per mole of acyl chloride have been investigated.

Should a smaller quantity of carbon disulphide be used in the above Friedel–Crafts' reaction, the co-ordinated compound hydrolyses too energetically even on pouring very slowly onto ice, with resulting formation of a dark-coloured product. The use of a greater quantity of carbon disulphide does not improve the colour of the ketone to any great extent; further, the loss of carbon disulphide during suction and distillation is also increased.

As indicated in the previous paper, molecular quantities of aluminium chloride and the acyl chloride should be used for the acylation of benzene. In practice 1·3 mols. of aluminium chloride were required—*i.e.*, the reaction is catalysed; should a greater quantity be used, the excess does not dissolve in the carbon disulphide and causes trouble in hydrolysis.

(a) *Purification of Alkyl Aryl Ketones.*—The unreacted acyl chloride in the reaction mixture is hydrolysed ultimately to free acid which contaminates the ketone; for removal, the crude ketone is treated with boiling sodium carbonate solution (10 per cent.) and the soap separated. Finally the ketone is washed several times with hot water. In the case of higher fatty acids, as pelargonic, lauric, and myristic acids, the soaps are comparatively difficult to dissolve in water and readily emulsify the ketone. The most suitable method of purification is to add to the emulsified ketone anhydrous calcium chloride with stirring and allow the mixture to stand in a warm place. The calcium chloride dehydrates and carries down the soap as a sediment. The ketone can then be separated by decantation.

(b) *Separation of Resinous and Colouring Substances from the Crude Ketone.*—Attempts were made to purify the crude ketone by crystallization from the usual solvents (alcohol, benzene, petroleum ether, etc.). The product thus obtained showed little improvement with regard to colour and melting point. This may be due to adsorption of a resinous substance by the precipitating crystals. This resinous substance is possibly a neutral sulphur compound formed by interaction between carbon disulphide and benzene in the presence of aluminium chloride. (Heinrich Jörg, *Ber.*, 1927, **60***B*, 1466.)

(c) *Purification by Distillation in Vacuo.*—The distillates are generally colourless, but in the case of *n*-octyl, *n*-undecyl, and *n*-tridecyl phenyl ketones the distillates are faintly coloured pink. The ketone can be obtained white on repeated crystallization from alcohol. Generally a 5 per cent. black resinous residuum remained in the distilling flask which residue contains sulphur. Freshly distilled ketones have an objectionable odour which can be removed by washing with dilute sodium hydroxide solution. To obtain the ketones in a pure state, recrystallization three or even four times from alcohol is necessary.

Yield of Pure Ketones Based on the Weight of Acid Chlorides employed.

Ketones.	% Theoretical.
n-Amyl phenyl ketone	80
n-Hexyl phenyl ketone	86
n-Octyl phenyl ketone	78
n-Undecyl phenyl ketone	71
n-Tridecyl phenyl ketone	69

n-Butyl phenyl ketone was purchased and purified by vacuum distillation.

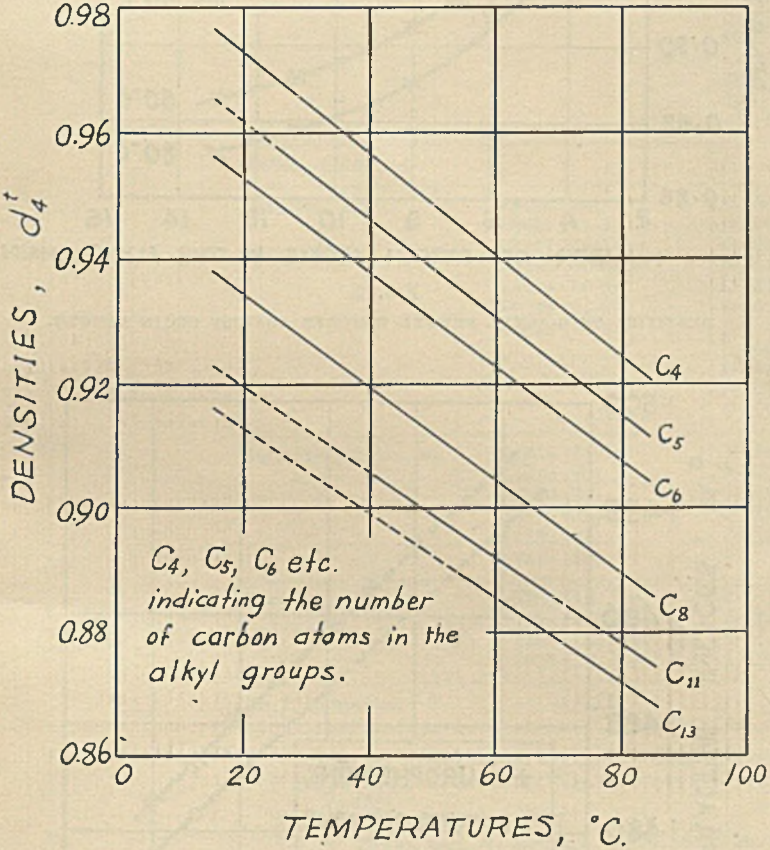

FIG. 1.

DENSITIES OF *n*-ALKYL PHENYL KETONES AGAINST TEMPERATURES.

Physical Properties of n-*Alkyl Phenyl Ketones.*

These are summarized in Table I.

A graph of the densities of the six ketones against temperatures is given in Fig. 1, the relationship being linear. The following data were interpolated or extrapolated.

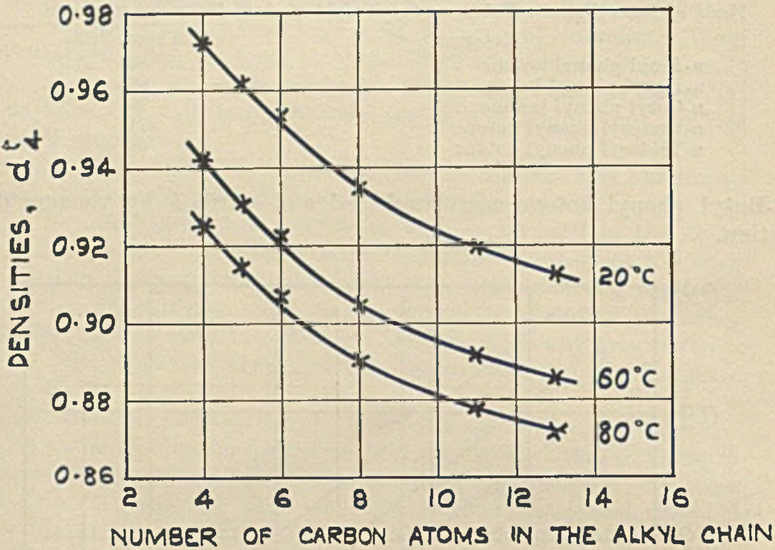

FIG. 2.

DENSITIES OF *n*-ALKYL PHENYL KETONES AGAINST CHAIN LENGTH.

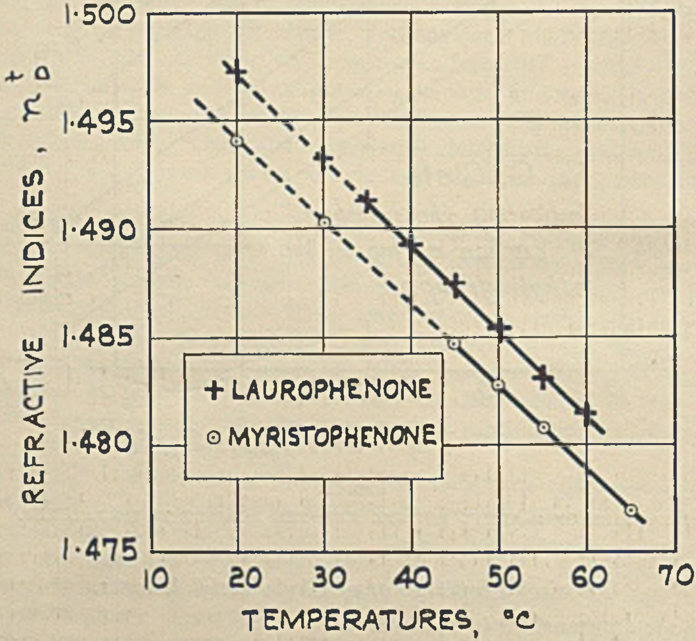

FIG. 3.

REFRACTIVE INDICES OF LAUROPHENONE AND MYRISTOPHENONE AGAINST TEMPERATURES.

TABLE I.

		n-Butyl phenyl ketone, $CH_3(CH_2)_2CH_2CO,C_6H_5$.		*n*-Amyl phenyl ketone, $CH_3(CH_2)_3CH_2CO,C_6H_5$.		*n*-Hexyl phenyl ketone, $CH_3(CH_2)_4CH_2CO,C_6H_5$.		*n*-Octyl phenyl ketone, $CH_3(CH_2)_6CH_2CO,C_6H_5$.		*n*-Undecyl phenyl ketone, $CH_3(CH_2)_9CH_2CO,C_6H_5$.		*n*-Tridecyl phenyl ketone, $CH_3(CH_2)_{11}CH_2CO,C_6H_5$.	
		Determined value.	Values in literature.	Determined value.	Values in literature.	Determined value.	Values in literature.	Determined value.	Values in literature.	Determined value.	Values in literature.	Determined value.	Values in literature.
Boiling point, ° C. (mm.)		116 (10)	248·5 [1] 144·5 (35) [3] 236–238 (720) [4] 242 [12] 131–133 (13) [13] 135–140 (25) [17]	111·5 (4)	132–134 (14) [8] 258–260 [14] 265·2 [16] 145–150 (19) [17] 122–124 (15) [18]	141 (9)	267 (740) [2] 155 (15) [5] 277 [10] 160 (30) [10] 273–275 [14]	166 (9)	298–300 [14]	193–194 (9)	201–202 (9) [9] 222–223 (21) [11] 174 (3) [19]	194–196 (4)	
Melting point, ° C.		−9		27	27 [8, 14] 24·7 [16]	17	17 [2]	14	46 [14]	44–45	47 [8, 14] 45 [9] 46 [11]	52–53	55·5 [14]
Densities, d_4^t		0·9731 (19·8) 0·9645 (30·1) 0·9566 (39·5) 0·9561 (40·6) 0·9479 (50·7) 0·9407 (59·7) 0·9393 (61·7) 0·9234 (81·0)	0·988 (d_{20}^{20}) [17]	0·9567 (26·8) 0·9527 (31·7) 0·9467 (39·5) 0·9450 (41·5) 0·9380 (50·3) 0·9308 (59·7) 0·9288 (61·9) 0·9148 (80·1)	0·95761 (25) [16] 0·95306 (30) [16] 0·981 (d_{20}^{20}) [17] 0·959 (18) [18]	0·9517 (21·2) 0·9393 (38·5) 0·9231 (59·7) 0·9076 (80·0)		0·9338 (20·5) 0·9328 (21·6) 0·9263 (30·2) 0·9197 (39·5) 0·9191 (40·0) 0·9109 (51·2) 0·9025 (62·4) 0·8890 (80·4)		0·9045 (41·5) 0·9012 (46·5) 0·8970 (53·0) 0·8933 (59·0) 0·8872 (66·8) 0·8848 (70·5) 0·8827 (73·0) 0·8762 (83·5)	0·87935 (78·5) [7] 0·8969 (52·2) [11]	0·8886 (55·0) 0·8848 (60·2) 0·8811 (66·2) 0·8765 (72·5) 0·8708 (81·2)	
Refractive indices, n_D^t		1·5148 (20) 1·5109 (30)	1·5152 (19) [3] 1·532 (20) [17]	1·5097 (20) 1·5050 (30)	1·538 (20) [17] 1·516 (18) [18] 1·5178 (13·1) [18]	1·5081 (20) 1·5037 (30·1)	1·505 (?) [10]	1·5019 (20) 1·4977 (29·8)		1·4910 (35) 1·4890 (40) 1·4870 (45) 1·4851 (50) 1·4831 (55) 1·4812 (60)	1·47001 (n_α78·5) [7] 1·4850 (52·4) [11] 1·4815 (n_α52·4) [11] 1·4943 (n_β52·4) [11]	1·4848 (45) 1·4828 (50) 1·4809 (55) 1·4789 (60) 1·4769 (65)	
Crystalline form		Liquid		Leaflets	Leaflets [8]	Flakes		Flakes	Crystalline [14]	Flakes	Crystalline mass [8, 9]	Needles	Crystalline [14]
Colour		Yellowish		Yellowish-white		White		White		White		White	
Semicarbazone	Melting point, ° C.	166	166 [3, 15] 157–157·5 [17]	132	132 [8, 15] 127–128 [17]	119	118–119 [10]	133·5	115 [14]	98		101	75 [14]
	Colour	White		White		White		White		White		White	
	Form	Needles	Needles [3]	Needles	Needles [8]	Needles	Needles [10]	Needles		Needles		Flakes	Flakes [14]
Oxime	Melting point, ° C.	55	52–52·5 [3] 51–52 [13] 52 [15]	52·5		54·5	55 [2]	53·5		64·5		69·5	
	Colour	White		White		White		White		White		White	
	Form	Needles	Needles [3, 13]	Needles		Needles		Short needles		Short needles		Short needles	
2 : 4-Dinitrophenylhydrazone	Melting point, ° C.	163·5		166		135	127–128 [10]	119·5		101–102		98–98·5	
	Colour	Orange		Orange		Orange		Orange		Yellowish-orange		Yellowish-orange	
	Form	Short needles		Fine needles		Flakes		Flakes		Powder		Powder	

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[1] Beilstein, 1925, VII, 328.

[2] Auger, *Bull. de la Soc. Chim. de France*, 1887, **47** (2), 50 (cf. Beilstein, 1925, VII, 337).

[3] Layraud, *Bull. de la Soc. Chim. de France*, 1906, **35** (3), 224–227 (cf. Beilstein, 1925, VII, 328).

[4] Perkin and Calman, *J. chem. Soc.* (*Lond.*), 1886, **49**, 161 (cf. Beilstein, 1925, VII, 328).

[5] Krafft, *Ber.*, 1886, **19**, 2987.

[6] Kipping and Russel, *J. chem. Soc.* (*Lond.*), 1895, **67**, 508 (cf. Heilbron, "Dictionary of Organic Compounds," 1936, II, 501).

[7] Eijkman, *Chem. Zentr.*, 1904, I, 1259 (cf. Heilbron, "Dictionary of Organic Compounds," 1936, II, 501).

[8] G. Schroeter, *Ber.*, 1907, **40**, 1589–1604 (cf. *C.A.*, 1907, **1**, 1989).

[9] A. Haller and E. Bauer, *Compt. rend.*, 1909, **149**, 5–10 (cf. *C.A.*, 1909, **3**, 2676).

[10] Colacicchi, *Atti della Reale Accad. dei Lincei* (*Rendiconti*), 1910, **19** (5), II, 503 (cf. Beilstein, 1931, VII, 180).

[11] von Auwers, *Ber.*, 1912, **45**, 2772 (cf. Beilstein, 1931, VII, 186).

[12] Mailhe, *Compt. rend.*, 1913, **157**, 220 (cf. Beilstein, 1931, VII, 173).

[13] Haller and Bauer, *Ann. de Chim. et de Phys.*, 1913, **28** (8), 410 (cf. Beilstein, 1931, VII, 173).

[14] P. Sabatier and A. Mailhe, *Compt. rend.*, 1914, **158**, 830–835 (cf. *C.A.*, 1914, **8**, 2673).

[15] M. Tiffeneau and J. Levy, *Compt. rend.*, 1926, **183**, 969–971 (cf. *C.A.*, 1927, **21**, 908).

[16] I. Simon, *Bull. soc. Chim. Belg.*, 1929, **38**, 47–70 (cf. *C.A.*, 1929, **23**, 4440).

[17] R. L. Shriner and T. A. Turner, *J. Amer. chem. Soc.*, 1930, **52**, 1267–1269 (cf. *C.A.*, 1930, **24**. 1856).

[18] R. Truchet, *Ann. Chim.*, 1931, **16**, 309–419 (cf. *C.A.*, 1932, **26**. 2176).

[19] I. G. Farbenindustrie A.-G. Fr.P. 801,499, 5th Aug., 1936 (cf. *C.A.*, 1937, **31**, 483).

[*To face p.* 518.

TABLE II.

	C_4H_9CO,C_6H_5.	$C_5H_{11}CO,C_6H_5$.	$C_6H_{13}CO,C_6H_5$.	$C_8H_{17}CO,C_6H_5$.	$C_{11}H_{23}CO,C_6H_5$.	$C_{13}H_{27}CO,C_6H_5$.
20° C.	0·9728	0·9619	0·9526	0·9342	0·9196	0·9124
60° C.	0·9403	0·9306	0·9228	0·9042	0·8918	0·8852
80° C.	0·9241	0·9149	0·9077	0·8894	0·8781	0·8716

A further graph comparing the effects of the number of carbon atoms in the alkyl group on the densities of ketones at 20°, 60°, and 80° C. is given in Fig. 2. The convex curvature shows that, on ascent of the homologous alkyl phenyl ketones, the difference of density between successive higher members decreases for the temperatures investigated.

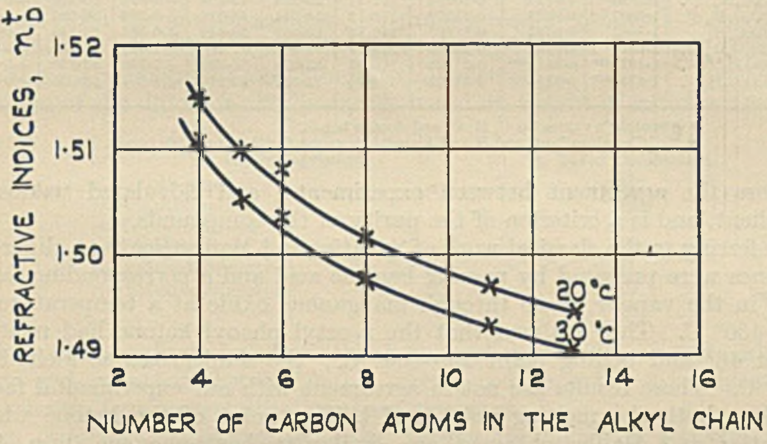


FIG. 4.

REFRACTIVE INDICES OF *n*-ALKYL PHENYL KETONES AGAINST CHAIN LENGTH.

The curves are roughly parallel, and there is no distinguishable differentiation between even and odd members in the chain length.

The variation of refractive indices with temperatures for laurophenone and myristophenone which is linear is shown in Fig. 3, from which the following data were extrapolated :—

	$C_{11}H_{23}CO,C_6H_5$.	$C_{13}H_{27}CO,C_6H_5$.
n_D^{20}	1·4970	1·4942
n_D^{30}	1·4931	1·4904

The effect of the number of carbon atoms in the alkyl chain on the refractive indices for the six ketones at 20° and 30° C. for D line is shown in Fig. 4. The curves are again convex towards the axis, and the difference of refractive index between homologues decreases on ascent of the series. It is to be noted that the refractive index for the hexyl (6) member does not lie on the curve; this difference (experimental value–interpolated value) lies outside the possible experimental error. This member also shows slight anomaly in relationship to other members with regard to its density.

It is interesting to compare the observed data for the molecular refractivity with calculated data using the Eisenlohr and Hulst values for atomic refractivities.

	Eisenlohr.	Hulst.
C	2·418	2·590
H	1·100	1·025
Double bond	1·733	—
Oxygen, ketonic . . .	2·211	—

Table III.

	n_D^{20}.	d_4^{20}.	$\frac{n^2-1}{n^2+2}\cdot\frac{l}{d}$.	Mol. weight.	Mol. refract., obs.	Mol. refract., calc.[a]	Obs.–Calc.[a]	Mol. refract., calc.[b]	Obs.–Calc.[b]
C_4H_9CO,C_6H_5 .	1·5148	0·9728	0·30988	162·11	50·234	49·408	+0·826	50·250	−0·016
$C_5H_{11}CO,C_6H_5$.	1·5097	0·9619	0·31078	176·12	54·734	54·026	+0·708	54·890	−0·156
$C_6H_{13}CO,C_6H_5$.	1·5081	0·9526	0·31297	190·14	59·507	58·644	+0·863	59·530	−0·023
$C_8H_{17}CO,C_6H_5$.	1·5019	0·9342	0·31585	218·17	68·908	67·880	+1·028	68·810	+0·098
$C_{11}H_{23}CO,C_6H_5$.	$1·4812^{46°}$	$0·8918^{46°}$	0·31923	260·21	83·070	81·734	+1·336	82·730	+0·340
$C_{13}H_{27}CO,C_6H_5$.	$1·4789^{46°}$	$0·8852^{46°}$	0·31302	288·25	92·327	90·970	+1·357	92·010	+0·317

[a] Eisenlohr's values for C, H, O, and double bonds.
[b] Hulst's values for C and H and Eisenlohr's values for O and double bonds.

Here the agreement between experimental and calculated values is excellent, and is a criterion of the purity of the compounds.

Referring to the classical work of Sabatier and Mailhe (*loc. cit.*), different ketones were prepared by passing benzoic acid and a corresponding fatty acid in the vapour phase through manganous oxide at a temperature of 400–450° C. They claimed that the *n*-octyl phenyl ketone had melting point 46° and boiling point 298–300° C.; the semicarbazone melted at 115° C. These results are not in agreement with our experimental facts, further, both the melting point and boiling point of the ketone which Sabatier and Mailhe obtained are similar to benzophenone (m.p. 48°, b.p. 305°), although benzophenone semicarbazone has m.p. 164°.

The carbon and hydrogen determinations are given below.

C_4H_9CO,C_6H_5	C, 81·50 (Theory 81·43) H, 8·69 (Theory 8·70)	$C_8H_{17}CO,C_6H_5$	C, 82·39 (Theory 82·51) H, 10·36 (Theory 10·16)
$C_5H_{11}CO,C_6H_5$	C, 81·61 (Theory 81·77) H, 9·32 (Theory 9·16)	$C_{11}H_{23}CO,C_6H_5$	C, 82·57 (Theory 83·01) H, 10·99 (Theory 10·84)
$C_6H_{13}CO,C_6H_5$	C, 81·98 (Theory 82·05) H, 9·76 (Theory 9·54)	$C_{13}H_{27}CO,C_6H_5$	C, 83·28 (Theory 83·26) H, 11·31 (Theory 11·19)

The authors are indebted to Mr. J. Khalili, B.Sc., for experimental work relating to the melting points, derivatives, and refractive indices of certain ketones and hydrocarbons.

Hydrogenation of Alkyl Aryl Ketones.

(1) *Reduction by Zinc Amalgam.*—Zinc foil cut into small strips was left for 1 hour with frequent shaking in contact with an equal weight of 5 per cent. aqueous mercuric chloride solution. The solution was then poured off and the zinc amalgam washed with fresh water.

Conical flasks fitted with ground joint reflux condensers were used. To the mixture of 100 c.c. concentrated hydrochloric acid 200 c.c. water and 150 grams of zinc amalgam; half mole of alkyl aryl ketone was added, and the whole boiled vigorously; 50 c.c. concentrate hydrochloric acid were added hourly until a total of 400 c.c. acid had been employed. Hydrogen is evolved only at the boiling point, and the reaction was allowed to proceed until the zinc was practically dissolved. The oily layer was separated, washed several times with hot water, dried over calcium chloride, and distilled *in vacuo*. Generally, yields of 65–75 per cent. of hydrocarbons, boiling within a range of 6° C., were obtained. The residues obtained on distillation were of high boiling point and of high viscosity. The oils partly crystallized on keeping. The constitution of these oily residua has not been investigated; they are probably pinacones the formation of which is favoured by this method of reduction.

The hydrocarbon was purified by heating for some hours with freshly cut sodium at 160° C. (approx.), then cooled and distilled *in vacuo* in contact with the molten sodium. A gummy residue (about 2–3 per cent.) remained in the flask. The distillate was redistilled *in vacuo* and the fraction, b.p. range not exceeding 1° C., collected.

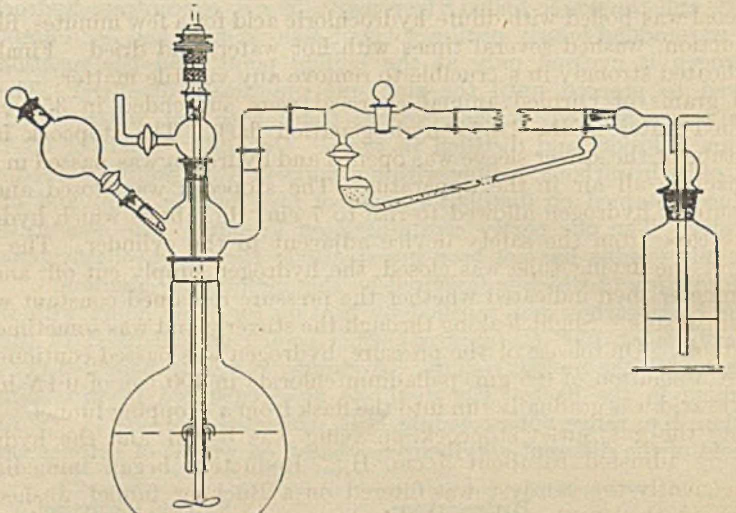
Yield of the different alkylbenzenes based on weight of ketones used :—

Hydrocarbons.	% Yield theoretical.
n-Amylbenzene	58
n-Hexylbenzene	56
n-Heptylbenzene	53
n-Nonylbenzene	51
n-Dodecylbenzene	41
n-Tetradecylbenzene	39

For efficient hydrogenation the ketone should be pure and sulphur free, and repeated distillations *in vacuo* and repeated crystallizations (frequently four recrystallizations) are necessary.

(2) *Catalytic Hydrogenation.*—The ketones in alcoholic solution were hydrogenated to corresponding alkylbenzenes under a pressure slightly above atmospheric in the presence of palladium deposited on animal charcoal. A stationary apparatus was designed for this purpose. All connections were fitted with ground joints, and rubber tubing was used only to connect the hydrogen cylinder to the safety device and the apparatus.

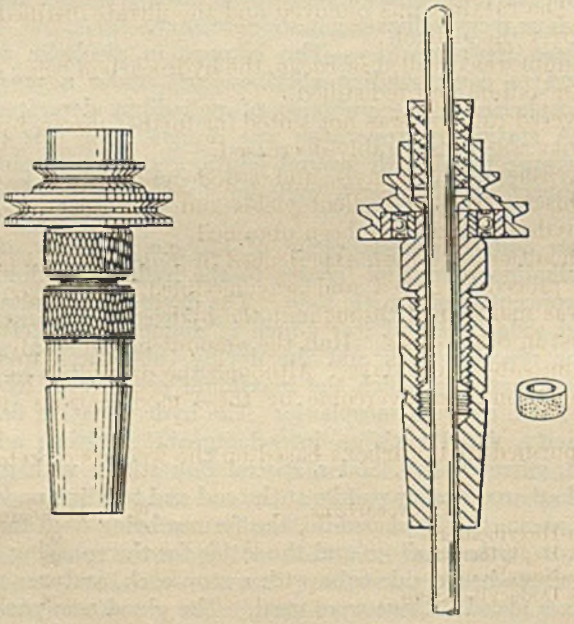
There were four Drechsel bottles of 125 c.c. capacity, of which two contained alkaline pyrogallol (nearer to the hydrogen cylinder), and the other two, concentrated caustic soda. The drying tube contained calcium chloride and soda lime and was $\frac{3}{4}$-inch in diameter and 2 feet in length. Between the reaction flask and the drying tube there was an inclined mercury manometer in which the maximum pressure of hydrogen could be read to 7 cm. above atmospheric. The hydrogenation flask was 1- or 2-litre capacity, fitted with an interchangeable multiple adapter, dropping funnel, stirrer sleeve, and a special link stirrer with gland fittings. The stirrer had an ordinary paddle at the end and two link paddles attached at 3 inches above the fixed paddle, the former being used for distribution of the catalyst in the medium and the latter for the spraying of the liquid. The stirrer sleeve had a side-tube with a stop-cock, and was used as a gas outlet. Brass gland fittings were used. The gland was packed with felt washer or asbestos string lubricated with soft wax, and incorporated an



THE HYDROGENATION APPARATUS.

aluminium pulley mounted by means of a ball race. The stirrer was locked to the pulley by means of cork.

Animal charcoal obtained commercially may contain traces of metallic sulphide which render palladium inactive. To remove this impurity, the



THE STIRRER GLAND.

charcoal was boiled with dilute hydrochloric acid for a few minutes, filtered by suction, washed several times with hot water, and dried. Finally, it was heated strongly in a crucible to remove any volatile matter.

10 grams of purified animal charcoal were suspended in 350 c.c. of distilled water in the 1-litre hydrogenation flask. The stopcock in the side tube of the stirrer sleeve was opened and hydrogen was passed in order to displace all air in the apparatus. The stopcock was closed and the pressure of hydrogen allowed to rise to 7 cm. Hg, above which hydrogen will escape from the safety device adjacent to the cylinder. The stopcock of the drying tube was closed, the hydrogen supply cut off, and the manometer then indicated whether the pressure remained constant within the apparatus. Slight leaking through the stirrer gland was sometimes unavoidable. On release of the pressure, hydrogen was passed continuously, whilst a solution of 0·5 gm. palladium chloride in 100 c.c. of 0·1*N*-hydrochloric acid was gradually run into the flask from a dropping funnel. After closing the gas outlet stopcock, spraying was begun, and the hydrogen pressure adjusted to about 5 cm. Hg. Reduction began immediately. Subsequently the catalyst was filtered on a Buchner funnel, washed free from acid, then twice with alcohol and once with ether; it was transferred to a desiccator, which was evacuated and kept in the dry condition until ready for use.

For hydrogenation, 50 grams of pure ketone dissolved in 800 c.c. absolute alcohol were introduced into a 2-litre flask, together with 5 gm. of the palladium deposited charcoal (equivalent to 0·25 gm. $PdCl_2$). The procedure of hydrogenation was similar to that for preparing the catalyst, the time required for completion of hydrogenation being generally from 20 to 30 hours. The catalyst was removed and the filtrate distilled on a water-bath to recover the alcohol.

The residuum was distilled *in vacuo*, the hydrocarbon being subsequently purified with sodium and redistilled.

The recovered catalyst was not suited for further use in hydrogenation, for its activity was considerably decreased.

n-Hexyl-, *n*-heptyl-, *n*-nonyl-, and *n*-dodecyl-benzenes have been prepared by this method. Excellent yields and very pure products for the first three hydrocarbons have been obtained.

Many difficulties have been experienced in hydrogenating laurophenone. The above procedure failed and was modified. Hydrogen pressure of 7 cm. Hg was maintained throughout the hydrogenation instead of 5 cm. Hg employed in other cases. Half the amount of the catalyst was added in portions on subsequent days. Although the difficulties in carrying out the hydrogenation were overcome by these modifications, yet the yield was low.

Yield of purified hydrocarbons based on the weights of ketones used :—

Hydrocarbons.	% Yield theoretical.
n-Hexylbenzene	95
n-Heptylbenzene	93
n-Nonylbenzene	92
n-Dodecylbenzene	76

Traces of sulphur compounds present in the mixture stop the hydrogenation completely. The ketones should be distilled *in vacuo* and recrystallized several times from alcohol (cf. Clemmensen's method) and tested for sulphur. No lubricant was used for glass joints and for gland fittings; a sulphur-free soft wax was used. To obtain efficient spraying, the level of the solution should be just below the top of the link paddles.

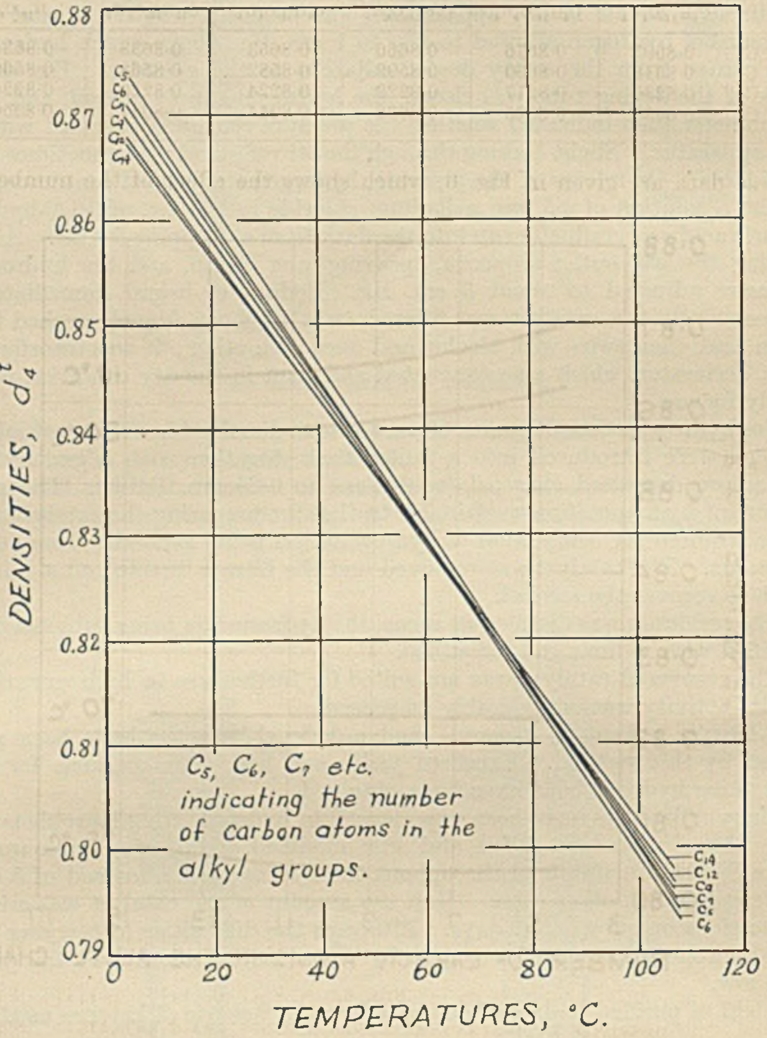


FIG. 5.

DENSITIES OF *n*-ALKYL BENZENES AGAINST TEMPERATURES.

Physical Properties of Hydrocarbons.

Various physical properties of the hydrocarbons so prepared have been determined, and are tabulated and compared with the values given in the literature (Table IV).

The densities of six *n*-alkylbenzenes plotted against temperatures is given in Fig. 5; change of density with temperature is linear of course. The following data were interpolated from this graph :—

TABLE V.

	C_5H_{11},C_6H_5.	C_6H_{13},C_6H_5.	C_7H_{15},C_6H_5.	C_9H_{19},C_6H_5.	$C_{12}H_{25},C_6H_5$.	$C_{14}H_{29},C_6H_5$.
10° C.	0·8695	0·8676	0·8666	0·8653	0·8638	0·8634
20° C.	0·8618	0·8600	0·8592	0·8582	0·8568	0·8566
70° C.	0·8230	0·8217	0·8222	0·8224	0·8220	0·8225
95° C.	0·8038	0·8025	0·8038	0·8044	0·8047	0·8056

These data are given in Fig. 6, which shows the effect of the number of carbon atoms in the alkyl chain on the densities at the four temperatures. The longer the chain attached to the benzene nucleus the lower is the density at lower temperatures (below 50° C.). This effect diminishes with increase of the chain length. For higher temperatures (above 70° C.), however, increase of chain length causes very little change in density, and at 70° C. the six hydrocarbons have practically the same density.

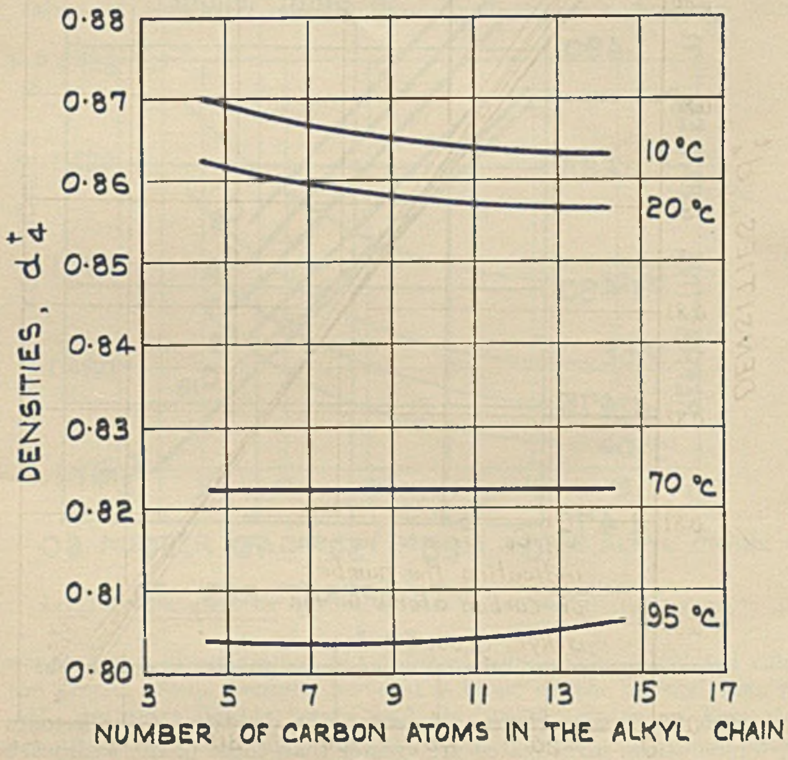


FIG. 6.

DENSITIES OF *n*-ALKYL BENZENES AGAINST CHAIN LENGTH.

At still higher temperatures (above 90° C.) increase of chain length, on the contrary, causes increase in density.

Comparison of Fig. 2 (ketones) and Fig. 6 (hydrocarbons) (cf. also Tables II and V) for densities and chain-length relationships shows how widely the two homologous series differ. Fig. 2 shows that density with increase of number of carbon atoms decreases rapidly, which is not the case with the hydrocarbons. Moreover, the densities of the ketones for all temperatures investigated are greater than those of the hydrocarbons.

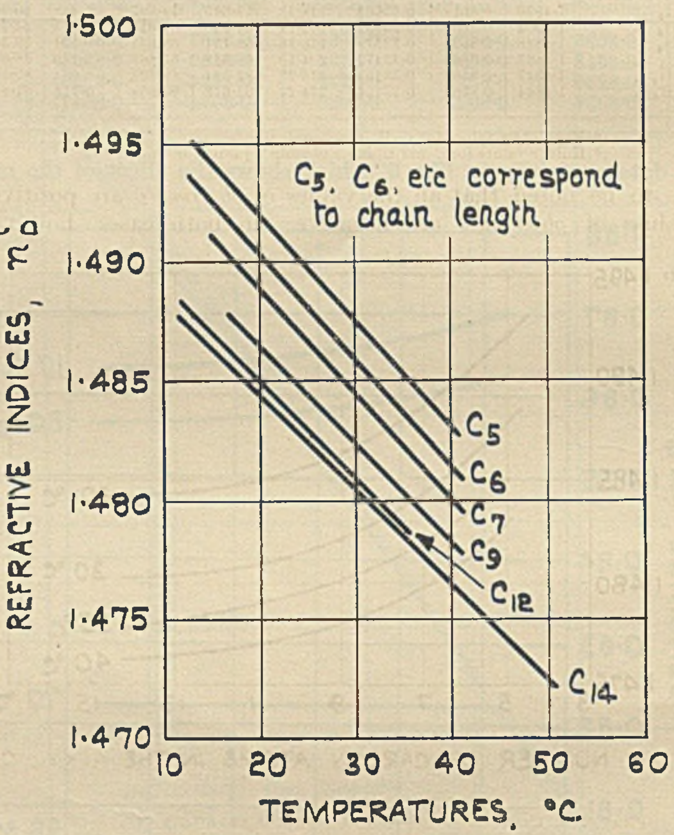


Fig. 7.

REFRACTIVE INDICES OF *n*-ALKYL BENZENES AGAINST TEMPERATURE.

The variation of refractive indices at different temperatures is shown as Fig. 7, the relationship also being linear. The effect of the number of carbon atoms in the alkyl chain on the refractive index for D line at 20°, 30°, 35°, and 40° C. (given in Table IV) is plotted in Fig. 8. The decrease in refractive index caused by the increasing chain length diminishes on ascent of the series. The curves are practically parallel, and whatever stereochemical structure these alkylbenzenes possess there is no apparent differentiation into even and odd members. In Table VI the experimentally determined and calculated values of the molecular refractivity are compared.

TABLE VI.

	n_D^{20}.	d_4^{20}.	$\frac{n^2-1}{n^2+2}\cdot\frac{l}{d}$.	Mol. weight.	Mol. refract., obs.	Mol. refract., calc.[a]	Obs.–Calc.[a]	Mol. refract., calc.[b]	Obs.–Calc.[b]
C_5H_{11},C_6H_5 . .	1·4920	0·8618	0·33663	148·13	49·865	49·397	+0·468	50·089	−0·224
C_6H_{13},C_6H_5 . .	1·4902	0·8600	0·33632	162·14	54·530	54·015	+0·515	54·729	−0·199
C_7H_{15},C_6H_5 . .	1·4888	0·8592	0·33579	176·16	59·154	58·633	+0·521	59·369	−0·215
C_9H_{19},C_6H_5 . .	1·4863	0·8582	0·33472	204·19	68·348	67·869	+0·479	68·649	−0·301
$C_{12}H_{25},C_6H_5$ . .	1·4847	0·8568	0·33434	246·23	82·324	81·723	+0·601	82·569	−0·245
$C_{14}H_{29},C_6H_5$ . .	1·4844	0·8566	0·33424	274·27	91·672	90·959	+0·713	91·849	−0·177

[a] Eisenlohr's values for C, H, and double bonds.
[b] Hulst's values for C and H and Eisenlohr's values for double bonds.

It is to be noted that all the values of *observed-a* are positive and all the values of *observed-b* are negative; in both cases, however, these differences range about a mean but different value. The calculated value for the phenyl group (benzene nucleus) is based on the refractivities for 6C, 5H, and three double bonds, and also on the statement that ring closure affects the molecular refractivity but slightly. It would seem, from a consideration of the sign of the differences obtained, that a better value for the refractivity of the phenyl group could be obtained from an experimentally determined average value for this group—viz., from a large number of refractive indices of aromatic compounds. Still the differences are only a small percentage of the molecular refractivity in each case. The using of Hulst's values for carbon and hydrogen gives results in better agreement with the observed values. The Abbé Refractometer at constant temperatures was used in these determinations.

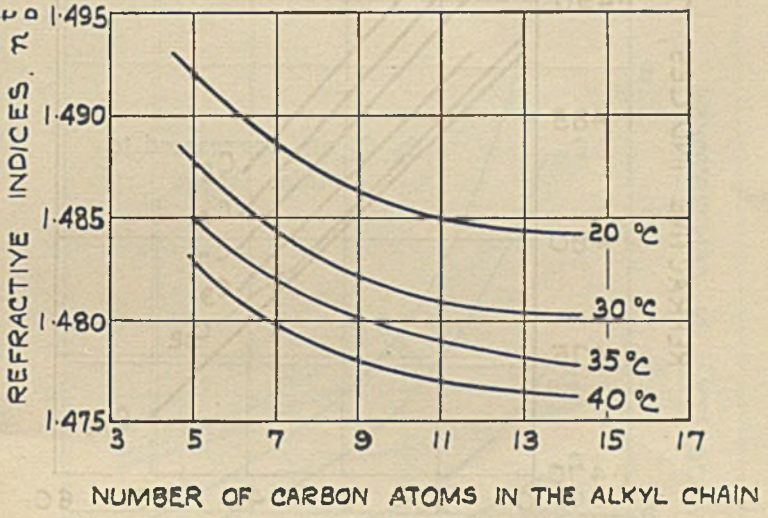


FIG. 8.

REFRACTIVE INDICES OF *n*-ALKYL BENZENES AGAINST CHAIN LENGTH.

Kurtz and Ward (*J. Frank. Inst.*, 1936, 222, 563) calculate the refractive intercept (the intercept on the ordinate axis of a plot of n_D^{20} against d_4^{20}) of the aromatics as 1·0627 and of the paraffins as 1·0461. They propose the refractive intercept, $b = n - \frac{d}{2}$. The values of b in the present investigation are :—

C_5H_{11},C_6H_5	1·0611	C_9H_{19},C_6H_5	1·0572
C_6H_{13},C_6H_5	1·0602	$C_{12}H_{25},C_6H_5$	1·0563
C_7H_{15},C_6H_5	1·0592	$C_{14}H_{29},C_6H_5$	1·0561

It is clear, with regard to this physical property, that the value regularly and consistently diminishes as would be expected, but the phenyl group predominantly influences the value even when the chain is long (C_{14}). The value never approaches that for paraffins.

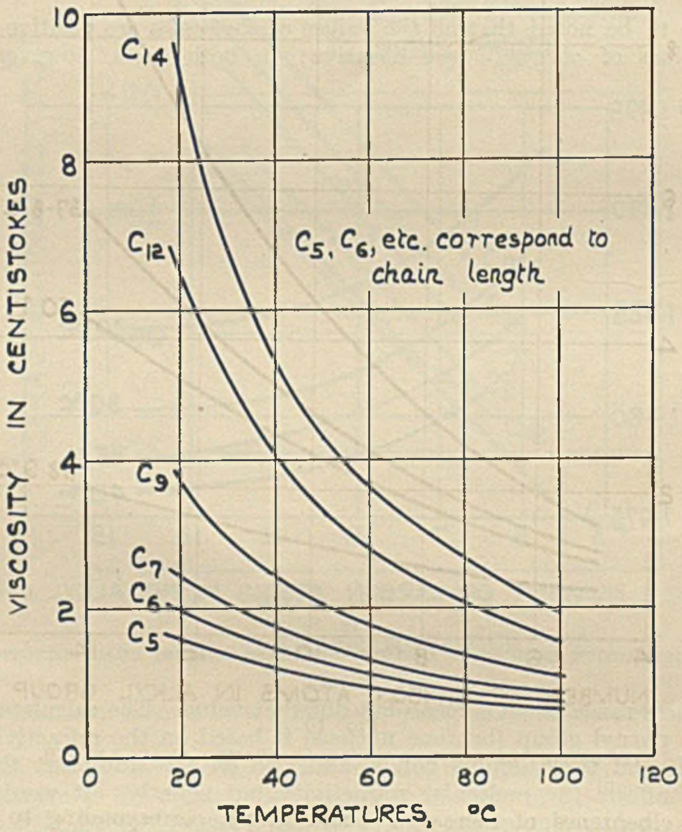


FIG. 9.

VISCOSITIES OF *n*-ALKYL BENZENES AGAINST TEMPERATURES.

Comparisons of Fig. 4 (ketones) and Fig. 8 (hydrocarbons) (cf. also Tables I and IV) shows the influence in the visible region of the absorption band of the carbonyl group in raising the refractive index, the molecular refractivity being, as would be expected, almost identical for ketones and hydrocarbons (cf. Tables III and VI).

The viscosities in centistokes of the hydrocarbons plotted against temperatures are given in Table IV and Fig. 9. The diagram obtained is typical of a series of normal homologues—ascent of the series causing increase of viscosity. The coefficient of change of viscosity with temperature increases as the series is ascended. The graph indicates the viscosities of the alkylbenzenes of increasing chain length corresponding to carbon atoms 5, 6, 7, 9, 12, and 14, but it does not indicate viscosities of successive members. This latter point for four definite temperatures—viz. 20, 37·8, 50, and 98·9° C.—is given in Fig. 10, and it is interesting to note the great effect of chain length in change of viscosity with respect to temperature. For amylbenzene the change of viscosity between 20° and 98·9° C. (left-hand side of diagram) is not more than 1 centistoke, whilst for tetradecylbenzene (right-hand side of diagram) it is more than 7 centistokes. Further, the coefficient of change of viscosity with chain

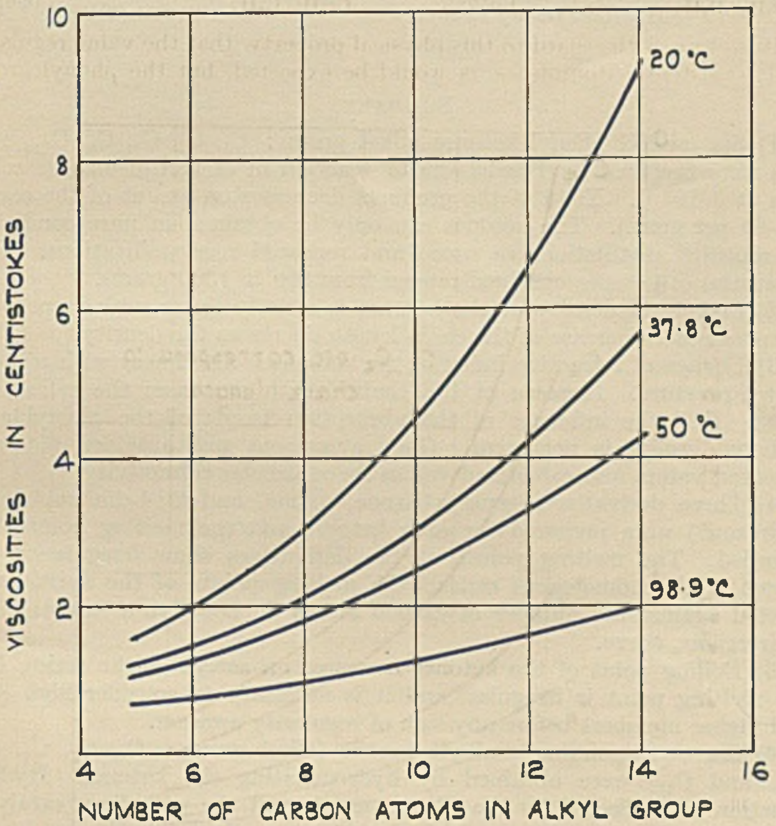


FIG. 10.

VISCOSITIES OF *n*-ALKYL BENZENES AGAINST CHAIN LENGTH.

length is smaller at the higher temperatures and increases with decreasing temperature.

The carbon and hydrogen determinations are as follows :—

C_5H_{11},C_6H_5	C, 89·09 (Theory 89·11) H, 10·86 (Theory 10·89)	C_9H_{19},C_6H_5	C, 88·05 (Theory 88·15) H, 11·78 (Theory 11·85)
C_6H_{13},C_6H_5	C, 88·91 (Theory 88·81) H, 11·30 (Theory 11·19)	$C_{12}H_{25},C_6H_5$	C, 87·70 (Theory 87·72) H, 12·37 (Theory 12·28)
C_7H_{15},C_6H_5	C, 88·54 (Theory 88·55) H, 11·58 (Theory 11·45)	$C_{14}H_{29},C_6H_5$	C. 87·62 (Theory 87·50) H, 12·50 (Theory 12·50)

SUMMARY.

(1) Six *n*-alkyl phenyl ketones (alkyl group : C_4, C_5, C_6, C_8, C_{11}, and C_{13}) were prepared by Friedel–Crafts' reaction in carbon disulphide solution at 5–10° C. Yield of the products decreases on ascent of the series (80–69 per cent.). The ketones can only be obtained in pure condition by repeated distillations *in vacuo* and repeated recrystallizations. The quantities of ketones obtained ranged from 800 to 1500 grams.

(2) Change of density of the ketones is strictly linear with respect to temperature. Increase of the chain length decreases the density.

(3) Change of refractive index of the ketones is also linear with respect to temperature. Increase of the chain length decreases the refractive index. Still the influence of the absorption bands of the phenyl and carbonyl groups is persistent. Good agreement was obtained between observed values and calculated values for molecular refractivity.

(4) Three derivatives (semicarbazone, oxime, and 2 : 4-dinitrophenylhydrazone) were prepared for each ketone, and the melting points are recorded. The melting points of the derivatives show irregularity on ascent of the homologous series; the melting points of the derivatives plotted against the number of carbon atoms do not give a smooth, but an irregular, curve.

(5) Boiling point of the ketones increases on ascent of the series, but the melting point is irregular, and it is necessary to consider high (C_8) and higher members before any sign of regularity appears.

(6) Six corresponding *n*-alkylbenzenes (alkyl group : C_5, C_6, C_7, C_9, C_{12}, and C_{14}) were obtained by hydrogenating the ketones. Hydrogenation was effected by the Clemmensen's and the palladium catalytic methods. Clemmensen's method gives a poor yield (39–58 per cent.). Excellent yields have been obtained by the catalytic method (92–95 per cent.). The ketones used should be pure and sulphur free in both cases.

(7) The experimentally determined linear relationship between density and temperature for all the six hydrocarbons is given. Increase of chain length decreases the density for temperatures below 50° C.; the effect diminishes when the temperature is increased and at 70° C. the hydrocarbons have practically the same density. At still higher temperatures (above 90° C.) the reverse is the case.

(8) Change of the refractive index of the hydrocarbons is also linear with respect to temperature. Increase of chain length causes a decrease in refractive index. Good agreement between observed and calculated

values for molecular refractivity was obtained, especially when Hulst's values of atomic refractivities for carbon and hydrogen were used.

(9) Both boiling points and melting points increase on ascent of the series.

(10) Increase of chain length increases the viscosity of the *n*-alkylbenzenes. This increase is more enhanced for the higher members than for the lower, and for the lower temperatures than for the higher.

(11) Critical solution temperature in aniline increases as the chain length increases.

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OBITUARY.

SIR ROBERT ABBOTT HADFIELD.

Sir Robert Abbott Hadfield, Bart., died at his home in Kingston, Surrey, on 30th September. He was an Honorary Member of the Institute, having been elected in 1929 in recognition of his distinguished services to metallurgy, and in particular for his discovery and development of the special alloy steels which find extensive application in petroleum technology.

Sir Robert, who was chairman and managing director of Messrs. Hadfields, Ltd., Sheffield, and occupied a prominent position in industrial circles for many years, was born in Sheffield on 28th November, 1858. He entered the works of his father, a small steel foundry at Attercliffe, and pursued a course of practical training in metallurgy and engineering. Early in life he was attracted by the possibilities of alloy steels, and at the age of 22 had not only produced manganese steel, but had studied its heat treatment. On the death of his father in 1888 Sir Robert took over the management of the Attercliffe works. The company rapidly expanded, and new works were commenced in 1897 at Tinsley, Sheffield. Sir Robert continued as chairman of the company throughout his life, maintaining a close personal interest in all its activities until a year or two before his death.

In the field of metallurgy Sir Robert will chiefly be remembered for his researches on manganese steel; on low-hysteresis silicon steel for transformers and electrical plant; and for heat-resisting steels of various types. In the course of his researches he gathered round him a team of metallurgists, chemists and engineers who, under the inspiration of his leadership, proved distinguished and energetic co-workers. In collaboration with Dr. S. A. Main, Sir Robert presented a paper on " The Use of Steel in the Oil Industry with a Special Reference to Heat-Resisting Steels " to the Second International Drilling Congress in Paris, 1929.*

During his long career Sir Robert presented over two hundred contributions to the Proceedings of learned and technical societies and institutions in this country and abroad. His earliest papers were the classical researches on iron–manganese and iron–silicon alloys, presented to the Institution of Civil Engineers and the Iron & Steel Institute in 1888 and 1889. Subsequent papers dealt with alloys of iron with chromium, aluminium, tungsten and copper, with hardness and impact testing. In later years he devoted considerable attention to the history of metals, and it was largely owing to his patient historical research that the metallurgical work of Faraday was made known to the world at the time of the Faraday Centenary in 1931.

Sir Robert was knighted in 1908 and created a baronet in 1917. He was elected F.R.S. in 1907, and received the degrees of the Universities of Oxford, Sheffield, and Leeds. He was awarded the Albert Medal of the Royal Society of Arts in 1935. Decorations of the highest order were conferred upon him by governments and scientific bodies all over the world—in the United States, France, Norway, Sweden, Italy, Japan, and U.S.S.R.

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* *Journ. Inst. Pet. Tech.* 1929, 15, 611–633.

ABSTRACTS.

AUTHOR INDEX.

The numbers refer to the Abstract Number.

The original papers referred to in the abstracts marked with an asterisk may be borrowed by Members from the Institute Library.

Geology and Development.

1432.* Recent Developments in South Mid-Continent. L. W. MacNaughton. *Bull. Amer. Assoc. Petrol. Geol.*, 1940, **24**, 1025–1032.—The South Mid-Continent occupies more than 250,000 sq. miles, and includes Arkansas, south-eastern New Mexico, and all of Mississippi, Louisiana, and Texas, except the Gulf Coast.

The more important developments were in Mississippi, New Mexico, and particularly in West Texas. By major extensions to old fields, presence of the deeper Permian " pay " in the North Cowden field, and the discovery of more production from the Ordovician, West Texas was much the most important district in the South Mid-Continent area.

A period of decreasing reserves, however, ensued in 1939, since production exceeded additions to reserves represented by new discoveries. More than 500 million brl. of crude oil came from the South Mid-Continent area in 1939; new fields replaced less than one-third of this production. G. S. S.

1433.* Developments in West Texas and South-Eastern New Mexico during 1939. D. M. Secor, W. C. Fritz, and W. W. West. *Bull. Amer. Assoc. Petrol. Geol.*, 1940, **24**, 1033–1043.—The results of drilling in 1939 led to important extensions to, and linking of, productive fields. Nine new pools were discovered in West Texas; two of these produced from the Ordovician, two from the Pennsylvanian, and five from the Permian. In south-eastern New Mexico, of 648 wells drilled, 551 were completed as oil wells and twelve as gas wells. Five new pools were discovered, all producing from Permian rocks.

More than 100 million brl. were obtained from the two districts in 1939, and there are indications that reserves may be expected to be materially greater than hitherto expected. G. S. S.

1434.* Developments in North and West-Central Texas, 1939. K. A. Mygdal. *Bull. Amer. Assoc. Petrol. Geol.*, 1940, **24**, 1044–1061.—At least 90% of the total production of this area to date has come from the major positive structural features, the Electra, Muenster, and Bend arches.

It is likely that important oilfields will continue to be discovered along the crests of these features, but increased attention is being given to the bordering basins, especially the Fort Worth syncline. From this huge depression, five new fields were found in 1939, representing as a group the most important of the new discoveries for the year.

New discoveries, important extensions, and new pay zones are listed in tabular form. Discussion is limited to the significant geological and economic deductions which can be drawn from these discoveries and from the important dry holes.

Drilling was active through 1939, and was increasing at its close. The total number of wells drilled in the North Texas district declined, though there was a moderate increase in the west-central district. No important change occurred in the total production figures for either district; drilling and production figures are furnished. G. S. S.

1435.* Developments in East Texas during 1939. H. J. McLellan and E. A. Wendlandt. *Bull. Amer. Assoc. Petrol. Geol.*, 1940, **24**, 1062–1068.—During 1939 less drilling was carried out in East Texas than at any time since the discovery of the East Texas field; one small oilfield and one small oil- and gas-field were discovered during the year. From new depths in three old gas-fields, gas and distillate production was obtained.

Few important exploratory tests were drilled, and in most fields only routine development occurred. On 1st January, 1940, there were forty-five active operations, thirty-six of which were in proved areas and nine were exploratory tests.

Brief reference is made to the new fields and producing areas, and to the field developments and more important exploratory tests. G. S. S.

1436.* Developments and Status of Oil Reserves in South Texas, 1939. L. B. Herring. *Bull. Amer. Assoc. Petrol. Geol.*, 1940, **24**, 1069–1078.—The South Texas area is divided into three districts, San Antonio, Laredo, and Corpus Christi. The former includes all pre-Eocene production, the Laredo all Eocene production, and the Corpus Christi district all post-Eocene production. They also have distinct types of crudes and in most instances distinct types of accumulation.

Thirty new pools were added during 1939, but no major discovery is known to have resulted; fifteen were gas wells and fifteen were oil wells. Data on these pools are supplied in tabular form.

It is estimated that 79 million brl. of crude oil and condensate were discovered in 1939. Oil reserves total 1260 million brl., which, based on the previous year's production, are equivalent of 15·5 years' supply. Present reserves are 300% more than on 1st January, 1934. G. S. S.

1437.* Review of Developments in 1939, Gulf Coast of Upper Texas and Louisiana. O. L. Brace. *Bull. Amer. Assoc. Petrol. Geol.*, 1940, **24,** 1079–1091.—Developments in this area during 1939 have shown little important change from those of previous years. Discoveries have slightly decreased in number, a total of thirteen for Louisiana and ten for Texas being recorded; the quality of discovery has, moreover, greatly depreciated. It is probable that no more than three or four of these fields will ultimately reach major importance.

In detailed descriptions of the discoveries, it is pointed out that a large number of the new fields are of the low relief, faulted type; these have subsequently become an increasingly important source of new reserves.

A notable feature of the year has been the development of important oil-bearing horizons on the flanks of old producing fields. G. S. S.

1438.* Developments in Southern Arkansas and Northern Louisiana during 1939. W. B. Weeks and J. Purzer. *Bull. Amer. Assoc. Petrol. Geol.*, 1940, **24,** 1092–1099.—Production for Southern Arkansas and Northern Louisiana during 1939 was only slightly less than that for the previous year, viz.: *1938*, 46,900,165 brl., *1939*, 46,608,465 brl.

In Southern Arkansas the main object of prospecting centred on the Smackover limestone. In Northern Louisiana the lower Glen Rose and Cotton Valley formations gave rise to increased activity. An analysis of wild-cat wells showing the deepest formations tested is given in tabular form.

Other tabular matter furnished indicates dry holes drilled during 1939 which are considered important in having assisted in establishing the limits of the Smackover limestone producing trend, the limits of possible producing area within the Cotton Valley section; or have provided tectonic or stratigraphic data not previously available. G. S. S.

1439.* Developments in Rocky Mountain Region in 1939. C. E. Dobbin. *Bull. Amer. Assoc. Petrol. Geol.*, 1940, **24,** 1100–1111.—This region in 1939 had no relatively important discoveries in unproved areas. In certain old fields, however, several discoveries were made, including: (1) a widespread and rather prolific oil zone in the Minnelusa sandstone (Pennsylvanian) in the Lance Creek field, Wyoming; (2) the development of deeper oil zones in the Tensleep sandstone (Pennsylvanian) in the Wertz field, Wyoming; and (3) the finding of oil in the second sand of the Dakota group (Up. Cretaceous) in the Fort Collins field, Colorado.

Important extensions were made to the Cut Bank and North Cut Bank fields, Montana, the Lance Creek field, Wyoming, and the Wilson Creek field, Colorado. At the north end of the main oil-producing part of the Cut Bank field and down dip slightly from three neighbouring oil wells, the Sunburst Sand yielded the largest gas well yet found in Montana. This had an estimated initial production of 80 million cu. ft. per day. G. S. S.

1440.* Significant Developments in California, 1939. E. R. Atwill. *Bull. Amer. Assoc. Petrol. Geol.*, 1940, **24,** 1112–1125.—Four new oilfields were discovered in California during 1939. They are all situated in the central part of the San Joaquin Valley: North-East Coalinga, Paloma, Strand, and South-East Mt. View. To date, one only, North-East Coalinga, has been definitely established as a major field.

The North-East Coalinga field produces from 200 ft. of continuous Gatchell oil sand

(Middle Eocene) at a total depth of 8237 ft. The initial production rate was 4225 brl. per day. Structurally, the field is a long south-east plunging fold (Coalinga anticline), having a definite bow on its east flank. The field will probably include 1200 acres and have an ultimate production of 100 million brl. of oil.

Paloma ranks as second in importance of the new fields, and appears likely to become one of major proportions. Structurally, the field is probably related to Coles Levee (Stevens zone, Upper Miocene). Initial production was 2280 brl. per day.

The Strand also produces from the upper part of the Stevens zone, and gave an initial production of 1306 brl. per day. The structure is a small flat anticline, approximately 300 acres in extent. Production may ultimately total 10 million brl. from the sands known at present.

South-East Mt. View gets its production from a non-marine series of sand in the Middle Pliocene. The initial yield was 3800 brl. per day. Probably less than 200 acres, however, will be included in the field, and its ultimate production may not exceed 2 million brl. of oil.

Extensions of known fields include Coles Levee, Greeley, Montebello, Dominguez, and Rosecrans.

Wild-cat drilling declined. Moreover, many of the wells drilled were located on doubtful geological prospects, indicating that the possibilities of new discoveries are remote. G. S. S.

1441. Gulf Coast Looms Larger in National Oil Picture. Anon. *Oil Wkly*, 23.9.40, 99 (3), 39.—The Gulf Coast area holds one-fifth of the present known producible crude oil reserves of the U.S.A. At present it is giving 11% of the country's crude. The rate of discovery of new fields shows no signs of the area being exhausted, and the reserves were estimated to be 3,873,085,099 brl. on 1st July, 1940.

Tables show the reserves for this area as compared with those of other States, and the reserves, annual production, wells drilled, and new fields found yearly since 1935. The number of new fields and new sands below 10,000 ft. are listed since 1936. Certain fields and counties are shown to be outstanding in reserves. Deep drilling and geophysical activity are discussed.

Drilling, production, and reserve data are given by fields and counties, and the production is given by fields by years. G. D. H.

1442. Gulf Coast Development Trend is Away from Salt Domes. J. M. Vetter, *Oil Wkly*, 23.9.40, 99 (3), 39, 47.—Within the past few years the search for accumulation on partly explored salt domes has continued, but this phase of exploration has been secondary to the development of a new type of structure which has no apparent relation to salt domes. Chronologically Gulf Coast prospecting falls into three stages : during the first the piercement type of salt dome was discovered ; in the second there was the deep-seated or non-piercement type; and in the third the non-salt dome structures with closure of the downthrown side of faults. There are, however, fields which do not conform strictly to any of these types, or are hybrids.

Before the application of geophysics in 1924, location of piercement type of domes was difficult, but geophysics soon added thirty discoveries to the thirty odd previously discovered. Since 1928 attention has been paid to the non-piercement type, and these fields have generally proved more prolific and larger in areal extent than the piercement type of domes. There are over a hundred of this type. In 1933 the third phase opened, although the structural significance was not at first appreciated fully. These structures have relatively little structural relief and are closed against faults, as at Amelia, Tepetate, and Joe's Lake. Structurally they are far less complicated than those caused directly by salt intrusion, but the lack of pronounced uplift increases the difficulty of discovery. G. D. H.

1443. Gulf Coast Oilfields, Salt Domes, and Prospects. Anon. *Oil Wkly*, 23.9.40, 99 (3), 83–179.—Brief notes are given for the fields, which are arranged alphabetically for each county, the latter being themselves in alphabetical order for each State. These notes deal with the means of discovery, structure, producing formations, sand thickness, extent of development, daily production, estimated ultimate recovery, estimated remaining reserve, oil gravity and outlet, the deepest well, number of wells running on 1st September, 1940, and the principal leaseholders. G. D. H.

1444. Mississippi Entering Settled Exploration Stage. G. Weber. *Oil Gas J.*, 8.8.40, **39** (13), 22.—The Upper Cretaceous play extending through Central Mississippi has revealed the existence of blanket sand bodies over a wide area in the Selma Chalk, Eutaw, and Tuscaloosa. Few outstanding structures like Tinsley or Jackson have been found, but less pronounced structures revealed by geophysical shooting have been proved productive by the discovery at Pickens. Several such prospects have not yet been satisfactorily tested.

The leasing wave has extended east from Mississippi into South and West Alabama, and may extend into Florida and Georgia. The Warrior or North-West Alabama basin, which extends into North-East Mississippi, has producing possibilities in the Palæozoic. Outcrops show asphalt. Gas shows have been found in the upper beds in Southern Alabama.

Tinsley has three producing horizons and a recoverable reserve of 24,000,000 brl. is estimated, and there are possibilities of further extensions. The daily potential is estimated at 37,500 brl., but production averages 8000 brl./day. The flowing life of the field will probably be short. The main pay is the Woodruff sand at the base of the Selma Chalk; in the Eutaw is the Stevens sand, and between the two is the Perry sand.

The present Pickens production is believed to be on the north-west flank of the structure. G. D. H.

1445. Two Recent Discoveries may Signal Michigan's Comeback. W. V. Howard. *Oil Gas J.*, 15.8.40, **39** (14), 31.—The Michigan basin has axes of warping running generally north-west–south-east with some crossfolds giving highs, many of which are productive. Three Devonian limestones, the Traverse, Dundee, and Monroe, give most of the oil. The first gives its main production in the south-east. The chief oil development is in a strip about 50 ml. wide, running almost at right angles to the structural trends.

Discoveries have been made this year in N.E., S.E., N.E. section 22-19-3e in Arenac County, and S.½, S.W., S.W. section 15-19-3w in Gladwin County. The first is on a trend running through Adams pool, 1 ml. to the south-east, and the second is on a trend traversing the north end of the Buckeye field, about 12 ml. to the south-east.

Since 1924 Michigan has given about 191,869,000 brl. of oil, and 110,663,000 brl. have been obtained since the beginning of 1937. The main production is from the Allegan–Van Buren district in the south-west, the Walker field near Grand Rapids, the Mount Pleasant district in the centre of the state, and the Freeman–Redding or Temple field in Clare County. G. D. H.

Geophysics.

1446. Advancements Continue to be Made in Geophysical Field. Anon. *Oil Wkly*, 23.9.40, **99** (3), 50.—In the seismograph field there has been instrumental development, but the outstanding advances are due to a better appreciation of the geological problem in hand—*i.e.*, to map low dip structures and to solve fault problems. There has been greater attention to field and calculation technique. Good reflections are being obtained from depths out of reach of the drill. On the Gulf Coast there are excellent reflections below 15,000 ft., and in California, with reflections down to 40,000 ft., mapping at 20,000–26,000 ft. is common. Effective receipt of these deep reflections requires a different choice of frequency discrimination from that in ordinary use. Automatic volume control is an important factor. A more daring interpretation of data has yielded several fields on the Gulf Coast in old producing districts.

Gravity meters are in extensive use for reconnaissance. A good average for current work is one to three stations per square mile, and it is common to cover thirty stations per day, at 4$ to 9$ per station. The instruments have an accuracy of ± 0·02 milligal, although most surveys are made to only 0·05 milligal. Gravity meters have been built for use under water. The torsion balance is still used for detailed work, and is valuable on prospects which are not resolvable seismically.

Soil analyses have been developed more and search for petroleum hydrocarbons, secondary products from these or the modifications of organic matter of local origin, and local abnormal concentrations of inorganic matter in the soil. Geochemical well logs are also being made.

The magnetometer is still used for determining the structure of magnetizable zones down to 20,000 ft. Electrical transient measurements are said to be of value, and gamma ray well logging has been introduced. G. D. H.

Drilling.

1447.* Well Saved by Side-Tracking Upper Fish to Catch Lower. T. P. Sanders. *Oil Gas J.*, 29.8.40, **39** (16), 47.—A short discussion of a new type of fishing job is given, where above a fish consisting of the bit, drill-collar, and a portion of drill-pipe, another was stuck consisting of wash-pipe. The method used to save the well was to side-track the hole and yet drill sufficiently near it so as to enter it again in the space between the upper fish and the lower one. Details of the steps taken are given.

The hole was reamed above the lower fish and an overshot was used to lift the lower fish through the 72 ft. of side-tracked hole. The hole was completed, and no difficulty was encountered in running casing.

A diagram illustrates this unusual process. A. H. N.

1448.* Steel-Pit Partitions. H. F. Simons. *Oil Gas J.*, 29.8.40, **39** (16), 48.—The fact that in many Illinois fields a rotary rig will drill at least one well per week has caused a premium to be placed on any method which will save time in rigging up and which will reduce the costs per well. Hence steel-pits have been developed which are quickly and easily installed and removed as required. Steel partitions are used in many other pits. With steel partitions, it is only necessary to dig a recess into the pit wall deep enough to allow the partition to be slid into place. The dimensions and other details of these partitions are given. A. H. N.

1449.* Fast Drilling Time in 12,000-ft. Wildcat. N. Williams. *Oil Gas J.*, 5.9.40, **39** (17), 17.—A 12,000-ft. wildcat well was drilled and completed in 68 days from the starting of rigging up. This time includes 17 days for casing and cement time, running of various coring, and other well surveys, leaving 51 days' actual drilling time.

Details of the drilling programme and equipment are given. A. H. N.

1450.* Use of Casing Mill for Multiple Sand Completions in Old Wells. H. F. Simons. *Oil Gas J.*, 5.9.40, **39** (17), 51.—The first well drilled in a field may show no oil in the shallow formations and find good productions in lower sands. Careful examination, however, of drill cuttings on subsequent wells may reveal that one or more good producing horizons were missed above the discovery horizon. The upper formations would, in these cases, be cased off in the older wells. To test for and produce oil from these cased-off sands, a tool has been developed to cut away the steel casing opposite the upper pay sands, thus permitting multiple sand production with a substantial saving in costs of drilling, casing, tubing, and equipping another well.

The tool is a special type mill with one or more sets of cutters which can be applied successively as the cutting operation progresses. Each cutter has five blades of a special alloy steel designed to cut the hardest casing. Mud is used as the circulating medium. Full details of the cutting operation are given.

The cost of cutting varies with each case, but it is generally moderate.

A. H. N.

1451.* Mast-Type Derrick Used on Deep Coastal Test. N. Williams. *Oil Gas J.*, 12.9.40, **39** (18), 46–47.—At a wildcat well drilled in Coastal Louisiana a 129-ft. cantilever-type mast and specially designed substructure were used. Capacity of the mast is rated at 10,000 ft., and it appears that the mast is the largest ever built. In keeping with rigs used for slim-hole exploratory drilling it is designed to speed and facilitate moving, drilling, and setting up or dismantling.

The wildcat well drilled by this unit was abandoned at a depth of 9200 ft. The well drilled 9⅞-in. open hole from 1435 ft., where 10¾-in. surface casing was cemented. More than 800 ft. of core were taken, all with a conventional core barrel.

The substructure incorporates features of portability, but is of full 8-ft. height, permitting installation of standard blow-out preventers and well-control assemblies below the derrick floor. Combining engine foundations with the substructure as a single unit, it is 45½ ft. long, exclusive of pump base, with an overall width of 18 ft. 2 in.

Details of equipment and mast are given. A. H. N.

1452.* Smaller-Diameter Holes Cut Deep-Drilling Costs. Anon. *Oil Wkly*, 2.9.40, **98** (13), 15–18).—Drilling of small holes has not been accompanied by the expected reduction of drilling time. Material costs have been reduced appreciably, but the drilling time has been longer in slim holes than in the larger holes. The latter fact has been caused largely by mechanical factors, but it is believed that drilling time in slim holes will gradually approach that in larger holes.

Details of slim-hole drilling programmes are given.

Because of the small diameter of the oil strings used in slim holes, all footage is made before running the casing. The casing is cemented well off bottom, however, above the oil zone. (Details are included in the description.) A new open-hole record was established recently when 11,800 ft. of uncased formation was penetrated. Much less casing is being run per foot of hole drilled than was run six years ago.

Rotating speeds are usually around 200–400 r.p.m., with some attaining a maximum of 500 r.p.m. No desire to use excessively high speeds is evidenced.

Use of an oil-base mud while drilling producing formations is a new California practice, which is still in the experimental stage. Mineral seal or absorption oil is used as a base for one drilling fluid of this type, but experiments have been carried out with asphalt as a base. Lamp-black and 300-mesh limestone are added for colloidal and weighting purposes, respectively. Derrick men usually object to its use because " it is messy to handle." Chemical treatment of mud is discussed.

A study is made of the desirability and method of keeping the hole straight on the usual lines—*i.e.*, of keeping the drill string in tension above the collar. Figures, however, are given for practical purposes. A. H. N.

1453.* Drilling the Lucas Gusher. A. W. Hamill. *Oil Wkly*, 2.9.40, **98** (13), 35.—An historical sketch of the drilling of Spindletop's discovery well in 1900–1901 is given by the driller. It was this well which started the industry on its rapid rise to present world prominence, although the original Drake well is recognized as the most important discovery in the oil industry. A. H. N.

1454.* Lost Circulation in Illinois Devonian Drilling. Anon. *Oil Wkly*, 9.9.40, **99** (1), 12–15.—The chief difficulty when drilling below 2400 ft. at Salem is that when the weight of the mud exceeds 9½ lb./gal., the column weight plus the pump pressure at the ports of the bit will overcome the formation tension and result in the loss of mud in the permeable formations being penetrated. The objective to be attained becomes to hold the viscosity at such a point that it will be most effective in plastering the walls of the hole, yet the mud remains sufficiently light in weight to obviate it being lost by excessive column pressure.

In many wells the zone of lost circulation has been sealed effectively by squeezing cement into the permeable formation. Lime slurry has also been used effectively. Both methods failed in many instances, however.

Additives which have been found very successful are now used. These are either flakes of mica or cellophane, frequently crinkled. Either additive is mixed with the mud in varying percentages, but seldom in greater quantities than 3–4% of the quantity picked up by the pump. A. H. N.

1455.* Practical Survey of Direct Mechanical Rotary Drilling Outfits. V. J. Beissinger. *Petrol. World*, August 1940, **37** (8), 31.—A brief historical review of the development of direct mechanical rotary drilling rigs using internal-combustion engines for prime movers is given at the beginning of this extensive paper.

The chief objectives of good mechanical rig design are given as : (1) portability ; (2) power transmission flexibility and provision for sufficient speed variation to permit engines to operate at optimum performance points; (3) low cost and maintenance requirements.

A discussion of multiple-engine outfits and methods of connections to be used follows. The data regarding the comparative values of driving through a reversing clutch and gear mechanism or through a chain transmission directly to the draw-works are meagre, and choice of either system is left to personal experience.

The principal economic considerations involved in the selection of mechanical drilling rig programmes are listed as: (1) location and accessibility, whether wildcat or development well; (2) fuel and water, cost and suitability; (3) completion programmes, total depth, casing, productivity, and curtailment effect; (4) materials and supplies, on hand and new purchases; (5) labour, cost and adaptability; and (6) tool rental charges, depreciation, obsolescence, repairs, and replacements. To illustrate these points a direct analysis is made of a typical case of an 11,168-ft. wildcat drilled in the Wheeler Ridge area, of another wildcat well in the Coalinga area, of a routine development well in a third area, and of others in less detail.

Based on the consideration of six examples of heavy and light duty mechanical outfit performance data, and on the writer's acquaintance with similar factual data for a number of other such jobs, the economy of operation peculiar to this type of rig appears to be well established.

The chief disadvantages of such rigs when compared to steam-driven rigs appear to be: (1) Steam power is more flexible. (2) I.C.E. must be geared to specific load limits. (3) Power-driven slush pumps are more costly, heavier, and subject to gear strength limitations. (4) Reverse gear and clutch mechanisms are subject to frequent adjustments. (5) More shock is experienced in drilling with such outfits than when using steam.

The rest of the paper describes the efforts made to minimize these disadvantages.
A. H. N.

1456.* Bulk Cementing. Anon. *Petrol. World.* August 1940, **37** (8), 47.—This system is simply a method of transporting cement from specially designed bins to the well in an efficient manner. It consists essentially of a railroad siding and a series of storage bins to store various brands and types of cement and of mechanical equipment to unload cement in bulk from freight cars to storage bins. From the bins the cement is conveyed to a "weight-batcher," from which it is unloaded into transport units which convey it to the wells. At the well, screw conveyors move the cement from the transport unit to the mixer or to smaller bins. Four hundred sacks of cement were used to cement 3020 ft. of 8⅝-in. casing by this method, and the cement was mixed in 18 min.

Although the initial cost of the system is high, it appears that it offers the advantages of eliminating spoilage of cement by weather, breakages of sacks in transport, waste of cement while mixing, and assures uniform feeding of cement into the mixer.
A. H. N.

1457.* Importance of Drill-Pipe String in California Deep Drilling. W. A. Sawdon. *Petrol. Engr*, September 1940, **11** (13), 23–26.—The high degree of efficiency attained in deep-drilling operations in California is stated to have been influenced to a considerable extent by the attention paid to the drilling string and its component parts. Advanced metallurgical work has supplied material of adequate strength and hardness; design has utilized the material for effective performance and long life, and drilling technique has applied the designs to consistently successful application in meeting the conditions encountered. These various points are illustrated.

Where higher rotating speeds than 400 r.p.m. are used, $5\frac{9}{16}$-in. drill-pipe is found most desirable, with 4½-in. drill-pipe being the smallest size used for comparatively high speeds up to 400 r.p.m.

Large volumes of circulating fluid are necessary for deep drilling operations, and although high pressures are expected, it is desirable to keep the pressure down as much as possible. Large-capacity pumps are used, but the pumping rate of the circulating fluid probably never exceeds 1000 gals./min. below 10,000 ft. The average rate is between 700 and 800 gals./min.

Details of the drill-pipe and its joints and collars as well as the drill-collar are studied from a point of view of the stresses generated in drilling deep wells. A. H. N.

1458.* Hydraulic Torque Converter Used on Illinois Drilling Rig. H. L. Flood. *Petrol. Engr*, September 1940, **11** (13), 31–32.—The important element that rendered possible the change from steam to internal-combustion engines at reasonable cost was the hydraulic torque converter that was incorporated into the drive between the engine and the draw-works.

The torque converter is essentially a hydraulic chamber comprising a centrifugal pump and a reaction turbine. In the impeller or the pump, as the fluid velocity increases the fluid absorbs kinetic energy, and thereby imposes a corresponding load on the engine or driving-member. In the runner or turbine, due to loss of rotational velocity as the fluid is forced to the inside, kinetic energy is released and becomes available to the output shaft.

The capacity of the converter is based on hydraulic principles, in accordance with which the horse-power is proportional to the cube of the speed, and the torque is proportional to the square of the speed. Both horse-power and torque are in proportion to the fifth power of the diameter. Similarly, the power absorbed by the impeller is proportional to the cube of its speed.

Characteristics of torque converter, giving efficiency, output torque, and engine torque against speed, are reproduced. The efficiency curves are the usual ones showing maxima at certain speeds. A. H. N.

1459.* Temperature Log Reveals Gas-Oil Contact Plane. W. A. Sawdon. *Petrol. Engr*, September 1940, **11** (13), 83–84.—Amongst the reasons for and applications of geothermal surveys undertaken during the last 2 years have been the location of the top of cement behind casing, detection of points of entry of gas or water, and the determination of other points at which conditions cause slight change of temperature. Surveys have been made in flowing, pumping and shut-in wells, in drilling wells, and also in wells ready for completion.

Such a survey revealed, recently, the location of the point of contact between gas- and oil-bearing strata of a producing zone by temperature indication, with the consequent shutting off of the upper gas so indicated to conserve gas by reducing gas–oil ratio. Although other means have previously been used for this purpose, the speed at which the survey was made and the accuracy with which other determinations were checked render this method of value.

The equipment consists of a recording thermometer run on a piano wire with a conventional measuring-line hoist. The temperature record is made on film moving at constant speed, which provides synchronization with depth measurements at any time by means of a stop watch started at the same time as the instrument.

A. H. N.

1460.* New Fast-Setting Cement. R. K. Henderson. *Petrol. Engr*, September 1940, **11** (13), 93–94.—A new calcium sulphate cement is being used to advantage in special cases where other types are not readily adaptable. This cement is composed of 98% dehydrated calcium sulphate, to which have been added other compounds to control the setting time. Setting is accomplished through the hydration of the material to a dense, hard, interlocking, crystalline structure. Setting time is standardized to four periods: 30, 60, 120, and 180 min.

Setting of the material results in volumetric expansion, thus producing a very tight bond to steel and adherence to the walls of the hole. The cement will set under agitation, and, when set, leaves no free water on the surface. Crushing strength of the material is approximately 2000 lb./sq. in. shortly after setting. Very little heat is developed during the setting process.

Contamination with salts, sulphates, and bicarbonates in appreciable amounts will accelerate the setting time, hence caution must be exercised in mixing and placing of this cement if the standard setting time is expected. Whenever possible a sample of the cement should be mixed with the water to be used and allowed to set, to determine the exact setting time on any job. A. H. N.

1461.* Casing Cutting Tool May Stimulate Exploitation of Cased-Off Sands in Older Fields. H. L. Flood. *Petrol. Engr*, September 1940, **11** (13), 107–108.—Two recent developments are of great potential importance in untapping formations which lie hidden behind cemented casing strings. These are the apparatus and technique for logging geologic formations behind casing by use of gamma ray, and methods of cutting casing at any desired depth. The last development is under two main lines; the first consists of a tool which can drill laterally at any desired point in a well, cutting casing and the hardest type formation in one operation, retaining a sample intact in the hollow cutter which is retractable and can be hoisted to the surface; the second consists of perfecting a method for milling or cutting-out and completely removing steel casing over any desired length.

Operation of the milling device requires the use of rotary drill-pipe to suspend the tool, supply the rotation required, and circulate the mud to actuate the tool and remove the cuttings from the hole. Two types of cutting mills are available—a cutting-through mill for starting a window in the casing, and an expanding casing mill comprising three sets of cutter blades. After the drilling equipment is in place and ready for operation, the cutting-through mill is lowered to the point corresponding with the upper edge of the desired window. The cutter is forced outward by means of mud pressure acting on a piston which restricts the passage of mud until the cutters are completely out. A. H. N.

1462. Drilling Patents. P. W. Appleby. U.S.P. 2,212,491, 27.8.40. Appl. 29.8.39. Well-washing device in combination with a rotary drilling apparatus.

H. W. Evans. U.S.P. 2,212,594, 27.8.40. Appl. 6.2.39. Offset drilling tool with a wall engaging means.

C. H. Black. U.S.P. 2,212,727, 27.8.40. Appl. 12.10.39. Drill bit with conical toothed cutters.

H. E. Chiles. U.S.P. 2,212,729, 27.8.40. Appl. 10.11.39. Drill bit with conical cutters.

V. W. David. U.S.P. 2,213,038, 27.8.40. Appl. 27.6.38. Formation sealing composition made of a colloidal jell of clay of the Frazier Mountain and Mojave types combined with cement, calcium chloride, unslaked lime, bentonite, litharge, and caustic which hardens on the addition of water into an impervious mass.

V. W. David. U.S.P. 2,213,038, 27.8.40. Appl. 14.11.38. Water shut-off method and composition for wells.

D. H. Reed. U.S.P. 2,213,049, 27.8.40. Appl. 9.5.38. Compensating outside pipe-cutter with releasable cutter arms.

J. T. Hayward. U.S.P. 2,213,138, 27.8.40. Appl. 1.7.39. Method and apparatus for detecting oil in well-drilling by subjecting the returned mud to fluorescence-exciting rays to render minute oil drops visible by fluorescence and subjecting the same field to visible light ray to check presence of oil in the field.

B. P. Bishop. U.S.P. 2,214,786, 17.9.40. Appl. 15.8.38. Apparatus for logging holes while drilling, the bit being in electrical continuity with the drill stem, and used as an electrode for measuring the self potential of the strata.

D. C. Sharp, L. K. James, and R. M. Garrison. U.S.P. 2,214,799, 17.9.40. Appl. 29.11.35. Slush pump valve with a resilient closing member.

A. J. Colmerauer. U.S.P. 2,214,811, 17.9.40. Appl. 13.9.38. Liner perforator and under-reamer.

J. Mooney. U.S.P. 2,214,970, 17.9.40. Appl. 25.4.39. Combination well-driving and boring tool.

S. W. Marshall. U.S.P. 2,215,047, 17.9.40. Appl. 17.12.38. Rotary well-drilling apparatus consisting of a rotary table and bearing lugs, a roller-supporting bracket below the table.

B. S. Minor. U.S.P. 2,215,049, 17.9.40. Appl. 28.4.37. Hook for rotary well-drilling.

J. Rogoff. U.S.P. 2,215,072, 17.9.40. Appl. 25.3.39. Wire splicer.

G. Prince. U.S.P. 2,215,251, 17.9.40. Appl. 7.2.38. End protector for threadless pipe.

R. P. Fisher. U.S.P. 2,215,264, 17.9.40. Appl. 16.11.38. Rotary drill-bit with a centrally flanged shaft for mounting cutters thereon with ball bearings between cutters and flange.

C. S. Penfield and U. M. Warren. U.S.P. 2,215,377, 17.9.40. Appl. 2.5.39. Mud wiper for tubing being withdrawn from a well containing drilling fluid.

C. R. Athy. U.S.P. 2,215,494, 24.9.40. Appl. 3.12.37. Drilling bit.

J. D. Brack and L. M. York. U.S.P. 2,215,632, 24.9.40. Appl. 7.6.38. Pipe-cutting tool for inside cutting jobs, with laterally moving cutters moved by a tapered body.

J. T. Ellis. U.S.P. 2,215,638, 24.9.40. Appl. 26.5.36. Pipe cutter for cutting pipe inside wells, the cutters being fluid-operated.

G. E. Mullinix. U.S.P. 2,215,649, 24.9.40. Appl. 3.8.36. Well-pipe elevator adapted to support a pipe by its collar.

G. W. Miller. U.S.P. 2,215,710, 24.9.40. Appl. 18.7.38. Sand pump bottom containing a disc type valve.

W. F. Sheffield. U.S.P. 2,215,770, 24.9.40. Appl. 29.9.39. Drilling shaft coupling for oil well drilling shafts.

A. J. Thomas. U.S.P. 2,215,824, 24.9.40. Appl. 29.12.38. Chain wrench for pipes.

H. H. Franks. U.S.P. 2,215,920, 24.9.40. Appl. 12.8.38. Derrick structure adapted for portability and having a mobile base.

J. W. Hornbrook. U.S.P. 2,215,928, 24.9.40. Appl. 19.12.36. Drilling apparatus of a portable mast type; rotary system.

P. A. Williams. U.S.P. 2,215,948, 24.9.40. Appl. 23.1.39. Drilling tool.

I. N. Clark. U.S.P. 2,216,067, 24.9.40. Appl. 12.7.39. Blasting bridge for oil wells comprising an expansible, longitudinally collapsible closed pre-filled chambered member having a gravity actuated fluid material for expanding the chambered member into engagement with a well wall. A. H. N.

Production.

1483. Study of Brine-Disposal Systems in Illinois Oilfields. S. S. Taylor, W. C. Holliman and C. J. Wilhelm. *U.S. Bur. Mines. Report of Investigations* No. 3534. August 1940.—The problem of brine in the oilfields of Illinois has recently attracted a great deal of attention, and accordingly the Bureau of Mines has made a general survey of disposal systems available and their use in this State. Where sufficient surface water is available to reduce the salt content of oilfield brines to a negligible amount, large volumes of brine can be discharged into surface streams. As a rule, however, this method is suitable only in cases where a relatively small volume of brine is produced.

Another method adaptable to several oilfields in Illinois is to return the brine to subsurface formations already containing brine. Subsurface disposal of this character cannot, however, be universally employed, since in certain fields no formation pervious enough for brine injection has been found.

Certain brines require chemical stabilization before injection into subsurface formations, because of the volume or type of brine or the characteristics of the disposal formation, but investigations are not yet sufficiently far advanced to give a definite ruling on this point.

The report, in addition to embodying the results of a number of chemical tests, includes some valuable suggestions and criticisms of brine-disposal systems at present in use in the State. In certain cases it was found that wells had an insufficient intake capacity to indicate that a large volume of brine could ultimately be injected into the formation. The suggestion is made that other formations should be tested for injection purposes.

It is recommended that brine-conditioning and disposal systems should be kept under continuous observation, so that with changing producing conditions adjustments can be made in brine treatment. The design of brine-disposal systems should moreover be formulated only after detailed studies of chemical characteristics and volumes of the brine to be injected, also of the brine in the disposal formation, etc.

Summarily it is concluded that no general system of brine conditioning and disposal can be recommended for all oil-producing areas in the State, owing to the widely varying chemical characteristics of the brines produced and the different characteristics of brine-disposal formations. H. B. M.

1464.* Capillary Behaviour in Porous Solids. M. C. Leverett. *Petrol. Tech.*, August 1940, A.I.M.M.E. Tech. Pub. No. 1223, 1–17.—The static equilibrium vertical distribution of fluids of different densities in porous solids is discussed largely from a thermodynamic standpoint. The concept of a characteristic distribution of two-fluid curvatures with water saturation is suggested. This curvature–saturation relationship for clean unconsolidated sands was examined experimentally for imbibition and drainage and hysteresis demonstrated. The extent of the two-fluid interfacial surface area was shown to be determinable from thermodynamic considerations of the curvature–saturation relationship. The " hydratable " clayey matter in natural sandstones strongly affects the curvature–saturation function, and may be the cause of large " connate " water saturations in some reservoir rocks.

The distribution of oil, gas, and water was calculated for a uniform unconsolidated sand.

The concepts developed are applied briefly to problems in the flow of mixtures of immiscible fluids in porous media, with emphasis on the proper accounting for the effects of capillarity on such flow. The existence of a *boundary effect*, characteristic of any discontinuity in the capillary properties of the solid medium, is pointed out, and the importance of adequately allowing for its influence in the interpretation of data from small-scale experiments is stressed. G. D. H.

1465. Pressure Distribution about a Slotted Liner in a Producing Oil Well. F. G. Miller. *Petrol. Tech.*, August 1940, A.I.M.M.E. Tech. Pub. No. 1222, 1–15. *Petrol. Engr*, September 1940, **11** (13), 109.—The presence of a slotted liner in a well disturbs the simple radial pressure distribution about the well by increasing the pressure gradient near it by a convergence factor and a sand-bridging factor. This problem was examined mathematically. Experimental work was also carried out using fluid flow through a sand apparatus made geometrically similar to the well problem, and also with an electrolytic conduction model simulating the same condition.

It was found that the additional pressure loss resulting from the formation of a sand bridge over a rectangular slot becomes small, nil, or even negative if the slot width used is equivalent to at least the grain size at the 10-percentile size of the sand, taken from its sieve-analysis curve. The pressure loss resulting from the bridge increases markedly when the slot width is reduced. The additional pressure loss resulting from the convergence of the streamlines in the sand near a slot decreases as the slot length is increased. Experimental results show that the additional pressure drop per unit rate of flow due to a slot of length equal to the sand thickness is about one-third the loss for a slot of the same width, but only one-half the length, placed so that its centre is midway between the upper and lower horizons defining the oil sand, if the effect of bridging is neglected. Increasing the width of the slots without increasing the length does not reduce the convergence loss greatly.

The pressure loss due to the slots themselves, which is similar to the pressure drop across an orifice in pipe-line flow of liquids, is small compared with the corresponding loss that would occur in the sand near the slot. A slotted liner does not affect normal flow conditions in the sand beyond a distance, measured from the well axis, of three times the well radius. G. D. H.

1466.* Major Economies Result from Adoption of Twenty-Acre Well-Spacing. J. A. Kornfeld. *Oil Wkly*, 2.9.40, **98** (13), 10–14.—Twenty-acre spacing is the pattern employed in more than one-fith of the proratable oil wells on production on the Central Kansas Uplift. A saving of over $16,000,000 in development costs are estimated to have resulted from the adoption of this pattern. Further, it is expected that this pattern will result in retarded encroachment of edge-water, thus achieving a greater recovery/acre of the original reservoir reserves.

Many factors are responsible for this relatively wide well-spacing programme, amongst which are shrinkage of market due to loss of out-of-State demand; low per well allowable; high cost of production; present ability to drain large areas, due to universal use of acid in large doses; forced development of leases due to short-term expiration, to protection from drainage, and to maintaining drilling density with offset leases; low withdrawal rate from principally lime reservoirs; and hydrostatic head being propelling force with little or no gas drive.

From an engineering standpoint, well-spacing conditions in Western Kansas are related to three objectives: First, to secure the most efficient development with the least number of wells—*i.e.*, at the lowest cost/brl. of reserves. Secondly, to achieve a full, uniform development of the entire property through the most efficient well-spacing pattern for that type of reservoir. Thirdly, to delay the rate of water encroachment, through the rate of property development and the rate of withdrawals.

The legal aspects of well-spacing and proration are discussed. A. H. N.

1467.* Conventional Pumping Proves Economical in Slant Holes. Anon. *Oil Wkly*, 9.9.40, **99** (1), 23.—Directionally drilled oil wells are being pumped at reasonable costs in the Huntington Beach field, California. Many of these intentionally deflected holes drift more than 45 degrees from the vertical, and extreme drift angles of more than 60 degrees have been attained in wells being pumped successfully with conventional rods and tubing. About 115 deflected wells are on the pump.

Lifting costs in the various wells range from 8 to 40 cents/brl., but operators are not in agreement about items included in the lifting costs.

A certain well has a horizontal drift of 3200 ft., a total depth of 5694 ft., and an actual vertical depth of 4250 ft. This well has been on the pump about 2 years, and has given little trouble, except immediately after completion. Rod and sand troubles have been overcome. Spiral rod guides are used to check rod and tubing wear. Most of the wear is near bottom, due probably to settling of dirt and sand.

Many rod failures have been traced to severe wear on the couplings.

Mechanical action of the submerged pumps has not been seriously affected by inclination of the holes, where other factors are favourable.

Details of the type of wear observed on various parts and data of production are given and illustrated. A. H. N.

1468.* New Potential Method Uses Data Obtained at the Surface. J. H. Page. *Oil Wkly*, 16.9.40, **99** (2), 17.—In measuring productivity indices, the amount of liquid a well will produce per unit drop in bottom-hole pressure is determined. The pressure is either measured directly by a bomb at the bottom or estimated from the height of the fluid level, using a wave-impulse instrument. To calculate the pressure from the height of the liquid column a knowledge of the mean density of the liquid column as well as that of superincumbant gas column is essential.

In this new method the density of the liquid column is measured in the following manner. A recording pressure gauge is attached to the casing-head, which is closed-in during the test. If sufficient gas is produced, a regulator is placed on the casing-head outlet and set to maintain the required back-pressure for the first pumping rate. When both pressure and hourly production are stabilized, the fluid level is determined by an impulse method.

After production during 3 hrs. of stabilization has been pumped and gauged, the regulator setting is changed and pressure stabilization is again reached, keeping the production rate constant. This change in casing-head pressure is necessary in order to effect a difference in pressure on the fluid surface. The density of the oil column is obtained by observing the distance which the fluid surface has been depressed by the change in pressure. When the fluid density has been measured for the first production period, the pump speed is changed and a second stabilization period is started.

Three stabilization periods are used as in other fluid-level tests. Bottom-hole pressures are computed by adding together the recorded casing-head pressure, the weight of the gas column above the liquid, and the weight of the liquid column above the producing formation. The specific gravity of the gas in the annulus between casing and tubing is calculated from the speed with which wave-impulses reach the well head after being reflected by the surface of the liquid in the well.

The well potential is computed by first averaging two indices, taken as the ratio of the increment in production rate to the increment in bottom-hole pressure; the average index is next multiplied by the bottom-hole pressure at the lower rate. Adding this product to the lower rate gives the potential. A. H. N.

1469.* Dyes Aid in Tracing Water. Anon. *Oil Wkly*, 16.9.40, **99** (2), 18.—To make it possible for future drillers to determine whether water encountered in a pay-sand is coming from a previously plugged well, operators are using dyes. The " detector " is made of 30–40 oz. of red or purple dyes with sufficient warm water to form a thick paste. This mass is packed into a waxed paper container, which is weighted and dropped down the hole. The casing is pulled out and the hole plugged in the normal manner.

The paper is soon ruptured, and any moving body of water will tend to take the dye in the stream. By placing detectors of different colours in certain wells, and by keeping such locations carefully preserved on a map, it is possible to estimate dips and high-spots in a sand, and also to prove the general direction in which the sand is draining as well as to find the source of contaminating waters in future wells.

A. H. N.

1470.* More Efficient Practices Used to Produce Gas Wells on Gulf. N. Williams. *Oil Gas J.*, 29.8.40, **39** (16), 43–44.—In the production of high-pressure gas wells which are not of the distillate type, control of the pressure drop is a major factor in the efficient recovery of liquid content of the gas. This control involves reduction of pressures without causing freezing in the gas lines and separators, and simultaneously without applying too much heat to the gas to allow easy separation of gas and liquid.

Bottom-hole chokes have not proved successful because of continuous need for changing the size of the orifice. The most popular system is one where just sufficient heat is imparted to the gases before expansion to keep the temperature on the exit side constant. The regulators are placed, in this system, on the discharge side of the heater coil.

A discussion of heaters and regulators used on the Gulf Coast for such systems shows continual progress in design of the heaters and regulators. A. H. N.

1471.* Co-operative Repressuring in Louisiana Field. G. Weber. *Oil Gas J.*, 5.9.40, **39** (17), 32.—The advantages gained from repressuring are illustrated by this study of the Homer field in North Louisiana. Current production averages 2400 brl./day, approximately 50% above the estimated production under an ordinary depletion programme. In addition to the more rapid pay-out, the increased production represents an increase in recoverable oil, by extending the field's economic life for several years. Reduction of vacuum has shown definite returns in the relatively fewer clean-out jobs and lower field-operating costs.

The paper includes an historical account of the development of the repressuring project, a study of the operations and practices involved, gas–oil ratio studies, and processing of the gas produced.

The principal operating problem is controlling the gas–oil ratio. In most cases, this control is achieved by reducing the orifice in the gas line from the well showing increased gas production. A. H. N.

1472.* Unfavourable Pumping Speeds May Cause Excessive Sucker-Rod Breakage. T. P. Sanders. *Oil Gas J.*, 5.9.40, **39** (17), 37.—An upper limit to the number of strokes per minute in pumping wells is known to exist, but an unfavourable pumping speed may also occur at lower values than this upper limit, where failure of sucker-rods may occur due to vibrations. When a sudden stress is applied to the rods, that stress is transmitted to the other end of the rod in the form of a longitudinal wave. The frequency of the wave was shown to be equal to the velocity of stress transmission divided by 4 times the length of the rod string. Thus, frequency = 237,000/length of rods.

In designing pumping equipment, speeds which give rise to severe vibrational stresses due to synchronous vibrations of the first order should be avoided. A chart is given to assist in choosing safe speeds for various depths. However, only a dynamometer test would be a certain way of choosing optimum values of speeds.

A. H. N.

1473.* Small Generating Plant for Pumping. H. F. Simons. *Oil Gas J.*, 12.9.40, **39** (18), 65–66. Efficient pumping of shallow oil wells by electricity is being accomplished through a carefully designed system of a small generating plant supplying powder to forty-six producing wells and to a pump at a salt-water disposal well. Approximately 1000 brl. of fluid are lifted daily by the pump. Loads of the individual wells vary widely, and the length of the stroke, the number of strokes/min., and the time the well is on the pump differ from well to well, due to characteristics of the producing horizon.

Each well is equipped with an individual pumping unit driven by an electric motor. Generally the motors are of 220–240 volt, 8·1–4·05 amp., 3-phase, 3-h.p., 60-cycle, 1675-r.p.m. induction-type, capable of running continuously with a 50° temperature rise. The generating plant is as centrally located as possible to reduce the length of the transmission lines.

Certain details of the equipment, internal-combustion engine and generator foundation and of switchboard and transmission systems used are described and illustrated.

A. H. N.

1474.* Distortion of Sucker Rods. T. P. Sanders. *Oil Gas J.*, 12.9.40, **39** (18), 66.—In a short note on distortion of sucker rods when pulling stuck pumps, it is pointed out that the force required should be within the limits of the sucker-rod's capacity. The best available practice to avoid sucker-rod distortion due to excessive pulling forces is to use a weight indicator on rod-and-tubing pulling units. Another method may be used when weight indicators are not available, *i.e.*, to limit the rod stretch. A chart gives the maximum allowable stretch for rods of various lengths and yield points.

The method consists of raising the elevators to take up the slack in the rods and tying a marker on to the string. Further force is applied and the stretch is noted. If the stretch is near the maximum allowable, then it will not be safe to continue, and a tubing job is indicated. A. H. N.

1475.* Deepening and Completing a Well in the Lisbon Field, Louisiana. Pt. 8. P. D. Torrey and F. H. Miller. *Petrol. Engr*, September 1940, **11** (13), 124.—This is the concluding part of the long paper prepared by the authors to describe every detail of deepening a certain well. In this part methods are suggested of increasing oil recovery from this well based on information gained from tests described in previous parts. Gas-repressuring and pressure maintenance are discussed.

In the summary it is concluded that in this particular field pressure maintenance can only be accomplished economically if the several operators in the field co-operated. Several independent plants would serve merely to increase the cost, and would not improve the efficiency of the operation. Losses in recovery due to non-employment of pressure maintenance are made clear, but the full study of the economics of repressuring cannot be given, as the data are too meagre. A. H. N.

1476. Repair of Oil Wells. B. L. Astiz. *Bol. Inform. Petroleras*, May 1940, XVII (189), 19–27.—This is a description of the methods adopted for the repair of oil wells, with special reference to the conditions obtaining in the field at Comodoro Rivadavia. A number of pipe filters are illustrated. H. I. L.

1477. Some Aspects of the Use of Mechanically-Operated Pumps for Raising the Oil in the Comodoro Rivadavia Oilfield. M. Soifer. *Bol. Inform. Petroleras*, May 1940, XVII (189), 28–35.—The author points out that little has been published concerning the conditions affecting mechanically-operated pumps. The bulk of the pumps at

Comodoro Rivadavia are of this description, and the relatively high viscosity of the petroleum raised introduces features of interest. Among the points discussed is the effect of acceleration of the pump and of the petroleum on the maximum stress that can be borne by the pump rods, and also the effect of viscosity. The use and advantages of the "insertable" type of pump are considered in detail and various improvements are dealt with. H. I. L.

1478. Production Patents. A. J. Hughes. U.S.P. 2,212,604, 27.8.40. Appl. 12.11.37. Apparatus for depth measurement by echo reception methods.

E. J. Roe. U.S.P. 2,212,619, 27.8.40. Appl. 4.3.37. Well-packing device.

B. W. McCune. U.S.P. 2,212,784, 27.8.40. Appl. 24.2.40. Well-casing perforation cleaner.

R. Wiken. U.S.P. 2,212,909, 27.8.40. Appl. 24.1.38. Power unit for multiple oil wells comprising an eccentric rotating on a vertical axis.

C. P. Stauffer. U.S.P. 2,213,022, 27.8.40. Appl. 31.10.38. Repair clamp for pipes.

T. B. Wayne. U.S.P. 2,214,783 and 2,214,784, 17.9.40. Appl. 20.7.38 and 29.7.38, respectively. Processes and reagents for resolving emulsions of petroleum.

W. J. Dunlap. U.S.P. 2,214,956, 17.9.40. Appl. 14.9.38. Plunger controlled valve for oil well pumps.

J. S. Wylie. U.S.P. 2,214,982, 17.9.40. Appl. 16.6.38. Pipe cleaner containing an elongated helical spring, and a number of scraping blades secured to the spring at various radial positions.

G. S. Shupe. U.S.P. 2,215,164, 17.9.40. Appl. 30.3.39. Pump with latches to remove the cylinder when required.

J. Sutherlin and F. I. McConnell. U.S.P. 2,215,487, 24.9.40. Appl. 9.3.38. Treatment of wells by acid where acid is forced under pressure and maintained until permeability of formation reaches a maximum, when the pressure is released and acid is withdrawn and treatment repeated.

A. Hollander. U.S.P. 2,215,505, 24.9.40. Appl. 13.1.38. Variable capacity pumping apparatus for deep wells with a submersible electric motor and pump unit.

R. R. MacGregor. U.S.P. 2,215,514, 24.9.40. Appl. 25.7.38. Well device for cleaning well tubing, casing, liners, and the like, comprising brushes on mandrel.

A. G. Miller. U.S.P. 2,215,558, 24.9.40. Appl. 29.12.38. Deep well pump with air in a compression chamber to act as a cushion.

C. O. Tullberg and R. D. Frampton. U.S.P. 2,215,599, 24.9.40. Appl. 29.8.39. Tubing bleeder for oil wells.

R. I. Brown. U.S.P. 2,215,913, 24.9.40. Appl. 4.10.38. Method and apparatus for operating wells whereby a string of casing consisting of alternating sections of ordinary casing and others of drillable casings is landed, the latter sections set against producing horizons and drilled subsequently.

L. A. Layne. U.S.P. 2,216,037, 24.9.40. Appl. 27.12.37. Means and method of gravelling wells consisting of a gravelling assembly of a smaller diameter than casing in the well and a gravelling tool.

L. A. Layne. U.S.P. 2,216,038, 24.9.40. Appl. 9.2.39. Gravel dump bucket and method of depositing granular material in a well bore around a strainer element.

A. H. N.

Hydrogenation.

1479. Patents on Hydrogenation. E.I. Du Pont de Nemours & Co. E.P. 526,495, 19.9.40. Appl. 17.3.39. Manufacture of hexamethylene imine by catalytically hydrogenating adiponitrile in the vapour phase in the presence of an excess of ammonia and of hydrogen.

J. C. Morrell and A. U. Grosse. U.S.P. 2,212,034, 20.8.40. Appl. 30.4.38. Treatment of aliphatic hydrocarbons by contacting them under dehydrogenating conditions with an alumina–silica composite supporting a minor proportion of an oxide of tin.

J. C. Morrell and A. U. Grosse. U.S.P. 2,212,035, 20.8.40. Appl. 30.4.38. Production of aromatic hydrocarbons from aliphatic hydrocarbons of at least six carbon atoms in straight-chain arrangement by subjecting the latter to dehydrogenation and cyclizing conditions in the presence of an alumina–silica composite supporting a minor amount of an oxide of tin.

V. Ipatieff and R. E. Schaad. U.S.P. 2,214,463, 10.9.40. Appl. 30.4.37. Production of more valuable products from butene trimers by subjecting them to destructive hydrogenation under conditions conducive to the formation of octanes by depolymerization and hydrogenation of the trimers. H. B. M.

Polymerization.

1480.* Production of Aviation Spirit by Alcoholization and by Polymerization of " Cracking " Gases in the Liquid Phase. A. Pinilla. *Bol. Inform. Petroleras*, May 1940, XVII (189), 5–19.—This is a detailed description of the process in which sulphuric acid is used as the condensing agent and where two types of gas are used—namely, a gas which is mainly *iso*butane and another which consists predominantly of butane. A mixture of these with ordinary high-grade petrol results in a high-class aviation spirit. H. I. L.

Synthetic Products.

1481. Patents on Synthetic Products. J. G. Fife. E.P. 525,403, 28.8.40. Appl. 7.1.39. Manufacture of refined products from hydrocarbon mixtures by separating the liquid mixture into fractions having different compositions by means of an extraction process involving the use of a solvent consisting of antimony trichloride with or without the addition of other substances.

A. Carpmael. E.P. 525,673, 2.9.40. Appl. 25.2.39. Manufacture of fatty aromatic monochloromethyl compounds. Fatty aromatic hydrocarbons which contain one or more alkyl residues with more than two carbon atoms are brought into reaction in the presence of zinc chloride or concentrated sulphuric acid with hydrogen chloride and an excess of paraformaldehyde.

Stafford Allen & Sons. E.P. 525,705, 3.9.40. Appl. 27.2.39. Preparation of propenylbenzene derivatives from alkylbenzene derivatives capable of isomerization by heating with caustic alkali in which a glycol or polyglycol is used as a diluent for the heated caustic alkali.

I.G. Farbenindustrie A.G. E.P. 525,733, 3.9.40. Appl. 27.2.39. Manufacture of synthetic rubber-like materials by subjecting butadienes 1 : 3 to co-polymerization in aqueous emulsion with other polymerizable compounds. The polymerization is effected in the presence of such tertiary amines as are soluble in at least one of the polymerizable compounds.

Compagnie Française de Raffinage. E.P. 526,084, 10.9.40. Appl. 9.3.38. Process for the synthetic preparation of hydrocarbons to obtain fuels having a high antiknocking power. Gaseous *iso*butylene is converted into *iso*-octane by a series of reactions—*i.e.*, hydration by means of sulphuric acid, for forming tertiary butyl alcohol; dehydration and polymerization of this tertiary butyl alcohol to produce di*iso*butylene; and hydrogenation of the latter.

H. E. Potts. E.P. 526,465, 18.9.40. Appl. 17.3.39. Improvement in the production of hydrocarbons with more than one carbon atom in the molecule by conversion of carbon monoxide with hydrogen. The improvement consists in converting a gas mixture containing 2 parts or less of hydrogen to 1 part of carbon monoxide and alternately a gas mixture richer in hydrogen, thereby reactivating the catalyst.

V. Komarowsky. U.S.P. 2,212,026, 20.8.40. Appl. 31.12.36. Conversion of aliphatic hydrocarbons into cyclic hydrocarbons by subjecting them at elevated temperatures and atmospheric pressures to contact with a catalyst consisting of a mixture of aluminium oxide and metallic nickel.

J. F. Clausen. U.S.P. 2,212,112, 20.8.40. Appl. 26.11.38. Method of increasing the cyclic hydrocarbon content of a hydrocarbon mixture boiling within the gasoline range and containing a substantial amount of aliphatic hydrocarbons of at least six carbon atoms. The hydrocarbon mixture is contacted with a preformed heavy metal salt of an acid of the class consisting of molybdic and tungstic acids at a temperature between 400° and 600° C.

C. M. Loane. U.S.P. 2,212,644, 27.8.40. Appl. 5.12.36. Preparation of a new composition of matter consisting of white oil and from 1 to 50 parts of an acid selected from the group consisting of sulphuric acid, chlor-sulphonic acid, and a mono-alkyl sulphuric acid in about one million parts of the oil.

E. Slatineanu. U.S.P. 2,213,415, 3.9.40. Appl. 15.12.36. Production of mixtures of hydrocarbons by subjecting a composition consisting of methane, at least one member of the group constituted by carbon monoxide and carbon dioxide, and at least one member of the group constituted by hydrogen and water at a temperature between 225° and 380° C. to a pressure of more than 500 atmospheres. This suffices to cause a polarization of the methane present. H. B. M.

Refining and Refinery Plant.

1481a. Patents on Refining and Refinery Plant. N.V. de Bataafsche Petroleum Maatschappij. E.P. 525,388, 27.8.40. Appl. 20.2.39. Process for separating fractions of relatively high paraffinic character from those of relatively low paraffinic character in hydrocarbon mixtures by crystallization and by the use of diluents. Crystallization is effected alternately from a solvent with good solvent power for paraffinic hydrocarbons and a solvent with good solvent power for non-paraffinic hydrocarbons.

K. W. Pepper. E.P. 526,117, 11.9.40. Appl. 7.3.39. Process of purification of unsaturated ketones adapted for use in the production of ketonic resins by subjecting the greenish-coloured ketone in the presence of water to the action of alkalis or basic materials or certain reducing agents.

Anglo-Iranian Oil Co. E.P. 526,165, 12.9.40. Appl. 3.2.39. Process for the alkylation of *iso*pentane or *iso*butane in which the *iso*paraffin is condensed with ethylene or with a mixture of olefines containing substantial proportions of ethylene at a relatively low temperature. The reaction mixture is vigorously stirred in the presence of sulphuric acid of high concentration, and cupric sulphate and mercurous sulphate are added to the mixture as reaction-promoting agents.

Dow Chemical Co. E.P. 526,387, 17.9.40. Appl. 14.3.39. Separation of butadiene from mixtures thereof with other hydrocarbons having four carbon atoms by fractionally distilling the liquefied hydrocarbons in the presence of liquid ammonia.

Edeleanu Gesselschaft m.b.H. E.P. 526,477, 19.9.40. Appl. 17.3.39. Improved process for the extraction and dewaxing of mineral oils. The improvement lies in interposing between the extraction plant and the dewaxing plant a compensating evaporator in which such a proportion of the sulphur dioxide contained in the raffinate solution is evaporated that a relatively small and constant addition of the solvent prevents liquid phase formation and the degree of dilution of the hydrocarbon mixture most suitable for the dewaxing process is not exceeded.

E.I. Du Pont de Nemours & Co. E. P. 526,496, 19.9.40. Appl. 17.3.39. Purification of an aliphatic dinitrile by bringing it into contact with a solution containing sulphurous acid or a water-soluble sulphite.

C. T. Anné. U.S.P. 2,213,798, 3.9.40. Appl. 18.6.38. Continuous method of removal of asphalt from oil in the presence of a solvent adapted to precipitate asphaltic constituents. H. B. M.

Chemistry and Physics.

1482. Polycyclic Aromatic Hydrocarbons. XXIV. J. W. Cook and R. H. Martin. *J. chem. Soc.*, 1940, 1125–1127.—Certain homologues of 1 : 2-benzanthracene give photo-oxides when oxygen is passed through their dilute solutions in carbon disulphide, exposed to light. This behaviour appears unrelated to the carcinogenic activity of the hydrocarbons. T. C. G. T.

1483. Dehydrogenation. II. The Elimination and Migration of Methyl Groups from Quaternary Carbon Atoms during Catalytic Dehydrogenation. R. P. Linstead and S. L. S. Thomas. *J. chem. Soc.*, 1940, 1127–1134.—Hydronaphthalenes containing methyl groups attached to quaternary carbon atoms have been dehydrogenated in the vapour phase over metallic catalysts. Over platinized charcoal the main reaction was dehydrogenation, accompanied by a straightforward elimination of methyl from the quaternary atom. When certain hydronaphthalenes were passed over platinized or palladized asbestos the reaction was accompanied by a migration of methyl to an adjacent carbon atom.

The catalytic dehydrogenation of various alkyltetralins in the liquid phase has also been examined. Those without a quaternary carbon atom were rapidly and quantitatively dehydrogenated. Those with such an atom were practically unaffected. T. C. G. T.

1484. Polycyclic Aromatic Hydrocarbons. XXV. 1- and 2-Alkyl Derivatives of 3 : 4-Benzphenanthrene. J. L. Everett and C. L. Hewett. *J. chem. Soc.*, 1940, 1159–1162.—Continuing the research into the carcinogenic properties of aromatic hydrocarbons, the authors have prepared derivatives of 3 : 4-benzphenanthrene. T. C. G. T.

1485. Mechanization of Polymerization. IV. Experiments Relating to the Constitution of the Solid Dimeride and the Liquid Trimeride of $\beta\gamma$-Dimethylbutadiene, and to the Separation of the Higher Polymerides. E. H. Farmer and J. F. Martin. *J. chem. Soc.*, 1940, 1169–1176.—The solid dimeride $C_{12}H_{20}$ obtained from $\beta\gamma$-dimethylbutadiene is possibly one of two methylenetetramethylbi*cyclo*heptanes. The trimeric portion of the polymeride is probably a mixture of isomeric hydrocarbons, although a part of it may be pentamethyl*iso*propenyloctahydronaphthalene. T. C. G. T.

1486. Mechanism of Polymerization. V. Dimerization of Unconjugated Pentadiene. A. Ahmad and E. H. Farmer. *J. chem. Soc.*, 1940, 1176–1178.—The pentadiene, when heated above 200° C., polymerizes like certain drying-oils. The product is a mixture of low-molecular polymerides, in which dimeride and timeride predominate. The dimeride consists mainly of 1-methyl-2-allyl*cyclo*hexene. A mechanism is suggested. T. C. G. T.

1487. Hydrogenation of Ethylene at Surfaces of Certain Oxides. I. Zinc Oxide and Zinc Chromite. J. R. Woodman and H. S. Taylor. *J. Amer. chem. Soc.*, 1940, **62**, 1393–1396.—Zinc oxide and chromite catalyse the hydrogenation of ethylene at and above room temperature. At 56° C. the reaction velocity on the oxide is independent of hydrogen, ethylene, and ethane partial pressures. On zinc oxide at 56° the number of active centres decreases owing to the deposition of polymers or to the decomposition of ethylene at the surface. This poison can be oxidized by air at 150° and above, and the product removed by evacuation at 450° C.

This is evidence that oxygen is strongly adsorbed on the active centres of zinc oxide above 150° C. Reduction of the zinc oxide takes place above 218°.

Ethylene polymerizes on zinc oxide at 218° without appreciable formation of permanent gases. At 445° polymerization is rapid, but accompanied by the formation of hydrogen and methane.

Small quantities of water vapour poison the surface of the zinc oxide completely at 56° and even at 400° C. T. C. G. T.

1488. Hydrogenation of Ethylene at the Surfaces of Certain Oxides. II. Molybdenum Oxide Compounds. J. F. Woodman, H. S. Taylor, and J. Turkevich. *J. Amer. chem. Soc.*, 1940, **62**, 1397–1399.—A catalyst prepared by the decomposition and reduction of ammonium nickel molybdate at 300° C. is active at — 80° in the hydrogenation of ethylene. Magnetic susceptibility measurements, together with poisoning experiments using hydrogen sulphide, have suggested that this activity is due to metallic nickel, very highly dispersed.

Catalysts prepared from ammonium phosphomolybdate and ammonium paramolybdate have shown negligible activity for ethylene hydrogenation below 256° C.

T. C. G. T.

1489. Intermediate Complexes in the Friedel and Crafts Reaction. J. R. Norris and J. E. Wood. *J. Amer. chem. Soc.*, 1940, **62**, 1428–1432.—The preparation and some properties of the complexes having the following formulæ are described: $Al_2Br_6 \cdot s\text{-}C_6H_3(CH_3) \cdot HBr$, $Al_2Br_6 \cdot s\text{-}C_6H_3(C_2H_5)_3 \cdot C_2H_5Br$, $Al_2Br_6 \cdot s\text{-}C_6H_3(CH_3)_3 \cdot C_2H_5Br$. The complex $Al_2Br_6 \cdot s\text{-}C_6H_3(C_2H_5)_3 \cdot HBr$ did not react with CO_2 at 60 atmospheres, but a mixture of Al_2Br_6 and $s\text{-}C_6H_3(CH_3)_3$ under the same conditions gave high yields of the dimesityl ketone and *s*-trinethylbenzoic acid.

When a complex which contains aluminium chloride and benzene, toluene, triethylbenzene, or nitrobenzene was treated with hydrogen bromide at room temperature an exchange of halogen atoms took place. When the complex which contained aluminium bromide was treated with hydrogen chloride exchange also took place.

When acetyl chloride was condensed with benzene by means of aluminium bromide 77 mole-% of the hydrogen halides formed were hydrogen bromide. When acetyl bromide and aluminium chloride were used the mole-% of hydrogen chloride was 70.

T. C. G. T.

1490. The Redistribution Reaction. VIII. The Relative Affinity of Mercury and Lead for Methyl and Ethyl Radicals. G. Calingaert, H. Soroos, and G. W. Thomson. *J. Amer. chem. Soc.*, 1940, **62**, 1542–1545.—Mixture of diethyl mercury with tetramethyl lead, and of dimethyl mercury with tetraethyl lead containing equal proportions of methyl and ethyl radicals and equivalent amounts of mercury and lead, undergo redistribution and yield the same random equilibrium mixture, in which the mercury shows a greater relative affinity than lead for methyl with respect to ethyl radicals.

T. C. G. T.

1491. The Redistribution Reaction. IX. Redistribution of Halides and of Esters. G. Calingaert, H. Soroos, V. Hnizda, and H. Shapiro. *J. Amer. chem. Soc.*, 1942, **62**, 1545–1547.—Experimental data are presented for the redistribution reaction in the following six halide or ester systems: ethylene dibromide and ethylene dichloride, ethyl chloride and ethylene dibromide, ethyl bromide and ethylene dichloride, dimethyl oxalate and dibutyl oxalate, ethyl acetate and methyl butyrate, furfuryl acetate and ethyl furoate. T. C. G. T.

1492. Hexa-*p*-alkylphenylethanes. X. *p*-*cyclo*Hexyl Derivatives of Hexaphenylethane. C. S. Marvel and C. M. Himel. *J. Amer. chem. Soc.*, 1940, **62**, 1550–1553.—The dissociation of di-*p*-*cyclo*hexylphenyltetraphenylethane, tetra-*p*-*cyclo*hexylphenyldiphenylethane, and hexa-*p*-*cyclo*hexylphenylethane into five radicals has been measured by the magnetic susceptibility method. The dissociation in benzene at 26–28° is 9 ± 1% in 0·1M solution, 10 ± 1% in 0·05M solution, and 50 ± 7% in 00·1M solution, respectively. T. C. G. T.

1493. Hydrogen Fluoride as a Condensing Agent. XI. The Reaction of Alcohols and Ethers with Benzene. J. H. Simons and S. Archer. *J. Amer. chem. Soc.*, 1940, **62**, 1623–1624.—Additional studies of the hydrogen fluoride catalysed alkylations have been carried out using primary, secondary, and tertiary alcohols and their ethers. Good yields were obtained with *sec.* and *tert.* compounds at room temperature, but with primary compounds except benzyl alcohol and ether 100° C. was necessary.

The alcohols were found to react more readily than the corresponding chlorides, but when aluminium chloride is used the chlorides react more readily than the alcohols.

It is considered that the ease of reaction of benzyl alcohol is a strong argument against the hypothesis that an olefine is an intermediate in the reaction.

T. C. G. T.

1494. Hydrogen Fluoride as a Condensing Agent. XII. Reactions of Methyl, Ethyl, and Phenyl Compounds with Benzene and its Derivatives. J. H. Simons and H. J. Passino. *J. Amer. chem. Soc.*, 1940, **62**, 1624.—Hydrogen fluoride has been found to be a suitable catalyst for ethylation, but not for methylation or phenylation.

T. C. G. T.

1495. Polymethyl Aromatic Hydrocarbons. I. Synthesis of 1 : 2 : 4-Trimethylnaphthalene and 1 : 2-, 1 : 3-, and 1 : 4-Dimethylnaphthalene. M. C. Kloetzel. *J. Amer. chem. Soc.*, 1940, **62**, 1708–1713.—1 : 3- and 1 : 4-dimethylnaphthalene and 1 : 2 : 4-trimethylnaphthalene have been synthesized from β-benzoylpropionic acid. A similar synthesis starting from 1-tetralone is described for 1 : 2-dimethylnaphthalene.

T. C. G. T.

1496. Spectrographic Study of the Formation of 1 : 3-*cyclo*Hexadiene from *cyclo*Hexene. H. Stücklen, H. Thayer, and P. Willis. *J. Amer. chem. Soc.*, 1940, **62**, 1717–1719.—Ultra-violet absorption spectra measurements indicate the presence of traces of 1 : 3-*cyclo*hexadiene and benzene in all samples of *cyclo*hexene prepared by the dehydration of *cyclo*hexanol. Benzene can be removed by fractionation, but long-continued distillation increases the diene content. The latter may be removed by maleic anhydride. The diene is also formed by the action of ultra-violet light and by sunlight. T. C. G. T.

1497. Spreading of Volatile Organic Liquids on Water in the Presence of Unimolecular Films. E. R. Washburn and C. P. Keim. *J. Amer. chem. Soc.*, 1940, **62**, 1747–1749.—A method has been developed for the measurement of spreading pressures by means of a film pressure balance and a small quantity of the spreading liquid put on a unimolecular film. By the method the following Harkins' spreading coefficients dynes/cm. were obtained : benzene 8·94, toluene 6·84, and nitrobenzene 3·76. The unimolecular films were palmitic or stearic acid. T. C. G. T.

1498. Acetylenic *cyclo*Hexane Derivatives. C. S. Marvel, R. Mozingo, and R. White. *J. Amer. chem. Soc.*, 1940, **62**, 1880.—Four new derivatives have been prepared : 1-(3-methyl-1-pentyn-3-ol)-2-methyl*cyclo*hexanol, 1-(3-methyl-3-penten-1-ynyl)-2-methyl*cyclo*hexene, 2-methyl-1 : 1′-di*cyclo*hexanolacetylene, and 2-methyl-1 : 1′-di*cyclo*hexenylacetylene. T. C. G. T.

1499. Heat Capacity and Entropy, Heats of Fusion and Vaporization and the Vapour Pressure of *n*-Butane. J. G. Aston and G. H. Messerly. *J. Amer. chem. Soc.*, 1940, **62**, 1917–1923.—The heat capacity of *n*-butane has been determined from 12° K. to its boiling point. The transition point of *n*-butane is 107·56 ± 0·1° K., the melting point is 134·87 ± 0·05° K., and the boiling point is 262·66 ± 0·03° K. The heats of transition, fusion, and vaporization at the boiling point are, respectively, 494 ± 1, 1113·7 ± 2, and 5351 ± 15 cal./mole. The vapour pressure of *n*-butane from 210° K. to the boiling point is given by $\log_{10} P$ mm. $= 2352{\cdot}900/T - 16{\cdot}49230 \log_{10} T + 0{\cdot}01111869\,T + 48{\cdot}64763$.

The molal entropy of the ideal gas at the boiling point calculated from the experimental data is 72·05 ± 0·2 e.u. The molal entropies of the ideal gas and the superheated liquid at 298·16° K. are, respectively, 74·0 ± 0·2 and 55·2 ± 0·3 e.u.

The rotation of the ethyl groups of *n*-butane is hindered by a potential of the order of 30,000 cal./mole. Reliable thermodynamic functions for *n*-butane at high temperatures may be obtained despite uncertainty in the vibrational frequency assignment.

T. C. G. T.

1500. Heat Capacity and Entropy, Heats of Fusion and Vaporization and the Vapour Pressure of *iso*Butane. J. G. Aston, R. M. Kennedy, and S. C. Schumann. *J. Amer. chem. Soc.*, 1940, **62**, 2059–2063.—The heat capacity of *iso*butane has been determined from 12° K. to the normal boiling point. The melting point is 113·74° K. and the boiling point 261·44° K. The heats of fusion and vaporization at the boiling point are 1085·4 and 5089·6 cal./mole, respectively. The vapour pressure of *iso*butane from 200° K. to the boiling point is given by $\log P$ mm. $= -1716{\cdot}687/T - 6{\cdot}38879 \log T + 0{\cdot}0024132T + 24{\cdot}260325$.

The molal entropy of the liquid at the boiling point is 47·94 ± 0·10 e.u. The molal entropy of the ideal gas at the boiling point calculated from the experimental data is 67·52 ± 0·10 e.u. The molal entropy of the liquid at 298·16° K. extrapolated from the experimental data is 52·09 ± 0·10 e.u., whilst that of the ideal gas is 70·43 ± 0·15 e.u.

T. C. G. T.

Analysis and Testing.

1501. Measurements of the Viscosities of Oils under Reservoir Conditions. C. R. Hocott and S. E. Buckley. *Petrol. Tech.*, Aug. 1940, A.I.M.M.E. Tech. Pub. No. 1220, 1–6.—A simple rolling-ball viscometer, the construction of which is described, has been used successfully for routine determinations of the viscosity of subsurface samples of oil under reservoir temperatures and pressures. This instrument is adaptable to the measurement of a wide range of viscosities by varying the roll angle, the diameter of the roll tube, or the size of the ball.

A large number of subsurface oil samples have been examined, and it has been found that the viscosity of an oil is a minimum at the saturation pressure, and that the release of dissolved gas attending reduction of the reservoir pressure results in increased viscosity of the residual oil. Because of the nature of the variations of the viscosity with pressure, direct measurements on subsurface samples appear to be the only feasible method for determining the viscosity of any particular oil under reservoir conditions.

G. D. H.

1502. Development of Modified Quantitative Oliensis Spot Test. A. H. Benedict. *Proc. Assoc. Asph. Paving Techn.*, 1940, **2**, 13–43.—Owing to the tendency of certain high-sulphur-content Californian bitumens, having good service records, to give positive results in the Oliensis spot test an investigation was made of various methods of detecting overheating of bitumen. Blends of Californian bitumen and severely cracked material were examined for relationship between solubility in petroleum ether and proportion of cracked material; degree of unsaturation as measured by: (*a*) aniline point, bromine and iodine numbers, and absorption in sulphuric acid of vacuum distillate from the blends, (*b*) photochemical tests using daylight and ultra-violet light, (*c*) change in characteristics due to air blowing; relationship between physical properties of asphaltenes and proportion of cracked material as indicated by acetone solubility and molecular weight; quantitative Oliensis spot test.

The only method which appeared capable of being adopted for the detection of overheating of bitumen was the Oliensis test, and further investigation was devoted to the development and determination of the advantages and limitations of the modified quantitative Oliensis test. Various solvents were examined with a view to finding a solvent which would give more accurate results and greater sensitivity to small amounts of cracked material than naphtha; normal heptane was found to meet these requirements and it was decided to adopt this solvent and a xylene equivalent of 35% as a tentative dividing line between suitable and unsatisfactory bitumens.

A. O.

1503. Identification of Bitumen in Paving Mixtures. A. W. Attwool and D. C. Broome. *Proc. Assoc. Asph. Paving Techn.*, 1940, **2**, 60–76.—An account is given of investigations of colorimetric methods of identifying bitumens and of the development of an instrument for this purpose termed a Panchrometer. A description of the instrument and method of operation is given and results obtained with various bitumens are tabulated. It is stated that in addition to differentiating between various types and grades of bitumen it is possible to identify mixtures and to determine the proportions and nature of the material used as flux with Trinidad asphalt. The Panchrometer may also be used to detect changes in bitumen resulting from overheating or weathering and to detect sedimentation in asphalt cements whether containing filler or otherwise. A further application of the instrument is in the study of the reaction between different types of bitumen and mineral aggregate. A. O.

Lubricants and Lubrication.

1504.* Machine Tool Oiling. Anon. *Auto. Engr*, 1940, **30** (397), 149.—With increasing accuracy demanded of machine tools, the complexity of units has increased, as also has the number of points requiring lubrication. Whereas the lubrication used to be left to the operator, sometimes resulting in over-lubrication and waste, this has now been largely replaced by automatic or mechanical methods.

With the use of circulating systems oils of lower viscosity can be used, resulting in lower fluid friction losses and lower consumption. An example of such a case is given, together with a description of centralized mechanical lubrication designed for use with both oil and grease. Alternatives to the latter are centralized hand-operated and air-operated systems, the latter employing electric timing devices for automatically starting and stopping the compressor. Oils of all viscosities can be handled, and there is automatic compensation for changes in temperature. H. L. W.

1505.* Cutting Fluids. Anon. *Auto. Engr*, 1940, **30**, (398), 175.—In view of the small cost of cutting fluids in relation to total production costs, it is surprising that so little attention is paid to their use; the advances made in machine tools, cutting speeds, etc., could not have been made without corresponding advances in cutting fluids.

It is suggested that the power exerted at the tip of the tool varies directly with cutting speed, a factor which has created problems for the cutting fluid manufacturers. With the increase in demand for and improvements in the methods of measuring surface finish the cry for high-quality work has been met without any rise in unit costs, to which cutting fluids have contributed in no small measure. As the fluid is primarily used to prolong tool life, a balance has to be struck between its properties as a coolant and as a lubricant. This naturally varies according to the machine and the work being done, and a proper selection of fluid will have an influence on tool life and, therefore, on production costs.

Although opinions differ as to the use of fluids with carbide-tipped tools, it is felt that, if the rate and direction of flow were properly controlled, much of the opposition to the use of fluids would disappear, and it appears that costs would be reduced. Tests in which surface roughness was measured have shown that the use of cutting fluids materially reduced surface roughness, and, therefore, the approach to true planar smoothness.

Advance in the manufacture of cutting oils has, moreover, made it possible to reduce considerably the number of different fluids required to cover the use of a wide range of metals and operations. The practice of different factories varies considerably, soluble oils and neat cutting oils being used for identical operations. In spite of such wide divergencies, general recommendations as to the type of fluid to be used can be given. In some cases where dry machining has been used, considerable saving has been effected by wet cutting; but this has required the alteration of tool rake, etc., to give maximum benefit. The quantity of fluid is important, a weak flow of little volume frequently giving worse results than dry machining. Alkaline media should not be used with aluminium, but a soluble oil has been developed which can be used for grinding non-ferrous metals, including aluminium.

The published research work on cutting operations is mainly American, and has shown that the saving in power can be considerable. American practice has been outlined in a paper to the S.A.E., which gives the results of a co-operative investigation carried out by an independent group of investigators. A table is reprinted from the paper showing the requirements for various operations.

The use of soluble oils is discussed, the merits and demerits of the various types being analysed. Examples of the saving in tool life, particularly with the clear type of emulsion, are given. Although straight mineral oils are still used for some light operations, the neat cutting oils used nowadays are mainly sulphurized oils. The viscosity of these oils is of considerable importance, and savings have been proved by using an oil of lower viscosity; the use of summer and winter grades has even been introduced.

Although cutting oils are frequently blamed as the cause of skin diseases, it has been shown that personal cleanliness is the greatest safeguard. Certain types of oil do, however, favour bacterial growth, and therefore act as carriers. It is doubtful if the oil is itself to blame, and investigations frequently show that the infection has been introduced through lack of cleanliness, for which a cleaning unit has been found an advantage. The opinion is expressed that by drawing on the vast fund of experience of the oil companies users would be doing a great service to industry. H. L. W.

1506. Patents on Lubricants and Lubrication. L. C. Brunstrum. U.S.P. 2,211,921, 20.8.40. Appl. 17.5.37. Preparation of a gear lubricant by making a substantially neutral cup grease and thereafter grading a blend of asphalt containing unneutralized asphaltogenic acids, aluminium soap, and oil. Neutralization of the asphaltogenic acids is thus avoided.

C. E. Andrews and M. R. Fenske. U.S.P. 2,211,944, 20.8.40. Appl. 3.6.38. Conversion of high-viscosity lubricating oils to oils of lower viscosity, but having substantially the same viscosity index. A mixture of the high-viscosity oil and methanol is heated at a temperature between 300° and 400° C. under a pressure of 250–2000 lb./sq. in. in the presence of a reducing catalyst.

W. B. Hendrey. U.S.P. 2,212,020, 20.8.40. Appl. 1.4.37. Preparation of a lubricant consisting of a mineral lubricating oil containing 0·1–1·0% by weight of lecithin and 0·5–5·0% by weight of lanolin in order to improve oiliness and anti-corrosive properties.

W. B. Hendrey, U.S.P. 2,212,021, 20.8.40. Appl. 1.4.37. Preparation of a lubricating-oil composition consisting of a mineral lubricating oil, 0·1–1·0% of a phosphatide and 1–5% of a fatty oil.

M. T. Flaxman. U.S.P. 2,212,899, 27.8.40. Appl. 20.9.37. Preparation of a sulphurized lubricating oil consisting of a mineral lubricating oil and from ½ to 20% jojoba oil containing combined sulphur.

C. F. Prutton and A. K. Smith. U.S.P. 2,213,532, 3.9.40. Appl. 31.12.32. Preparation of a lubricant consisting of a major proportion of a hydrocarbon oil and a minor proportion of a halogenated aromatic hydroxy-compound.

B. H. Lincoln and G. D. Byrkit. U.S.P. 2,213,804, 3.9.40. Appl. 23.2.38. Preparation of a lubricating oil consisting of a hydrocarbon oil and a small quantity of an organic compound containing at least two sulphur atoms in a heterocyclic ring.

E. W. Cook. U.S.P. 2,213,856, 3.9.40. Appl. 6.7.38. Lubricating bearing surfaces having the corrosion susceptibility of cadmium-silver, cadmium-nickel, and copper-lead alloys. A lubricant having incorporated a sufficiently oil-soluble alkyl arsenite is applied to the bearing surfaces in corrosion inhibiting proportions.

B. H. Lincoln, A. Henriksen, and J. W. Wolfe. U.S.P. 2,213,988, 10.9.40. Appl. 16.9.38. Preparation of a lubricating composition containing a major proportion of a mineral oil and a halogenated thio-ether.

F. R. Moser. U.S.P. 2,214,379, 10.9.40. Appl. 22.11.37. Preparation of an extreme-pressure lubricant containing a major proportion of a mineral lubricating oil and a minor quantity of mixed organic sulphonyl halides prepared from an aromatic normally liquid mineral-oil fraction soluble in liquid SO_2 and boiling substantially above the gasoline range.

R. Cannon and K. A. Varteressian. U.S.P. 2,214,401, 10.9.40. Appl. 2.3.37. Preparation of a lubricating oil in which is incorporated a quantity of oxalic acid sufficient substantially to stabilize the oil.

K. A. Varteressian. U.S.P. 2,214,443, 10.9.40. Appl. 20.2.37. Preparation of a lubricating oil having a lake-forming substance in solution therein in quantity sufficient to stabilize against bearing corrosion.

K. A. Varteressian. U.S.P. 2,214,444, 10.9.40. Appl. 2.3.37. Stabilization of a lubricating oil by adding thereto sufficient of a stabilizing substance resulting from attaching three phenolate groups to a single arsenic atom to inhibit corrosion.

H. B. M.

Gas, Diesel and Fuel Oils.

1507. Patents on Gas, Diesel and Fuel Oil. Standard Oil Development Corp. E.P. 525,962, 9.9.40. Appl. 1.3.39. Continuous process for the production of gasoline of high octane number. A liquid mixture of *iso*butene and an olefine is fed into a pool of concentrated sulphuric acid and the temperature of the pool maintained within the range 60–175° F. under a pressure substantially equal to the vapour pressure of *iso*butane at the reaction temperature. Any increase in temperature of the reaction mass causes vaporization of the *iso*butane. Subsequently the vaporized *iso*butane is withdrawn from the pool, liquefied, and returned to the fresh feed. Normally liquid substantially saturated hydrocarbons suitable for motor fuel are continuously withdrawn from the pool.

Texaco Development Corp. E.P. 526,149, 11.9.40. Appl. 9.3.39. Process for the manufacture of high anti-knock gasoline hydrocarbons by subjecting *iso*butane and normally gaseous olefines heavier than ethylene to the action of strong sulphuric acid, whilst maintaining an excess of *iso*butane.

T. W. Pfirrmann. U.S.P. 2,213,407, 3.9.40. Appl. 10.7.37. Process for improving the ignition properties of diesel power fuels by treating in the liquid phase with a gas comprising oxygen in such proportions and for such a reaction period that no substantial proportions of oxygen-containing hydrocarbon compounds are formed and the boiling curve of the distillable portion of the original material is substantially unaltered.

E. Lieber. U.S.P. 2,214,059, 10.9.40. Appl. 14.7.38. Fuel for diesel engines consisting essentially of a hydrocarbon fuel with which is blended a minor proportion of a tertiary alkyl nitrosyl mercaptan. H. B. M.

Asphalt and Bitumen.

1508. Report of Committee on Anti-Skid Properties of Road Surfaces. G. E. Martin. *Highway Res. Board, Proc. Nineteenth Annual Meeting,* 1939, 126–128.—A preliminary account is given of an investigation of the anti-skid properties of thirty-six road surfaces which included Portland cement concrete, asphaltic concrete, bituminous macadam, and oil mat, ranging from surfaces not opened to traffic to surfaces in use for eighteen years.

The apparatus consisted of a specially constructed trailer towed behind a light truck, with a dynamometer placed in the towing bar to record the tractive resistance of the trailer. The tests were made by locking one wheel of the trailer while towing at a constant speed, speeds of 10 to 40 miles per hour being used under wet and dry conditions. Retreaded tyres were used to obtain a smooth surface, and a sprinkling tank was driven ahead of the test vehicle for tests on wet surfaces.

The main series of tests was made with a wheel-load of 800 lb., but a few tests were made with a load of 400 lb. It is stated that the tests confirm that any of the pavements are satisfactory at reasonable speeds and under dry conditions, but at high speeds and with wet surfaces variations in skid resistance were observed. Sand-textured surfaces having coefficients of friction of 0·40–0·60 when dry drop to values of 0·20–0·30 when wet, whereas coarser-textured surfaces are only slightly affected by water. Surfaces which permit the draining of water are more skid-resistant when wet than when dry.

The coefficient of friction decreased from 25 to 40% on dry surfaces and from 15 to 25% on wet surfaces when the wheel-load was doubled.

Tests of the length of skid of a car with wheels locked, on eleven types of surfacing are also reported. The hydraulic brakes on the car were operated by air and the length of skid was determined by pistol-shot marks on the pavement. Tyres which had been worn smooth were employed and surfaces were wetted prior to tests. Results are tabulated. A. O.

1509. Use of Tar in Base Stabilization. T. F. Loughborough, A. C. Miller, N. F. Schafer, and A. C. Tilley. Arranged P. Rapp. *Highway Res. Board, Proc. Nineteenth Annual Meeting*, 1939, 504–516.—Details are given of costs and methods of construction of tar-stabilized road bases. A. O.

1510. Fundamentals in Asphalt Heating Equipment. H. G. Levitt. *Proc. Assoc. Asph. Paving Techn.*, 1940, **2**, 1–12.—The author discusses the factors involved in the design and operation of asphalt heating equipment.

The results of examination of two commercial heaters are considered. It is thought that direct heating has certain advantages, and risk of local overheating may be eliminated by specifying operation and design limitations. A. O.

1511. Characteristics of Various Asphalts as Regards Emulsification. R. M. Heino. *Proc. Assoc. Asph. Paving Techn.*, 1940, **2**, 77–85.—It is pointed out that differences in crudes and methods of refining affect the ease of emulsification of asphaltic bitumen as well as the mechanical, thermal, and chemical properties. This is attributed to variation in the amounts of easily saponified material in the bitumens, and generally bitumens containing small amounts are more difficult to emulsify; the estimation of these substances is very difficult.

Discussing the results of tests on emulsions prepared from various types of bitumen, it is stated that the residues from distillation may differ in penetration, although the same bitumen has been used in two emulsions, while different bitumens of the same grade may also give residues of different penetration. The ductility of the residue may be affected by variation in penetration, amount and nature of stabilizing agent, or by blending bitumens. The demulsibility also depends on the amount and nature of the stabilizing agent used. The author inquires whether viscosity is a function of absorption, adsorption, and free liquid, or of bitumen content and particle size. Settlement is said to vary with penetration and specific gravity, and may be affected by the nature of the bitumen. The cement test is stated to be a function of the bitumen when differences in ease of emulsification are shown, whilst dehydration depends on the penetration and specific gravity of the bitumen and on the nature and proportion of stabilizing agent used. A. O.

1512. Surface Treatment Studies. T. E. Shelburne. *Proc. Assoc. Asph. Paving Techn.*, 1940, **2**, 44–59.—A brief account is given of surface-treatment investigations in Indiana and of investigation of the crushing of bituminous-coated aggregates under road rollers.

The term surface treatment is applied to the process of road mixing aggregates and fluid bituminous materials to obtain a wearing course less than 1 in. in thickness.

Surface-treatment failures were extensive in the spring of 1936, and investigations were undertaken to determine the cause and, if possible, to extend the life of the surfaces. Few surfaces had lasted more than 2 years, although it was considered that the average life should be at least 3 years. Samples were examined for thickness, condition of surface, bitumen content, and sieve analysis, and an attempt was made to correlate bitumen content and surface area of the aggregate with the behaviour of the treatment, but no definite relationship could be established.

A lack of uniformity of texture was observed, bitumen content ranged from 3 to

12%, and surface area of the aggregate varied from 1000 to over 6000 sq. cm./100 gms., whereas the original aggregate had a surface area of approximately 300 sq. cm./100 gm.

The most prevalent type of failure, excluding base failure, was ravelling, and it was found that treatments constructed in late autumn and under adverse weather conditions ravelled more than those constructed earlier in the season.

In order to determine the effect of type, quantity, and method of application of bituminous material and size and amount of aggregate, fifty-one test sections 1000 ft. in length were constructed with three types of bituminous material and with aggregates of different gradings from two sources.

Measurements of texture were made with a profilometer.

The degradation of surface treatment aggregates was investigated by examination at periodic intervals of samples from test roads constructed with various aggregates coated with liquid bitumen and emulsion. Degradation under the roller was also investigated by examination of coated and uncoated aggregates compacted on flexible and rigid bases by means of 5- and 10-ton rollers.

The results indicated that the rate of degradation is greater with soft than with hard aggregates and also greater with large- than with small-sized aggregate from the same source. Particle shape influenced degradation, crushed gravel being affected to a greater extent than uncrushed gravel from the same source. Degradation under the roller was much greater on a rigid than on a flexible base, and the Los Angeles abrasive machine operated at 100 revs. gave a good indication of the amount of degradation under the roller.

Degradation during mixing, rolling, under traffic, and in the Los Angeles machine tended ultimately to correspond to Fuller's grading for maximum density. It is suggested that rolling should be reduced and a more suitable grading selected in preference to the practice of producing ultimate grading by crushing under the roller.

A. O.

1513. Patent on Asphalt. N. T. Anderson. E.P. 526,351, 17.9.40. Appl. 14.3.39. Preparation of light road-surface material consisting of a bituminous binder and a mineral aggregate consisting wholly or partly of burnt flint. H. B. M.

Special Products.

1514. Patents on Special Products. Parke Davis & Co. E.P. 526,024, 9.9.40. Appl. 12.16.39. Preparation of 5 : 5-diphenyl hydantoins or thiohydantoins in which the phenyl groups may be substituted or unsubstituted by reacting a benzoin with urea or thiourea in an alkaline solution containing an oxidizing agent.

Röhm and Haas Gesellschaft. E.P. 526,122, 11.9.40. Appl. 9.3.38. Preparation of β-chloropropionic acid by oxidizing β-chloropropionaldehyde with nitric acid of about 70% strength.

N.V. de Bataafsche Petroleum Maatschappij. E.P. 526,215, 12.9.40. Appl. 10.3.39. Production of saturated hydrocarbons with branched chains from saturated straight-chain hydrocarbons boiling below 200° C. The initial hydrocarbons are contacted at temperatures below 150° C. with double compounds of aluminium halides with aromatic hydrocarbons.

E.I. Du Pont de Nemours & Co. E.P. 526,497, 19.9.40. Appl. 17.3.39. Manufacture of aliphatic amines by bringing a liquid-heated mixture comprising essentially ammonia, hydrogen, and an aliphatic nitrile continuously into contact with a stationary solid hydrogenation catalyst.

The Mathieson Alkali Works. E.P. 526,662, 23.9.40. Appl. 24.3.39. Stabilization of alkali-metal alcoholate compositions by introducing therein a minor proportion of a catalytic anti-oxidant selected from the class consisting of amines, amino hydrochlorides, and amides.

B. W. Story. U.S.P. 2,211,798, 20.8.40. Appl. 2.3.37. Preparation of an oil composition by admixing with a highly refined petroleum oil a material selected from the class of disulphides consisting of the alkyl disulphides and the thiuram and thiazo-disulphides. The latter is added in sufficient quantity to diminish substantially the production of acidic compounds in the oil as the result of atmospheric oxidation at elevated temperature.

E. W. Gardiner and G. H. Denison. U.S.P. 2,211,972, 20.8.40. Appl. 4.10.38. Preparation of a compounded mineral oil in which is incorporated an aluminium phenate containing a substituted phenolic radical having more than 10 carbon atoms.

B. A. Dombrow. U.S.P. 2,214,634, 10.9.40. Appl. 21.5.40. Production of a soluble cutting oil base composed of a water-insoluble soap of an acid selected from the group consisting of naphthenic acids and unsaturated higher fatty acids, an emulsifier, and a mineral oil. H. B. M.

Detonation and Engines.

1515. Effect of Traffic Delays on Gasoline Consumption. A. J. Bone. *Highway Res. Board, Proc. Nineteenth Annual Meeting*, 1939, 99–125.—A study has been made of gasoline consumption and travel time on a route in Boston, Mass., the streets of which are narrow, crooked, and congested. Test runs were arranged to obtain a representative sample of busy traffic conditions; other tests were made when there was no congestion. Under ordinary conditions a driver required about 7 minutes to travel a mile, spending 2½ min. in traffic stops, 1½ min. in first or second gear, and 3 min. in high gear. The average consumption was 12·1 miles per gallon in city traffic and 18·2 m.p.g. without traffic interference.

Further tests were made on by-pass roads (Parkways) and a more congested parallel route. These showed an average consumption of 20·1 m.p.g. and an average speed of 38 m.p.h. on the Parkways compared with 18·4 m.p.g. and 25 m.p.h. on the alternative route. K. A.

Coal and Shale.

1516. Patents on Coal. Yorkshire Tar Distillers, Ltd. E.P. 525,813, 5.9.40. Appl. 28.12.38. Purification of coal-tar hydrocarbons from sulphur compounds. These are passed at an elevated temperature and in the presence of hydrogen or of a gas containing free hydrogen over or through a catalyst consisting of or containing a metallic thiomolybdate.

Yorkshire Tar Distillers, Ltd. E.P. 525,814, 5.9.40. Appl. 28.12.38. Process for the purification of coal-tar hydrocarbons from sulphur compounds in which these are passed at an elevated temperature and in the presence of hydrogen or of a gas containing free hydrogen over or through a catalyst consisting of or containing a metallic thiotungstate.

H. Dreyfus. U.S.P. 2,213,272, 3.9.40. Appl. 29.1.38. Treatment of crude liquid coal products by transforming phenolic compounds contained therein into liquid hydrocarbons without utilization of hydrogen. The crude liquid coal products are heated with a finely divided metallic zinc. H. B. M.

Economics and Statistics.

1517. Reports from Mexico, Uruguay, and Chile. Anon. *Bol. Inform. Petroleras*, May 1940, XVII (189), 51–58.—*Mexico:* A table is published showing the annual production of oil in cubic metres since the commencement in 1901, and in a note it is pointed out that a gradual recovery in production and export since the drop due to expropriation imposed by the Government is recorded, indicating, according to their statement, that the alleged boycott by the big companies has failed.

Uruguay: Decree authorizing changes in the basic prices of heavy fuel oil, gas oil, etc.

Chile: Decrees suspending import duties on coal and fixing maximum prices for sale of fuel oil and diesel oil. H. I. L.

INSTITUTE NOTES.

November, 1940.

CANDIDATES FOR ADMISSION.

The following have applied for admission to the Institute or transfer to another grade of membership, and in accordance with the By-laws the proposals will not be considered until the lapse of at least one month subsequent to the issue of this *Journal*, during which any Fellow, Member, or Associate Member may communicate by letter to the Secretary, for the confidential information of the Council, any particulars he may possess respecting the qualifications or suitability of any candidate.

The object of this information is to assist the Council in grading candidates according to the class of membership.

The names of the candidate's proposer and seconder are given in parentheses.

Bangert, Norman Roy, B.Sc., Chemist, 26, Harrington Square, London, N.W. 1. (*R. G. Stickland ; H. E. Priston*) (*Trans. from Student.*)

Bookless, Douglas Ernest, Works Manager and Director, Petroleum Engineering and Trading Co., Ltd., London. (*N. Matheson ; R. J. Stallard.*)

Fossett, Hubert, Engineer, Associated Ethyl Co., Ltd., London. (*F. H. Garner ; S. J. M. Auld.*)

Gunby, Frank, Tanker Engineer, c/o Anglo-American Oil Co., Ltd.

Howard, Frederick George, M.Sc., Chemist, I.C.I., Ltd. (*A. W. Nash ; T. G. Hunter*) (*Trans. from Student.*)

O'Connor, Dominic Desmond Taaffe, Production Engineer, Trinidad Petroleum Development Co., Palo Seco, Trinidad. (*H. V. Lavington ; L. K. White.*)

Robinson, James Terence Trimble, Refinery Superintendent, Trinidad Leaseholds, Ltd., Point-a-Pierre, Trinidad. (*B. G. Banks ; F. L. Melvill*) (*Trans. from Member.*)

Shorthose, John William, B.Sc., Chemist (Anglo-Iranian Oil Co., Ltd.), 48, Wellington Road South, Hounslow, Middlesex. (*A. E. Dunstan ; F. B. Thole.*)

Smith, Bernard William, Engineer, British Diesel Oil & Petrol Co. (*G. S. Pound ; Harold Moore.*)

Smith, Reginald John, Supervisor, Petroleum Depot. (*Trinidad Leaseholds, Ltd.*) (*J. McConnell Sanders ; W. B. Heaton.*)

Williams, Charles Garrett, M.Sc., A.M.I.Mech.E., Engineer, Shell Refining and Marketing Co. (*J. A. Oriel ; E. Le Q. Herbert.*)

Candidates for Admission as Students.

Farmaian, F. M.	The University of Birmingham Dept. of Oil Engineering and Refining.
Fellowes, M. L.	,, ,, ,, ,,
Green, S. J.	,, ,, ,, ,,
Hartley, D. A.	,, ,, ,, ,,
Jones, R. E.	,, ,, ,, ,,
Morgan, C. R.	,, ,, ,, ,,
Over, J. R.	,, ,, ,, ,,
Pearce, A. W.	,, ,, ,, ,,
Spencer, F.	,, ,, ,, ,,
Thurston, P.	,, ,, ,, ,,

Twinn, G. B. The University of Birmingham Dept. of Oil Engineering and Refining.
Weaver, A. G. T. ,, ,, ,, ,,
Whitehead, R. C. ,, ,, ,, ,,

All the above candidates are proposed by *Prof. A. W. Nash* and seconded by *Dr. A. H. Nissan.*

Keen, S. Royal School of Mines. (*S. E. Coomber ; G. D. Hobson.*)
Sasson, A. ,, ,, ,, ,,

STUDENTS' MEDAL AND PRIZE.

The Council offers a Medal and Prize (to the value of Five Pounds in books) for the most meritorious essay submitted by a Student Member of the Institute on one of the following subjects :

1. Limitations to Deep Drilling.
2. Problems of Water Shut-off.
3. Deep Well Surveying.
4. Theory and Practice of Gas-lift.
5. Theory and Practice of Water Drives.
6. Catalytic Processes for Conversion of Petroleum Fractions.
7. Commercial Utilization of Lubricating Oil Extracts.
8. Recent Developments in Thermal Cracking.
9. The production of high-octane motor spirit.
10. Economy of fuel and lubricants in engines.

Entries must be received by the Secretary of the Institute not later than 1st May, 1941.

The maximum length of the essay is not specified, but generally essays should be from 4,000 to 6,000 words in length.

Entries must be typed, and one carbon copy must be furnished in addition to the original copy. The Council is prepared to give financial assistance to students who experience difficulty in getting their MSS. typed.

BURGESS PRIZE.

Entries are also invited for the Burgess Prize (of value up to Five Pounds in books) for an essay dealing with some aspect of the economics of the petroleum industry, including the transport and distribution of petroleum products.

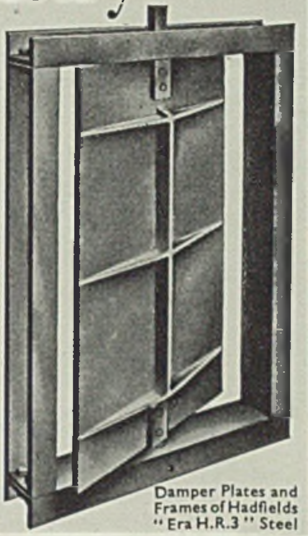
The conditions of entry for the Burgess Prize are the same as for the Students' Medal and Prize.

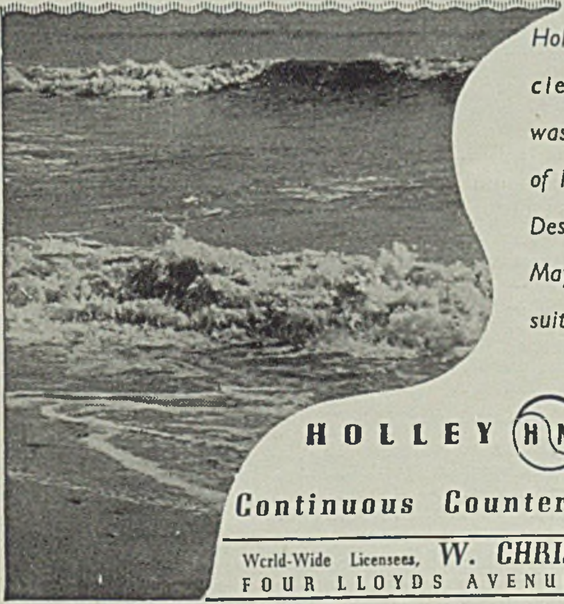
The Council reserves the right to withhold the award of either of these prizes, or to award prizes of such lesser value as it may decide.

NOMINATIONS FOR COUNCIL.

Every Fellow, Member or Associate Member of the Institute may send in writing to the Council the name of a Fellow or Member whom he desires to recommend for election to the Council. This nomination must be signed by at least nine other Fellows, Members or Associate Members, and delivered to the Secretary not later than 31st December, 1940. No member may sign more than one Nomination Paper. Nomination papers may be obtained from the Secretary.

ARTHUR W. EASTLAKE,
Honorary Secretary.





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	PAGE
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International Paint & Compositions Co., Ltd.	v
Lane-Wells Co.	—
Lucey Export Corporation	xiii
Lummus Co.	xi
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National Supply Corporation	—
Nordberg Manufacturing Co.	—
Oil and Petroleum Year Book	—
Oil Well Supply Co.	—
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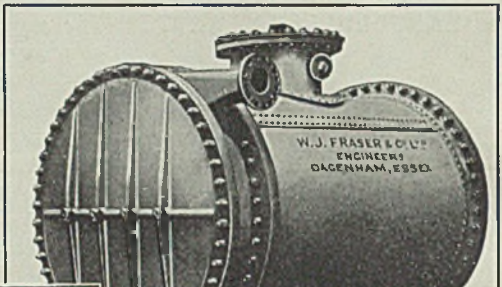
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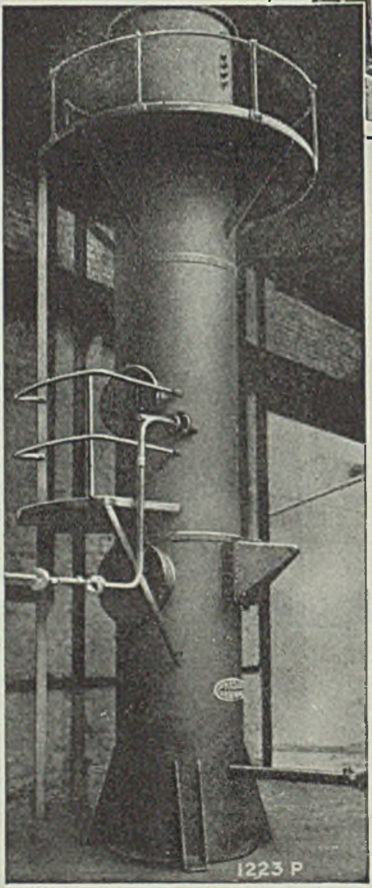
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EVERY operation with this up-to-the-minute, light-weight draw works is completed smoothly and easily.

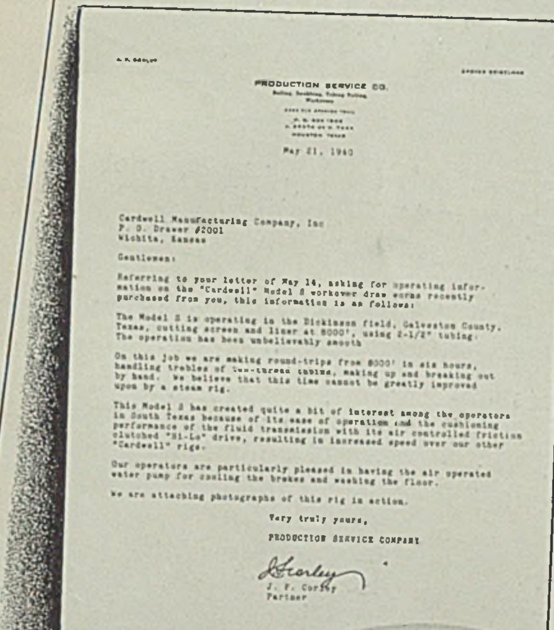
The full range of engine speeds, driving through the hydraulic transmission, is controlled by the accelerator, eliminating the shifting of gears. Gear transmissions are also available with all engines.

Smooth operating friction clutches, controlled by compressed air, provide a double range of drum speeds. This "Hi-Lo" drive make it possible to instantly double the line speed without stopping the block or rotary table.

The friction clutch driven drum and rotary table allow the drill pipe to be lifted any distance within the kelly length while the table is rotating, as when milling out liners, reaming or "drilling-up" through cavey formations.

The new "Cardwell" braking system provides dual safety brakes that can operate independently and hold the full capacity load should one brake fail.

The lightweight and one-piece design of the Model S makes it quick to rig up and easy to transport. The heat-treatment of every wearing part, to the last pin and pinhole in the controls, saves thousands of dollars in down time and repair costs.



PRODUCTION SERVICE CO.

May 21, 1940

Cardwell Manufacturing Company, Inc
P. O. Drawer #2001
Wichita, Kansas

Gentlemen:

Referring to your letter of May 14, asking for operating information on the "Cardwell" Model S workover draw works recently purchased from you, this information is as follows:

The Model S is operating in the Dickinson field, Galveston County, Texas, cutting screen and liner at 8000', using 2-1/2" tubing. The operation has been unbelievably smooth

On this job we are making round-trips from 8000' in six hours, handling trebles of ten-thread tubing, making up and breaking out by hand. We believe that this time cannot be greatly improved upon by a steam rig.

This Model S has created quite a bit of interest among the operators in South Texas because of its ease of operation and the cushioning performance of the fluid transmission with its air controlled friction clutched "Hi-Lo" drive, resulting in increased speed over our other "Cardwell" rigs.

Our operators are particularly pleased in having the air operated water pump for cooling the brakes and washing the floor.

We are attaching photographs of this rig in action.

Very truly yours,

PRODUCTION SERVICE COMPANY

J. F. Corley
Partner

● Model S is available with engines up to 225 h.p. and is recommended for rotary workover and well servicing to 10,000 feet; for rotary drilling with $3\frac{1}{2}$" drill pipe to 6,000 feet and to 4,500 feet with $4\frac{1}{2}$" drill pipe.

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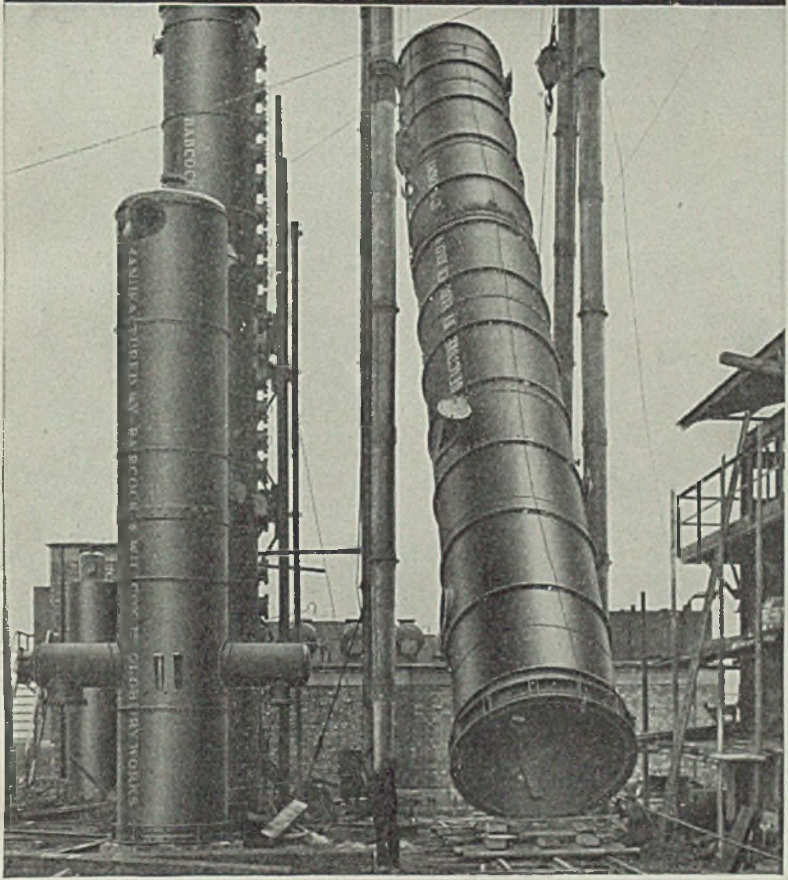

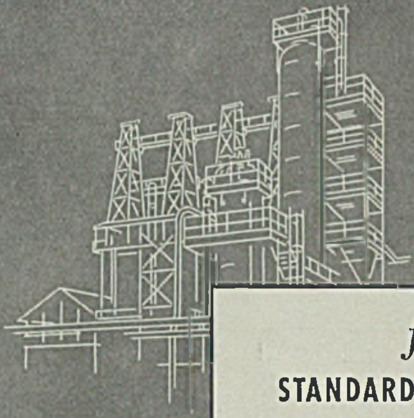

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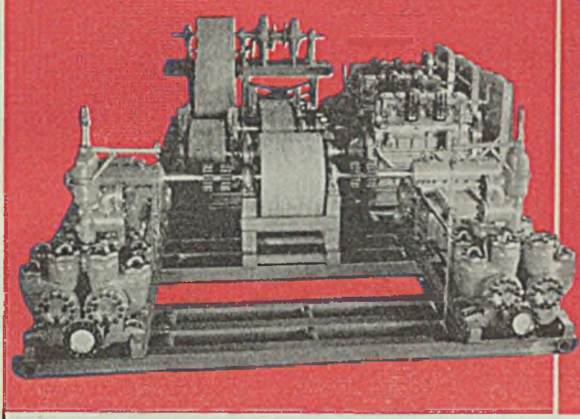
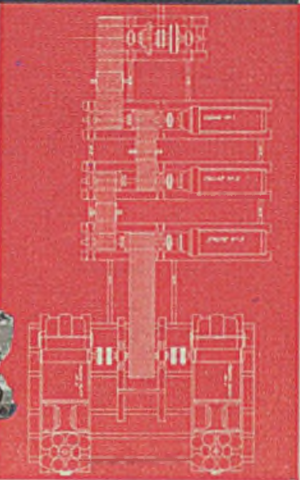
LUCEY DRILLING EQUIPMENT





This Wheland-Lucey Rotary Drilling Rig is a Diesel-mechanical three-engine hook-up of rugged construction and capable of high-powered economical operation for drilling to a depth of ten thousand feet. The hook-up makes this unit extremely flexible in operation and permits the use of either pump at will. Many variations of this hook-up are available to meet specific requirements.

The Wheland-Lucey HP-15000-CE 7¾" × 16" Power Slush Pumps shown are recommended for high-pressure deep drilling and have many valuable features assuring you a steady, uninterrupted mud flow. Here's why:

- Totally enclosed construction providing oil-bath lubrication for gears, connecting rods and crossheads.
- Cranks of alloy steel carried on four Timken bearings.
- Solid forged steel connecting rods fitted with cap over crank-pin and lined with brass for both crosshead and crank-pin.
- Pinion shaft of alloy forged steel fitted with four Timken bearings.
- Complete shaft assembly, with bearings, reversible without disturbing bearing adjustment; permits driving from either side.
- Standard or High Pressure fluid end optional.
- Exclusive Wheland patented valve.

Let us show you how a Lucey Rotary Drilling Rig will do your drilling efficiently and economically.

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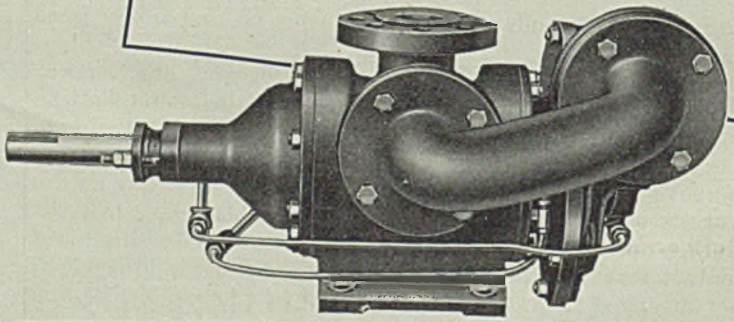


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