A Study of the Reactions that Lead to 'Knock' in the Spark-Ignition Engine

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A STUDY OF THE REACTIONS THAT LEAD TO 'KNOCK' IN THE SPARK-IGNITION ENGINE

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CONTENTS

Previous work has demonstrated that knock in the spark-ignition engine is a phenomenon confined to the last part of the charge to burn, and that it is the chemical reactions in this 'end-gas' which determine whether or not knock will occur. The purpose of this paper is to try to elucidate the nature of these reactions and to discover some of the critical chemical factors controlling the occurrence of knock. This has been done in three main ways: (*a*) the sequence of chemical reactions occurring in the 'end-gas' prior to knock has been followed by means of a specially designed electromagnetic gas-sampling valve which can abstract samples of this gas at various stages in the combustion cycle, (*b*) the effect of the addition of various substances to the cylinder charge on the knock-limited compression ratio of the engine has been determined and (*c*) a study has been made in a motored engine of the limits of cool and hot flame formation. Ricardo E. 6 variable-compression engines were used for all these investigations.

Preliminary tests with small quantities of additives, such as azomethane, alkyl nitrites and nitrates, carbon tetrachloride and chloropicrin, demonstrated that substances which would be expected to give rise to free radicals in the engine cylinder are strong pro-knocks. This and the anti-knock action of minute quantities of additives such as lead tetraethyl show the chain nature of the reactions leading to knock. Experiments are described to demonstrate that these reactions are substantially independent of the nature of the cylinder walls.

Qualitative sampling tests indicated that knock depends not so much on the formation of some new substance which was not present under non-knocking conditions but rather on the attainment of a critical rate of formation of products present under both conditions. Further experiments with additives in which various intermediate products of reaction, such as aldehydes, nitrogen peroxide and organic peroxides, were tested, showed that with normal fuels the organic peroxides were the only products which were strongly pro-knock and formaldehyde the only product which had an anti-knock effect. This led to the subsequent sampling investigation being concentrated largely on the estimation of these two products in the 'end-gases'.

A method for analyzing for organic peroxides in small concentration and in the presence of other reaction products, such as nitrogen peroxide, was developed. Use of this method with a higher paraffinic fuel showed that peroxide formation was two-stage in nature. The first stage culminated in the formation of a point of inflexion or small peak in the curve of peroxide concentration about 1° after top dead centre. In the second stage the curve normally rose again to a higher peak at about 7° l. Lead tetraethyl had a much greater depressing effect on the peak at 7° l. compared with that at 1° l. The mixture strength giving maximum knock was the same as that giving maximum peroxide concentration. Analyses were also made for aldehydes, shown to be mainly formaldehyde. The main growth of the formaldehyde formation took place in the second of the two stages of peroxide formation.

A much smaller quantity of peroxide appeared to be formed when methane was the fuel, and this was eliminated when lead tetraethyl was added to suppress the knock. Benzene formed no peroxides, and none was detected with the alkyl benzenes up to cumene.

This difference between benzene and methane on the one hand and the higher paraffinic fuels on the other in regard to peroxide formation was paralleled by the different effect of additives on the two classes of fuel. Formaldehyde was an anti-knock in the latter class and a pro-knock in the former class; acetaldehyde and benzaldehyde were ineffective in the latter but strongly pro-knock in the former; nitrogen peroxide has only a slight pro-knock effect in the latter but was strongly pro-knock in the former.

Experiments with the higher paraffinic fuels on a motored engine showed that if conditions of temperature and pressure were such as to simulate those obtaining in the 'end-gas' prior to knock, cool flames were formed at a time in the cycle approximately corresponding to the point of inflexion of the peroxide sampling curves. No cool flames were detected with benzene or methane. Bright blue flames were observed near the ignition point over certain ranges of mixture strength with benzene and methane as well as with the higher paraffins.

Non-engine work has shown the existence of two main types of combustion, namely, so-called 'low'- and 'high'-temperature types. Of these the first is associated with peroxide and cool-flame formation, ignition taking place by a two-stage process, whereas ignition of the second type is a single-stage process and not usually associated with cool flames or peroxide formation. From the evidence of (1) the peroxide analyses, (2) the experiments with additives and (3) the experiments with a motored engine, it is clear that normal fuels knock by the 'low'-temperature process but that benzene and methane knock by the 'high'-temperature process.

Experiments in which formaldehyde was used as a fuel and the effect of various additives on its knock limit determined, showed that its oxidation is best classified as of the 'high'-temperature type and yielded further understanding of the nature of the reactions leading to knock.

The effect of hydrogen as an additive with other fuels and the effect of various additives on its own highest useful compression ratio was determined. No peroxides were detected in engine samples when hydrogen was used as the fuel.

1. Introduction

Since the end of the 1914 war the phenomenon of 'knock' has been recognized as the prime factor limiting the power output and economy of the spark-ignition engine, and consequently a great deal of work has been done both to combat it (by improved fuels and engine design) and to elucidate its mechanism. A large measure of success has attended the former aim, so that the effects of the chief engine variables and design requirements can be predicted with fair accuracy. Progress towards the latter has been much slower, partly owing to the difficulty of making precise observations of knock in the cylinder and to the difficulty of reproducing knock in apparatus specifically designed as laboratory equipment.

It is now common ground among all workers in this field that the immediate cause of knock is the extremely rapid combustion of the last part of the charge to burn. The normal flame velocity and the pressure development in the cylinder prior to the inflammation of the 'end-gas' give no indication of whether knock will take place. The occurrence of knock appears to depend on the temperature-pressure-time relationship of the mixture in the 'end-gas'. Any condition which raises the temperature or pressure, such as increasing the compression ratio or the intake pressure, or any condition which increases the induction-time interval, such as increasing the length of flame path or lowering the engine speed (provided this does not affect other factors), will encourage knock. What is not so certain, however, is the exact nature of knock, i.e. whether it consists simply of the spontaneous ignition of the mixture as the pressure and temperature exceed certain critical values or whether a true detonation wave (initiated either in the flame or in the 'end-gas' and propagated because the 'end-gas' has been pre-sensitized by the reactions occurring in it) has to occur. Recent photographic studies (Miller 1947; Male 1949) of the sequence of events in the 'end-gas' would appear to support the second alternative.

Whichever of these explanations is accepted, however, it is the chemical reactions occurring in the 'end-gas' which determine whether or not knock will occur. The purpose of this paper is to try to elucidate the nature of these reactions and to discover the chemical mechanisms controlling the occurrence of knock. That preliminary oxidation of the fuel does occur under 'end-gas' conditions was demonstrated by Ricardo & Thornycroft (1928), who showed the presence of aldehydes and the effect of lead tetraethyl in reducing their concentration. About this time various workers (for example, Callendar 1926; Egerton & Gates 1926) stressed the importance of peroxides as products of this preliminary oxidation and, of the experimental demonstrations, that of Egerton, Smith & Ubbelohde (1935) was the most notable. In the present investigation improved methods of sampling and analysis have been used.

The problem has been approached in three main ways:

(1) The sequence of chemical reactions taking place in the 'end-gas' of the engine prior to knock has been studied by abstracting samples of gas at various stages in the combustion cycle and analyzing them for intermediate and final products of combustion.

(2) The effect of the addition of various substances to the cylinder charge on the knock-limited compression ratio of the engine has been determined.

(3) Pressure and temperature measurements within the engine cylinder have been made and related to the occurrence of luminosity.

These investigations are closely interrelated. Thus, substances which the sampling experiments have shown to be present as intermediate products in the combustion process have been tested as additives in the fuel. Conversely the effect on intermediate product concentrations of the addition to the fuel of substances which the additive tests have shown to exert an important effect on knock, has been determined in the sampling engine.

Some preliminary results of the sampling and additive experiments have been briefly reported elsewhere (Wheeler, Downs & Walsh 1948; Downs & Walsh 1949).

Hand in hand with the engine experiments, extensive work has been proceeding on combustion in a glass apparatus (Chamberlain & Walsh 1949*a*, *b*, *c*, 1950; Malherbe & Walsh 1950). The engine and non-engine investigations are complementary, and each has helped the understanding of the other.

2. Apparatus

2·1. *Engine*

Two Ricardo E. 6 type variable-compression engines (Downs & Robinson 1949) were used in the investigation, one for the sampling and the other for the additive tests. The engine (figure 1) had a bore of 3 in. and a stroke of $4\frac{3}{8}$ in., giving a capacity of 507 ml. The compression ratio could be varied between 4·5 and 20 while the engine was in operation.

The combustion chamber was cylindrical in shape, being bounded by the flat surfaces of the cylinder-head and piston. This gave a compact combustion chamber having good anti-knock qualities and also ensured that the chamber retained the same general form as the compression ratio was varied. The sparking plug was situated at the side of the combustion chamber, between the valves. A similar hole on the other side of the combustion chamber enabled a sampling valve, pressure-recorder or other instrument to be fitted when required. For sampling tests, an additional small hole was drilled through the cylinder-head near to the sampling valve position to enable an ionization gap to be fitted for flame arrival measurements.

2·2. *Equipment for sampling tests*

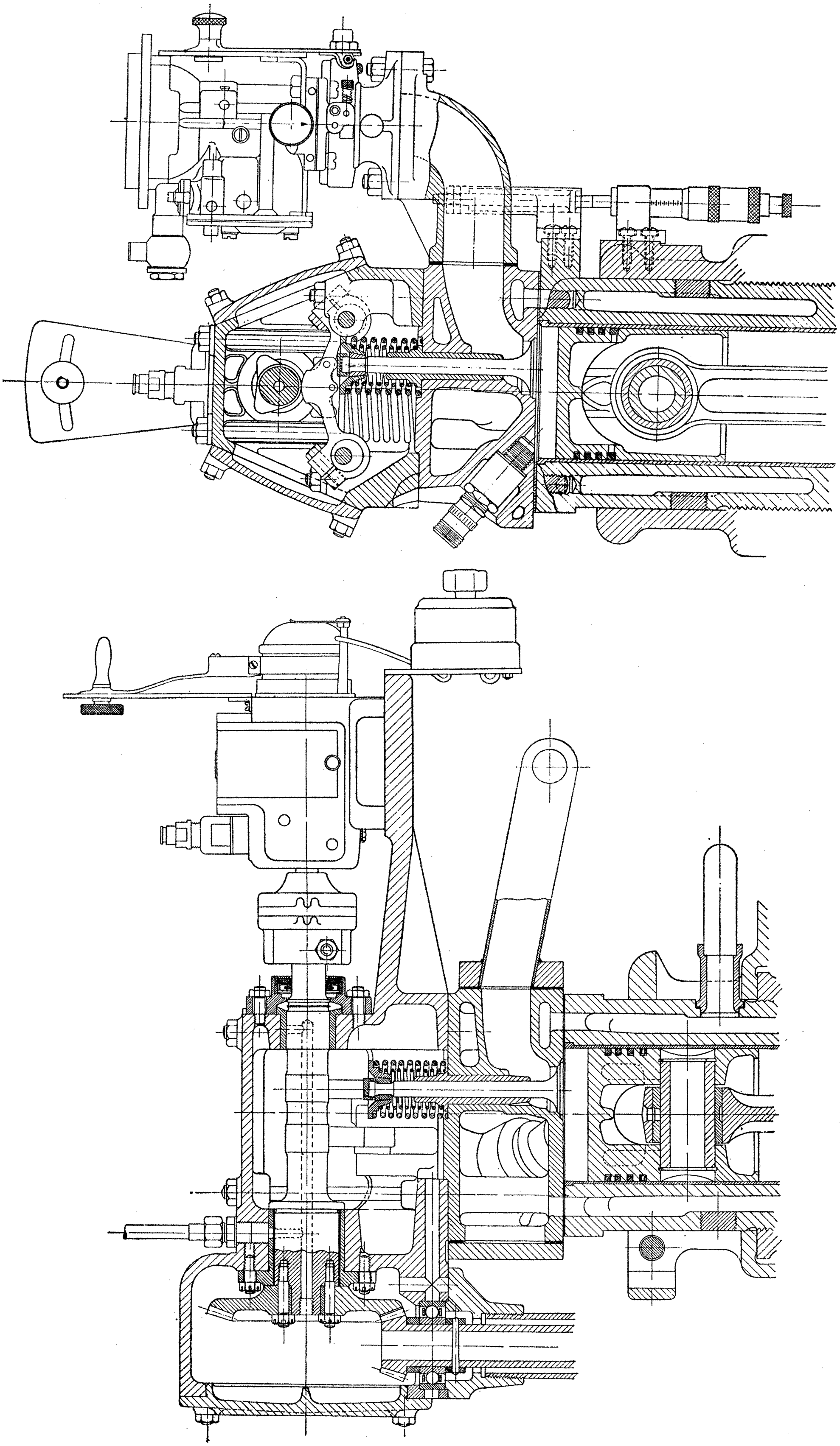
(*a*) *Adaptation of engine*

On this unit every effort was made to obtain the best possible cyclic regularity of combustion, since this was fundamental to any sampling investigation. Cyclic variation in spark timing was reduced to negligible proportions by replacing the usual contact breaker assembly by a magnetically triggered electronic ignition system. This consisted of a cold-cathode thyratron discharging a condenser through the primary of a conventional ignition coil. The thyratron was fired by a signal produced by a small blade on the engine flywheel passing the pole-piece of a pick-up unit consisting of a solenoid and small permanent magnet.

In an effort to obtain a fuel/air charge as homogeneous as possible, the mixture, after being formed in the carburettor, was drawn through a mixing chamber fitted with baffles before passing into the inlet port (figure 2). The admixture of the fuel and air was further assisted by the use of a shrouded inlet valve. As a result of these precautions the cyclic regularity of combustion, as judged by the time of flame arrival at the sampling point, was $\pm 2^\circ$ crank angle. That this remaining irregularity occurred principally in the initiation of the first nucleus of flame and not in the travel of the flame across the combustion chamber was shown by a test in which an ionization gap was placed near the sparking plug. The variation in time of flame arrival was found to be as great as when the ionization gap was placed on the opposite side of the combustion chamber. It was not found possible to reduce the remaining variation in time of initiation of the flame.

(*b*) *Sampling valve*

The sampling valve was evolved from the Atlas electromagnetic fuel injector (Vogt & Rogers 1939) with a number of detailed modifications designed to enable it to meet the changed conditions of operation.



cross-section

longitudinal section

FIGURE 1. Arrangement of cylinder head of Ricardo E. 6 variable compression engine.

In its final form (figure 3) the valve consisted essentially of three parts: (i) the body containing the solenoid and moving armature; (ii) a gas chamber of stainless steel screwed to the valve body through which the sampled gas passed before being led out into the absorbing apparatus; and (iii) an adaptor which held the nozzle to the gas chamber and which was screwed externally with an 18 mm. thread so that it could be used in a standard spark-plug hole. The valve itself consisted of a needle, seating in a nozzle. The needle was 0·125 in. in diameter and had a tip of 90° included angle seating in a hole 0·025 in. in diameter. Of the many materials tried it was found that a stainless steel needle in combination with a cast iron nozzle gave the best results under all operating conditions.

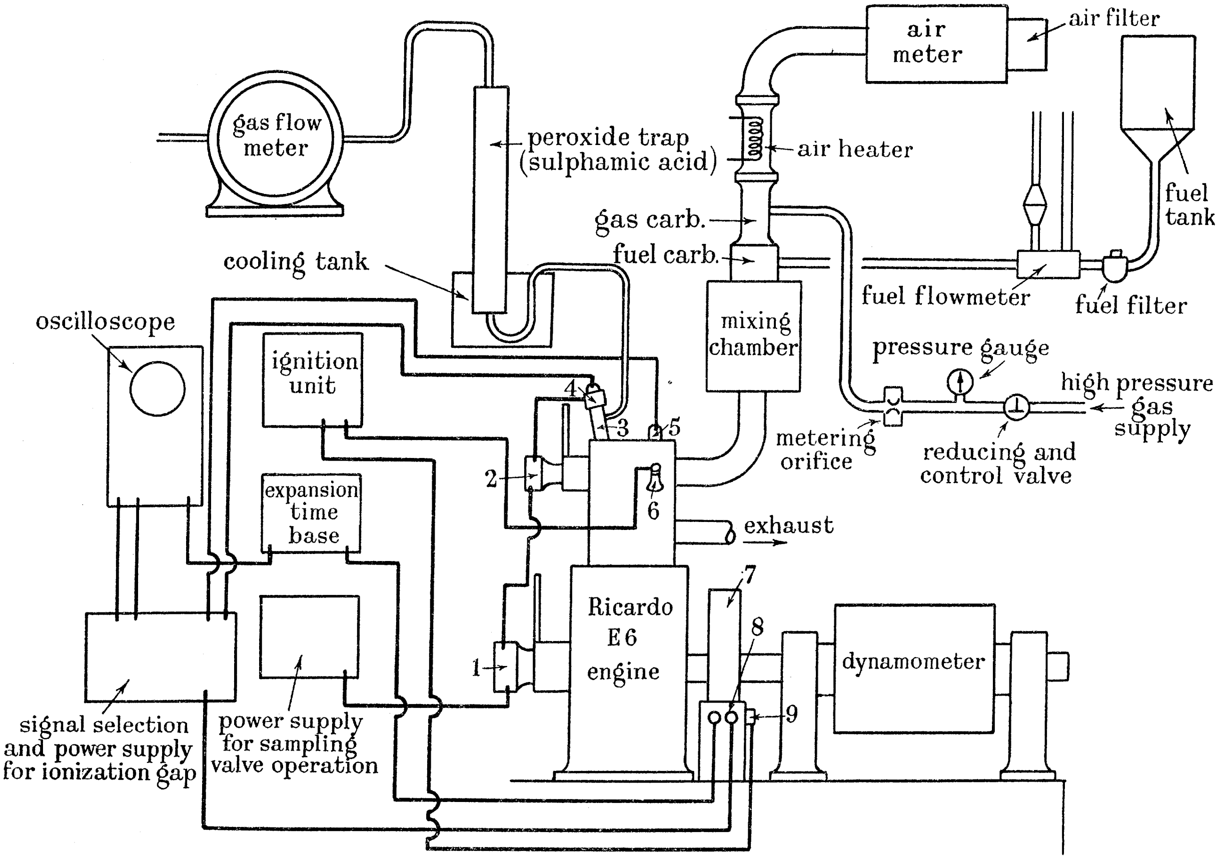


FIGURE 2. Diagrammatic arrangement of sampling unit.

Key. 1, contact breaker controlling valve operation; 2, stroke selector for valve; 3, sampling valve; 4, Sunbury pick-up; 5, ionization gap; 6, sparking plug; 7, flywheel; 8, Sunbury pick-up units for time base sweep, and degree marker; 9, timing pick-up for ignition unit.

The needle was brazed into one end of a tubular stainless steel spindle which passed axially through the moving armature situated in the solenoid. At the upper end of the spindle was attached a flanged bush which was spring-loaded, thus forcing the needle on to its seat. A slight axial clearance was allowed between the flange and the armature to ensure that the valve was seated when at rest. This clearance could be varied by placing washers between the nozzle and the gas chamber, best results being obtained with a clearance of 0·005 in. A greased neoprene washer prevented the corrosive sampled gas from passing into the solenoid chamber.

The valve was operated by the solenoid, the sequence of operations being as follows: The discharge of a bank of condensers sent a direct current through the solenoid. This set up a magnetic flux across the armature which, by reason of the fact that the circumferential serrations on the armature were slightly out of line with those on the solenoid wall, caused the armature to rise, so striking the flange of the spindle and lifting the needle from the nozzle seat. Two springs quickly returned the spindle and armature to their original position, so closing the valve. In the short time that the valve was open, a small sample of gas passed into the body of the valve under pressure from the cylinder and was subsequently led through a stainless steel tube to the absorbing and measuring apparatus. The compression in the spring retained the needle on its seat until the next discharge of the condensers.

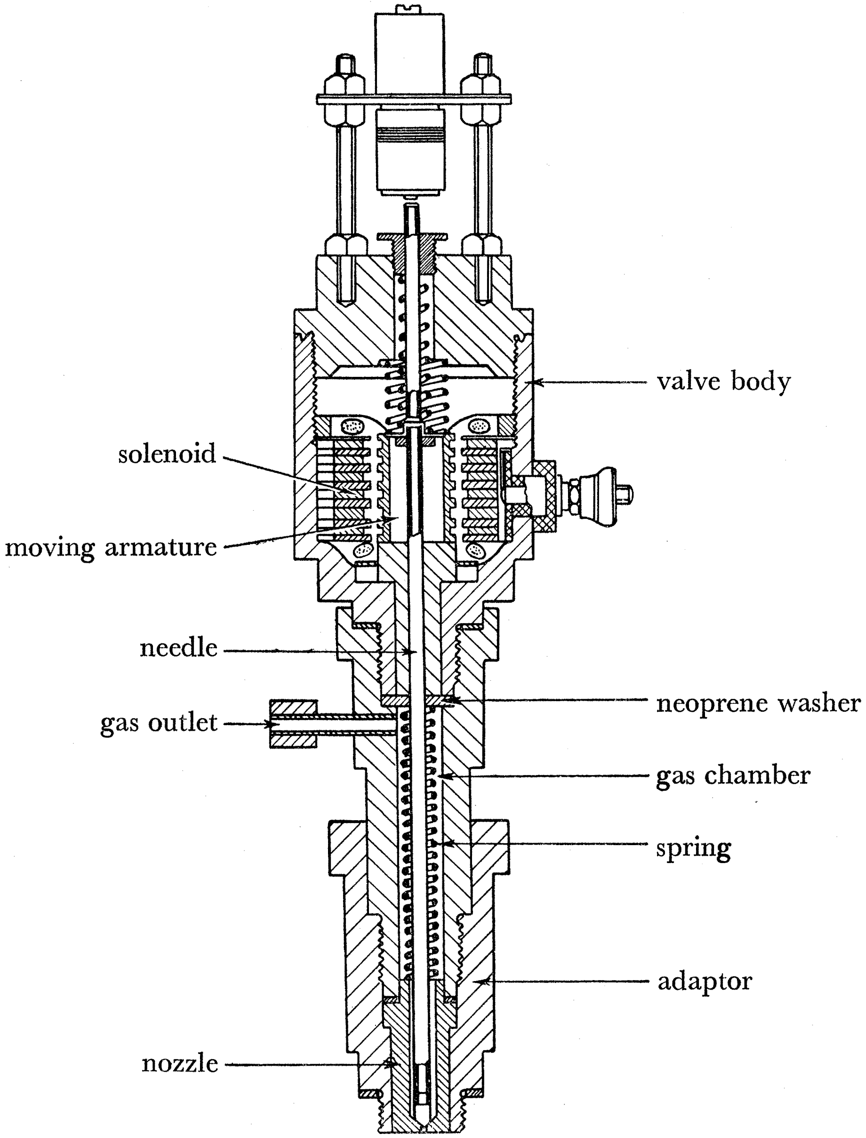


FIGURE 3. Sampling valve.

The discharge of the condensers was timed by a Bosch contact breaker, driven by the crankshaft, which could be adjusted to 'make' at any desired crank angle. The use of this one contact breaker would mean that the valve would also operate on the exhaust stroke and, in order to avoid this difficulty, a second contact breaker was driven by the camshaft and this 'made' early in the compression stroke. The two breakers were wired in series so that the sampling valve opened only at the required angle in the compression or working strokes and not on the exhaust or induction strokes. Originally only the camshaft-driven contact breaker was used, but, owing to the backlash in the gears and the coupling driving the shaft, a ± 2° variation in sampling time was obtained. Use of the crankshaft-driven contact as the 'master' control effectively removed this source of error.

The d.c. power was provided by the transformer-rectifier and regulator set housed in one casing. The various condensers were continually charged from the rectifier through a variable resistance, the required amplitude and time of opening being obtained by switching in different values of capacity whilst the charging resistance gave a fine control.

The time of opening of the valve was indicated as follows: The valve stem cap was provided with a small tube of non-magnetic material which projected a short distance through the top of the valve body. This tube carried at its free end a cap of steel. Above this a Sunbury magnetic pick-up assembly was carried in a brass holder with its pole-piece close to the steel cap. When the valve opened, the movement of the cap generated a small e.m.f. in the coil which, after amplification, was fed to a cathode-ray tube. The cathode-ray oscilloscope (c.r.o.) had a horizontal sweep provided with crank-angle marks generated when holes drilled in the engine flywheel passed a magnetic pick-up unit. The start of the sweep was controlled by a further pick-up unit which was energized when traversed by a single hole in the flywheel. This impulse operated a Ricardo time-base expansion unit, which gave an extended crank-angle scale, thus enabling the timing of the opening and closing of the valve to be fixed with accuracy.

The majority of the tests were made with a flow rate of sampled gas of 200 ml./min. Under these conditions, the period of valve opening indicated on the c.r.o. was about 6 crank degrees when sampling near the point of maximum cylinder pressure. There is reason to believe, however, that the true period of opening was much less, and that a high figure was indicated due to compression and tension forces in the needle which is $5\frac{5}{17}$ in. long between the actuating point and the nozzle seat. This was demonstrated by a special test under conditions where only a very small current was passing through the solenoid. In this case an indication of valve opening over a period of 3° was given although there was no flow of sampled gas, indicating that the valve cannot have left its seat. If this is regarded as the 'instrument error' and is subtracted from the value indicated under sampling conditions a figure of 3° is obtained for the true sampling period at a flow rate of 200 ml./min. This figure was subsequently confirmed by a special rig test when the actual lift of the valve from its seat could be measured electrically. That the opening period was at least small is borne out by the sharp peaks observed on many of the sampling curves.

In all the work described in this report the sampling valve was located in the 'end-gas' on the side of the combustion chamber opposite to the spark plug. That knock occurred in this region was demonstrated by a special test in which the engine was operated at a high compression ratio with severe knock over an extended period. The piston was found to be pitted over an area just below the sampling valve.

An ionization gap placed near the sampling valve measured the time of flame arrival at the sampling point. In all tests the ignition advance was adjusted to give a flame arrival at this point 10° after top dead centre (t.d.c.). Both the ignition timing and the time of flame arrival were indicated on the c.r.o.

2·3. *Equipment for additive tests*

For the majority of the tests, two carburettors, one for petrol and one for gas, were fitted to the engine. The petrol was metered into the carburettor by means of a volumetric flow device. The gas flow was metered using orifices of a size such that the flow through them was sonic and was, therefore, directly proportional to the applied pressure. A range of sizes to suit all flow conditions was used. Each jet was calibrated against a Wright water-displacement gas meter on all gases for which it would be used and in the engine tests, therefore, the gas flow was obtained from the measurements of gas pressure and temperature at the orifice. This latter reading enabled a temperature correction to be applied to the flows.

The gas passed from the high-pressure storage cylinders through a reducing valve which lowered the pressure to 20 to 100 lb./sq.in. Downstream of the reducing valve the gas passed a pressure-controlling valve which regulated the pressure operating on the metering orifice, this pressure being read on a gauge. The temperature of the gas was measured immediately downstream of the orifice.

The temperature of the induction air could be controlled at any desired value by adjustment to two electric air heaters placed in the line. A large air capacity placed just downstream of the large electric heater served to damp any air pulsations in the intake pipe. The air consumption was measured by means of an Alcock viscous flow air meter.

2·4. *Description of fuels used in the tests*

The composition and physical inspection data of the liquid fuels used for both the sampling and additive tests are given in table 1.

So far as the sampling work is concerned, mixed octanes (containing several octane isomers but principally 2.2.4-trimethyl pentane and 2.2.3-trimethyl pentane), were used as the representative fuel for most tests.

In the early additive tests, standard no. 1 was used as the base fuel. It was selected as a representative *iso*-paraffinic fuel of high octane number. The components of this fuel were exhausted towards the end of 1944 and standard no. 4, a fuel of similar anti-knock quality and roughly similar composition, was substituted. Later still, supplies of technical *iso*-octane, *c.* 99% 2.2.4-trimethyl pentane, became relatively more plentiful, and so, as this was a much purer material, it has been used for all subsequent tests where an *iso*-paraffinic fuel was required.

A number of commercial grades of fuel of other hydrocarbon types, such as cyclohexane, benzene, toluene, cumene, etc., were also tested. These varied considerably in purity; some, such as benzene and toluene, being almost 100% pure, whilst others contained large quantities of impurities. Such information as is available on the composition of these fuels is given in table 1.

The methane gas used was supplied by the Mogden Works of the West Middlesex Main Drainage Co. Analyses of two samples of the gas selected at different times in the course of the experiments are given in table 2. The average methane percentage is 90. In the

Table 1. Properties of liquid fuels used in the tests

fuel	sp.gr. at 15° C	octane no. (c.f.r./m.m.)	composition	i.b.p. (° C)	distillation % volume recovery at T (° C)									f.b.p. (° C)
					10	20	30	40	50	60	70	80	90	
iso-octane	0·696	100	c. 99 % 2.2.4-trimethyl pentane	94	97	97	97	97	97	97	97	97	97	105
mixed octanes	0·714	95	—	94	105	107	107·5	108	108·5	109	109·5	110·5	112	119·5
hot acid octane (h.a.o.)	0·7125	—	mixed octane isomers	88	102·5	104	105	106	106·5	107	107·5	108·5	110	120
neohexane	0·659	—	—	49	49	49	49	49	49	49	49	49	49	53
cumene	0·864	—	—	146	148	149	149	149	149	150	150	151	153	181
toluene	0·869	—	—	106	108	108	108·5	108·5	108·5	108·5	108·5	108·5	109	113
benzene	0·882	—	—	77·5	78·5	78·5	79	79	79	79	79	79	79	83
benzex bottoms	0·857	—	c. 90 % xylenes	131	—	—	—	—	—	—	—	—	—	147
cyclohexane	0·783	79·2	—	79	80	80	80	80	80	80	80	80	80·5	87
carbon di-sulphide	1·263 at 20° C	—	—		boiling-point 46° C									
methyl alcohol	0·799	—	—	64	64·5	64·5	65	65	65	65	65·5	66	66·5	68·5
power methylated spirits (p.m.s.)	0·820	—	75 % v. ethyl alcohol 25 % v. aromatics	67·5	69·5	70·5	71·5	73	74	75·5	76	77	77	84
hydropetrol (produced by cracking and hydrogenation processes)	0·736	79·0	24 % v. aromatics 24 % v. naphthenes 52 % v. paraffins	42	58	63	70	78	87	96·5	109	112	119·5	139
alkylates (produced by the alkylation procedure from gaseous by-products of other cracking processes)	0·703	91	—	49·5	84	93	99	103	105·5	107·5	110	112	117	153
standard no. 1	0·684	92	50 % alkylates 50 % neohexane	49·5	57·5	60·5	63·5	67·5	74·5	81·5	97·5	108	115	166
standard no. 2	0·686	91	25 % neohexane 55 % alkylates 20 % *iso*pentane alkylates	45	52	60	70	80	90	100	106	113	122	c.160
standard no. 4	0·699	92	75 % mixed octanes 15 % *iso*pentane 10 % hydropetrol	35	62	77·5	93	102	105·5	107·5	108·5	110	112	131·5
B.A.M. 100/3 Air Ministry 100 octane reference fuel	0·723	98·6 99·2 by CFR 1-C 3-C RM Rating S+1·50 ml. TEL/IG	15·2 % aromatics 5·47 ml. TEL/IG	c. 50	28 % at 75° C, 64 % at 105° C, 94 % at 145° C									168
D.T.D 230 base	0·717	75	6 % aromatics 33 % naphthenes 1 % olefins 60 % paraffins	42	64	72	79	86	92	97·5	103	110	122	155
low octane gasoline	0·727	50	18 % w. naphthenes 12 % w. aromatics 70 % w. paraffins	39	71·5	81·5	91·5	101	109·5	118·5	129	140	154	179

graphs and tables relating to methane, the concentration of additive has been expressed as a molecular percentage of the methane component of the gas supplied.

The hydrogen gas, which was supplied by the British Oxygen Co., was prepared electrolytically and was 99 % pure, the only impurity present in any appreciable proportion being oxygen.

TABLE 2. PROPERTIES OF GASEOUS FUELS USED IN THE TESTS

Gas		composition (% vol.) sample 1	sample 2
hydrogen	H_2	99·5	—
	O_2	0·5	—
methane	CH_4	89	89·8
	N_2	6·6	4·7
	CO_2	3·3	4·1
	O_2	0·8	0·4
	CO	0·3	0·6
	H_2	Nil	0·4

3. KNOCK-RATING PROCEDURE

3·1. *The determination of highest useful compression ratio*

The audibility method of knock rating was used in all tests. When running on a particular fuel or blend the compression ratio was raised until the standard intensity of detonation f.s./o.m.d. (frequent slight/occasional moderate detonation) as judged by ear was reached. This limiting compression ratio, termed the 'h.u.c.r.' (highest useful compression ratio), was taken as a measure of the knocking tendency of the fuel or blend.

It was found that the ear formed a remarkably accurate means for measuring the intensity of knock and that h.u.c.r. observations could be checked within close limits, *c.* 0·10 to 0·20 for compression ratios in the region of 5·0 to 9·0 and 0·20 to 0·30 for higher compression ratios. Day-to-day variations in both the ear and the engine were allowed for by taking readings on a reference fuel and correcting all h.u.c.r.'s on test fuels to a standard h.u.c.r. on the reference fuel.

The mixture strength used was that giving maximum knock (except where otherwise stated). This was obtained either by determining the knock-limited compression ratio at a series of mixture strengths and obtaining the minimum from the resultant curve of h.u.c.r. against mixture strength, or by setting the mixture strength and compression ratio directly to the h.u.c.r. at maximum knock mixture, a direct adjustment relatively easy to make with experience.

The ignition timing used was the optimum for maximum power mixture strength at each compression ratio and for each fuel (except where otherwise stated).

A word of explanation is probably necessary concerning the variety of engine and test conditions used for the various tests. The 'standard' test conditions for the engine, used almost exclusively in the early work, were 2500 r.p.m. and inlet air temperature 30° C. In some of the later tests the speed was lowered to 1500 r.p.m. in order to reduce the amount of fuel required for a test.

When the tests on methane came to be carried out, it was found that the h.u.c.r. with an inlet air temperature of 30° C and an engine coolant temperature of 70° C was in the region of 18. This compression ratio was inconveniently high for continuous working, particularly in view of the fact that it was proposed to try the effect of anti-knock substances in the fuel. Accordingly, the inlet air temperature was raised to 120° C and the engine coolant temperature to 90° C. The h.u.c.r. of methane under these conditions was 14 to 15, a more convenient range for continuous testing.

The conditions under which a particular test was carried out are given in the table or graph concerned.

Where both fuel and additive were liquid, the latter was usually added to the fuel before test. With gaseous additives, like formaldehyde, and gaseous fuels, like methane, this was not possible; the additives were, therefore, introduced into the inlet air stream in the following manner. The additive was contained in a tightly corked flask into which fitted two glass tubes. One of these tubes communicated directly with the atmosphere, and the other was connected to the induction pipe of the engine at a point just upstream of the gas carburettor. The difference in pressure between the outside air and the induction pipe caused a current of air to flow through the flask and into the engine intake, drawing with it some vapour of the additive. The flow rate was controlled by means of a stopcock in the exit pipe leading from the flask. Very low flow rates were obtained by chilling and high flow rates by heating the flask. The flow was obtained by determining the weight loss of the flask in a measured time. The additives were introduced in this manner not merely when methane was the fuel but also in many of the comparative tests on the liquid fuels. This ensured that the tests were carried out as far as possible under comparable conditions.

3·2. *The knocking behaviour of the test fuels*

A distinction is sometimes made in the literature between 'knocking' and 'non-knocking' fuels. The normal commercial petrols (containing higher paraffins, naphthenes, olefins and aromatics) belong to the first class, and fuels such as benzene, methane and methyl alcohol are sometimes said to belong to the second. In our experience all fuels will knock if the conditions are made sufficiently severe. A difficulty arises in obtaining knock in certain cases due to the proneness of some of the so-called 'non-knocking' fuels to give pre-ignition. This experimental difficulty probably accounts for the failure of some investigators to obtain knock with these fuels. Pre-ignition, can, however, usually be eliminated if care is taken to remove all hot spots from the combustion chamber, particularly hot-running sparking plugs.

A further difficulty with some of the fuels of high h.u.c.r. is that running tends to be rough, and combustion noise due to the high rates of pressure rise during combustion tends to mask the true 'knock'. With practice, however, it is relatively easy to distinguish the high-pitched note of knock from the duller noise due to rough running.

In cases where there was any real doubt, a special test was carried out in which the power output and heat transfer to the cylinder wall were measured at increasing compression ratios. The onset of knock was characterized by a drop in power and a very rapid rise in the rate of heat transfer. In general, the knock intensity used in the audibility tests was that corresponding to the peak of the power curve.

Figure 4 shows the results of h.u.c.r.-mixture strength tests on a typical selection of the base fuels used for the additive tests.

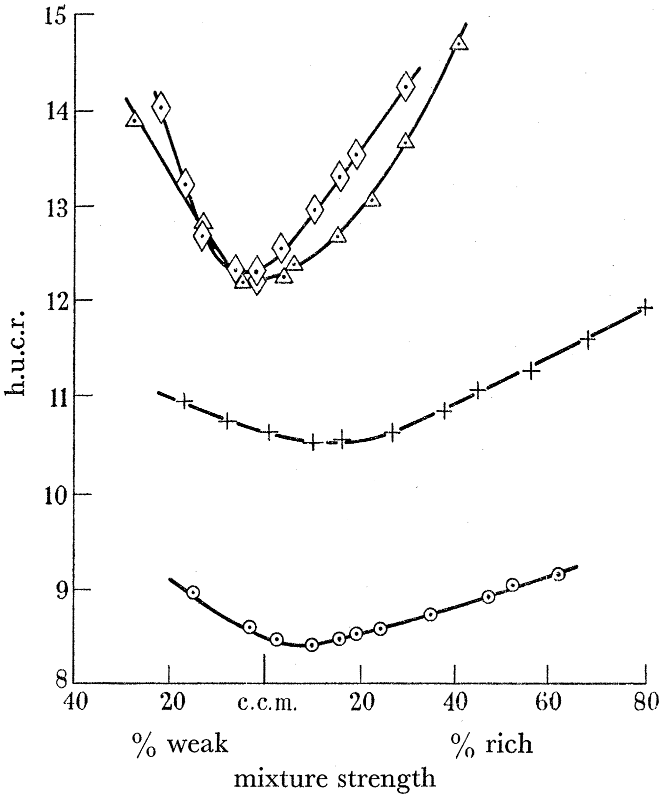


FIGURE 4. H.u.c.r.-mixture strength curves on representative fuels. Test conditions: engine speed 1500 r.p.m.; inlet air temperature 120° C; engine coolant temperature 90° C; Solex carburettor; ignition advance to give maximum cylinder pressure 13° after t.d.c. in all cases. Fuels: ⊙ *iso*-octane; + *iso*-octane + 4 ml. lead tetraethyl/imp. gal.; △ benzene; ◇ methane.

4. PRELIMINARY INVESTIGATION

4·1. *The chain nature of the reactions leading to knock*

The anti-knock action of minute quantities of lead tetraethyl (0·01 % by volume of fuel) and the knock-promoting effect of small concentrations of substances which would be expected to give rise to free radicals in the engine cylinder provide strong evidence of the chain nature of the reactions leading to knock. Tests on some of these free radical-forming substances are summarized in table 3.

Azomethane and diazomethane, sources of methyl and methylene radicals respectively, are both pro-knocks. The results are qualitative only, because of uncertainty as to the proportion of azomethane and diazomethane surviving the compression stroke to be present in the 'end-gas' at the critical time.

The effects of the alkyl nitrites and nitrates can be ascribed to their readiness to yield (either directly or under the influence of oxygen) free radicals:

$$R\mathrm{ONO_2} \rightarrow R\mathrm{O} + \mathrm{NO_2},$$

followed by subsequent decomposition of the *R*O radical (see George & Walsh 1946 and Walsh 1948 for the probable mode of this). The pro-knock effect of the nitrite and nitrate compounds in the clear fuel increases as the series ethyl→*n*-propyl→*i*-propyl-*t*-butyl is ascended. The reason is presumably in part that the ease of dissociation probably increases in this series; it is known to do so at least from methyl to ethyl to *n*-propyl (Phillips 1947).

The inertness of the mono-nitro-paraffins as knock agents, relative to the alkyl nitrites and nitrates, is probably due to the greater strength of the C-N bond as compared with the O-N bond (see, for example, Walsh 1948). The dissociation of nitro compounds to yield free radicals is likely, therefore, to be much less easy than for nitrites and nitrates.

TABLE 3. TESTS ON NITRITES, NITRATES, NITRO AND NITROSO COMPOUNDS, CHLORINE COMPOUNDS, AZOMETHANE AND DIAZOMETHANE

engine speed 2500 r.p.m.
coolant temperature 70° C
maximum knock mixture.
inlet air temperature 30° C
ignition advance—optimum for maximum power mixture at each c.r.
Fuels: standard no. 1 and standard no. 1 + 4·7 ml. lead tetraethyl/imp. gal.

	reduction in h.u.c.r. with 1% additive	
dope	clear fuel (8·5)	leaded fuel (12·5)
methyl trinitro-methane	2·1* ratios	— ratios
ethyl nitrate	1·5	2·55
n-propyl nitrite†	1·8*	2·4*
iso-propyl nitrite†	1·9*	2·55*
t-butyl nitrite	1·9	1·4
amyl nitrite‡	2·0	1·4
amyl nitrite	2·1	3·2
amyl nitrate	2·1	—
nitro-ethane	0	0·8
nitro-benzene	0	0
nitroso-benzene	0·4	—
chloropicrin	1·9	5·0
carbon tetrachloride	0	3·25
diazomethane	0·25*	1·15*
azomethane†	0·30*	0·70*

* Estimated.
† 517 W heat input to induction air in these tests.
‡ Alkylates (11·1) used as base fuel for these tests.

At higher compression ratios (about 12·5 instead of 8·5), the higher value being attained by addition of lead tetraethyl, nitroethane shows a definite pro-knock effect. That this is due to its increased dissociation at the higher temperatures involved, and not to the presence of lead was demonstrated by a test with a leaded fuel of the same h.u.c.r. as clear Standard no. 1 (about 8·5). Nitroethane was ineffective in the fuel.

The inertness of the nitroparaffins applies only to the simplest members. Thus methyl trinitro-methane has a considerable pro-knock effect. Chloropicrin has an effect approximately the same as that of amyl nitrite in an unleaded fuel but very much greater in a leaded fuel.

Carbon tetrachloride is ineffective in an unleaded fuel, but a strong pro-knock in the same fuel leaded. This result was confirmed by a more extensive series of tests (figure 5) which also showed that at high concentrations (>1·25%) the h.u.c.r. of the leaded fuel fell below that of the unleaded fuel. Such evidence strongly suggested that with a leaded fuel the lead tetraethyl reacted with the carbon tetrachloride, and that this reaction not only neutralized the effect of the lead tetraethyl but yielded products with a definite pro-knock effect. This pro-knock effect is probably to be ascribed to the alkyl groups released from the lead tetraethyl.

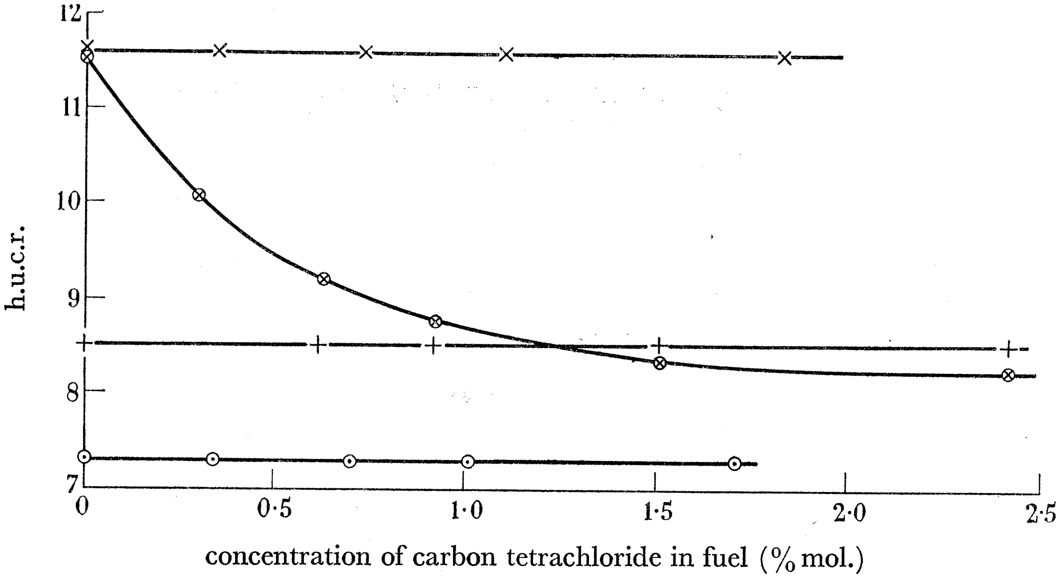


FIGURE 5. Effect of carbon tetrachloride on the h.u.c.r.'s of various fuels: Test conditions: engine speed 2500 r.p.m.; inlet air temperature 30° C; engine coolant temperature 70° C; Solex carburettor; additive admitted with fuel. Fuels: + hydropetrol; ⊗ hydropetrol + 5·5 ml. lead tetraethyl/imp. gal.; ⊙ 67 octane unleaded gasoline; × mixed octanes.

TABLE 4. TESTS ON ORGANIC PEROXIDES

engine speed 1500 r.p.m.
coolant temperature 70° C
maximum knock mixture
inlet air temperature 75° C
ignition advance—optimum for maximum power mixture at each c.r.
Fuel: cyclohexane

peroxide	change in h.u.c.r.
ethyl hydroperoxide	1·97
n-propyl hydroperoxide	2·23
i-propyl hydroperoxide	2·15
n-butyl hydroperoxide	2·25
i-butyl hydroperoxide	2·12
sec.-butyl hydroperoxide	1·97
t-butyl hydroperoxide	2·29
amyl nitrite	2·40

Another series of radical-producing compounds, the organic peroxides, was systematically explored. Egerton *et al.* (1935) had earlier demonstrated the qualitative pro-knock effect of certain peroxides. In the present investigation a whole series of hydroperoxides from ethyl to *t*-butyl was tested. Table 4 gives the reduction in h.u.c.r. consequent on the addition of 1·5% mol. of each of the peroxides to cyclohexane. The concentrations quoted were based on estimations of the active oxygen content by the iodine method. It can be seen that the pro-knock effectiveness of all the organic peroxides is much the same at this concentration, and that all the h.u.c.r.'s lie within 0·32 ratios. In all cases they are less effective than amyl nitrite.

Although the figures are very close, it is possible to pick out certain trends. Thus the results for the straight-chain compounds suggest that the effectiveness increases with length of chain up to *n*-propyl, thereafter being virtually constant. The effectiveness also increases from the ethyl to the *i*-propyl to the *t*-butyl compound.

The profound promoting effect on knock of all these free radical-forming substances shows the chain nature of the reactions leading to knock. The same is shown by the anti-knock action of minute quantities of other additives, e.g. lead tetraethyl. It is also shown by the correspondence between the reactions concerned in knock and those studied in non-engine investigations, where the usual criteria of chains (e.g. well-defined pressure limits of ignition, sensitivity to surface, induction periods, etc.) are amply obeyed. This is discussed further in a later section.

Having described the effect of various additives upon the h.u.c.r., it is convenient at this point to digress from the main argument to mention their effect upon the mixture strength giving maximum knock.

Mixture strength

The effect of mixture strength on the knock-limited compression ratio is well known (figure 4). The effect of additives on the mixture strength for maximum knock is of some interest. Generally speaking, it is found that when the additive is included with the fuel, a strongly anti-knock additive will cause the mixture strength for maximum knock to move towards a weaker mixture while a strongly pro-knock additive will cause it to move towards a richer mixture. When the additives are introduced to the intake air as vapours, such differences in maximum knock mixture strength are not usually observed.

This difference in effect of the two methods of introducing the additive into the engine may be explained as follows. When an additive is put into the fuel a reduction in fuel flow also effects a reduction in the amount of additive introduced into the cylinder per cycle. In the case of an anti-knock additive, such as lead tetraethyl, on weakening the mixture, one would expect a fall in h.u.c.r., due to a reduction in the quantity of anti-knock present as well as to the normal reduction in h.u.c.r. which occurs on weakening from a rich mixture. This process would obviously have the effect of weakening the maximum knock mixture strength. In the case of a pro-knock additive, on weakening the mixture, an increase in h.u.c.r. due to a reduction in the quantity of pro-knock present would take place. This will lead to the maximum knock mixture strength occurring at a richer mixture than with a clear fuel. Where the additive is introduced separately into the air stream, the quantity of additive entering the cylinder per cycle is unaffected by changes in fuel flow; consequently the introduction of additive does not affect the maximum knock mixture strength.

It would appear, therefore, that it is the concentration of additive per unit of fuel-air charge rather than the concentration in the fuel alone which determines the extent of the knock action.

4·2. *The substantial independence of the reactions leading to knock upon the nature of the cylinder walls*

The concentrations of reaction products detected in the 'end-gases' of engines do not begin to rise until about the time of normal spark ignition. At this time the 'end-gas' pressure, even with a compression ratio as low as 6·0, has reached some 10 atm., and thenceforward the pressure rises rapidly to many times this figure. In view of this and of the exceedingly short time intervals available in the engine for diffusion to or from the surface (at 2500 r.p.m. the 'end-gas' reactions begin and end in about a hundredth of a second), one would not expect the nature of the cylinder walls to have any important effect on the chemical reactions taking place. This expectation was confirmed by experiments in which the combustion chamber walls were coated with the following substances.

(*a*) *Sodium chloride*

The salt was introduced as an emulsion in the fuel, prepared in the following manner. 120 ml. of oleic acid were dissolved in 1 gal. of fuel (Standard no. 1), and 23 ml. of 0·880 ammonia were added drop by drop, the mixture being stirred all the time. A saturated salt solution was then added slowly with vigorous stirring. The mixture, which contained approx. 1% by weight salt, eventually cleared to a very slight turbidity. It was necessary to use the solution immediately as salt was precipitated on standing. A blank fuel for comparative tests was made up in a similar manner to the above but without the addition of the saturated salt solution.

The engine was run for about 20 min. on the fuel containing salt to allow time for deposits of salt to be formed on the inner walls. Comparison of the h.u.c.r.'s of the fuel containing salt and that of the 'blank' fuel showed that neither a coating of salt on the internal surfaces of the engine nor the presence of salt particles in the combustible mixture itself had any effect on the 'knock' tendency of the fuel. Inspection of the engine after test confirmed that a thin layer of salt had been deposited over the internal surfaces of the engine.

(*b*) *Ferric chloride*

By running the engine on fuel containing ferric chloride for about 20 min. a coating of iron compounds was built up on the combustion chamber walls. It was found that neither the presence of ferric chloride in the fuel nor a coating of an iron compound on the combustion chamber walls had any effect on knock.

(*c*) *Cobalt and chromium*

The engine was run for a considerable time on fuel containing a mixture of cobalt acetyl acetonate and chromium acetyl acetonate. Chemical analysis of the internal deposits showed that a considerable deposition of cobalt and chromium compounds had taken place everywhere on the cylinder walls, head and valves. The effect on knock, however, was nil.

(*d*) *Thorium and cerium*

The introduction of a mixture of 99% thorium oleate and 1% cerium oleate into the fuel in the proportion of 0·25% by weight, formed a deposit of thorium and cerium compounds on the combustion chamber walls but led to no detectable change in the h.u.c.r. of the fuel.

It may be concluded from these experiments that any effect of the cylinder walls on the reactions taking place in the 'end-gas' is generally at least small.

4·3. *Knock due to intensification of existing reactions*

At the beginning of the sampling investigation qualitative tests were carried out on samples taken from the engine cylinder under various conditions of operation, both knocking and non-knocking, and in circumstances in which on the one hand knock was suppressed by the addition of lead tetraethyl, and on the other was encouraged by adding amyl nitrite to the fuel. The tests were carried out on commercial fuels of both paraffinic and aromatic bases.

In all cases the qualitative results were similar in that no substance peculiar to any one of the above conditions was found in any of the samples taken over a range of timings extending from 70° e. to 20° l. Aldehydes (mainly formaldehyde), ammonia in the region of t.d.c., and ketones, formic acid and formates (at late timings) were all detected. Nitrites and peroxides were present; acetates, propionates and cyanides were always absent. Unsaturated hydrocarbons were detected and estimated; their quantity increased rapidly from 10° e. to 13° l., an observation which confirmed that reactions were taking place to a considerable extent in the gas before the arrival of the flame.

The logical conclusion from this preliminary work seems to be that knock depends not so much on the formation of some new substance which is not present under non-knocking conditions but rather on the attainment of a critical rate of formation of products present under both conditions.

4·4. *Effect of products upon the reactions leading to knock*

The products of reaction in the 'end-gas' which *a priori* might be expected to have a pro-knock action are aldehydes, nitrogen peroxide (from unscavenged NO) and organic peroxides. Formaldehyde, so far from being a pro-knock, is actually an anti-knock with a normal paraffinic fuel (figure 6). The higher aldehydes are either very slightly pro-knock or ineffective. Nitrogen peroxide, when introduced into the air stream as a gas, has only a slightly pro-knock effect in unleaded paraffinic and naphthenic fuels. In leaded fuels, nitrogen peroxide has a stronger pro-knock effect due to a reaction between nitrogen peroxide and lead tetraethyl which destroys the effectiveness of the latter (see below).

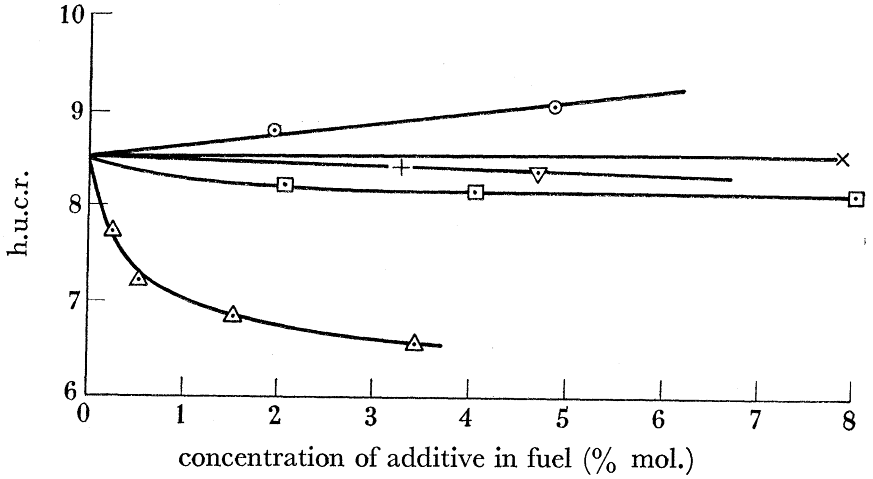


FIGURE 6. Effect of various additives upon the h.u.c.r. of a paraffinic fuel. Fuel: Standard no. 1. Additives: ⊙ formaldehyde; × propionaldehyde; + nitrogen peroxide; ▽ acetaldehyde; ⊡ butraldehyde; △ *t*-butyl hydrogen peroxide.

It should be mentioned here that a different result is obtained when nitrogen peroxide is introduced with the fuel through a carburettor (i.e. when added to and mixed with the fuel before test). Figure 7 shows the response in *iso*-octane. It can be seen that the addition of the first 0·2 to 0·4% of nitrogen peroxide has a profound pro-knock effect, but that subsequent additions have a negligible further effect. Nitrogen peroxide is known to react in the liquid phase with certain hydrocarbons. Presumably some such reaction took place in the fuel upon adding nitrogen peroxide, and this was the cause of the fall in h.u.c.r. observed. Evidence for this was supplied by the observation of a gummy deposit settling out during storage of the petrol to which peroxide had been added.

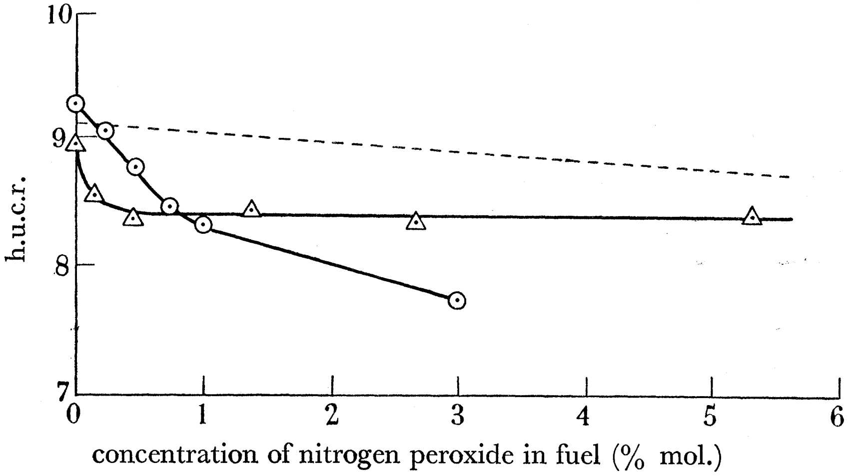


FIGURE 7. Comparison of the pro-knock effect of nitrogen peroxide introduced (*a*) with the fuel and (*b*) with the inlet air, also showing the effect of trimethylethylene nitrosate. Test conditions: engine speed 1500 r.p.m.; inlet air temperature 120° C; engine coolant temperature 90° C; Solex carburettor. Fuel: *iso*-octane; ---- NO_2 introduced with intake air; △ NO_2 introduced with fuel; ⊙ trimethylethylene nitrosate introduced with fuel.

The occurrence of a saturation point in the curve might be due to reaction of nitrogen peroxide with some particular constituent of the fuel present in small concentration, but tests on a number of different fuels failed to suggest what this constituent might be. The degree of pro-knock effect did not appear to correlate with the olefinic content of the fuel, although it was shown that a nitrosate compound of the type which might be formed as a result of reaction between nitrogen peroxide and olefin had a pro-knock effect comparable with that of the first small additions of nitrogen peroxide to the fuel (figure 7).

Another interesting point which emerges from a study of figure 7 is that the response of *iso*-octane to nitrogen peroxide after the saturation point is much less than that of gaseous nitrogen peroxide. This suggests that, even in the gas phase, reaction occurs between nitrogen peroxide and some constituents of the fuel, although at a much lower rate than when they are added together in the liquid phase.

Additional evidence that the nitrogen peroxide formed in the combustion process in the engine is only an incidental accompaniment to the oxidation process and plays no important part in the promotion of knock is provided by experiments in which the engine was run on a mixture of argon/carbon dioxide/oxygen having the same volumetric percentage of oxygen and having approximately the same thermodynamic properties as air (Downs & Pignéguy 1949). By this means all except about 1 % of the nitrogen was eliminated from the engine charge, yet the h.u.c.r. of a fuel such as *iso*-octane was practically unaltered.

Additive tests demonstrating the strong pro-knock action of organic peroxides are described in the preceding section. Although no specific tests have yet been carried out on the gas sampled from the combustion chamber of the engine, the indications are that the peroxides formed during the combustion process include hydrogen peroxide. Polarographic and other work (Shtern & Pollyak 1943; Damköhler & Eggersglüss 1942) has also been claimed to show the presence of H_2O_2 in engine condensates. It is important to remember that titanous sulphate, the reagent commonly used to detect hydrogen peroxide, is unreliable in the presence of formaldehyde (Wheeler *et al.* 1948) which is always present in engine solutions.

This makes it of interest to determine the effect of hydrogen peroxide when added to the engine charge. The experiment is not easy to accomplish, owing to the fact that hydrogen peroxide is but sparingly soluble in petrol and also is very unstable and explosive in the presence of organic matter. Some tests were, however, carried out in which a 30 % aqueous solution of hydrogen peroxide was sprayed into the induction manifold of the engine and its effect on the h.u.c.r. determined (figure 8). Blank tests were carried out with the injection of distilled water. These tests showed the well-known anti-knock behaviour of water vapour.

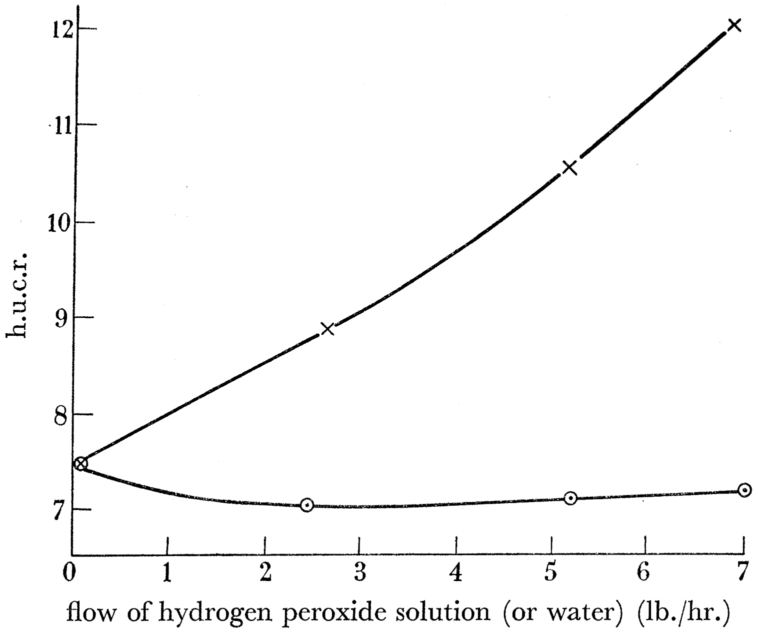


FIGURE 8. Effect of hydrogen peroxide on knock. Test conditions: engine speed 1500 r.p.m.; inlet air temperature 85° C; engine coolant temperature 100° C; Solex carburettor; additive admitted with air. Fuel: DTD 230. × water; ⊙ 30 % hydrogen peroxide solution.

In contrast the hydrogen peroxide vapour had either a pro-knock effect or only a small anti-knock effect. It is reasonable to suppose that the difference between the curves for water and the 30 % solution of hydrogen peroxide represents the action of the hydrogen peroxide. It can be seen that for a given small addition the effect is very much less than that of any organic peroxide tested. The tests of a comparatively dilute aqueous solution of hydrogen peroxide may not, of course, give the full effect of the pure substance.

Thus it can be seen that of all the stable intermediate products of reaction formed in the 'end-gas' of the engine prior to knock organic peroxides (and hydrogen peroxide) are the only ones which have a strong pro-knock action. Their effect implies that auto-catalysis, due to peroxide formation, of the reactions concerned in knock occurs.

Of the various products known to be formed in the 'end-gas' of an engine, formaldehyde is the only one which, in small quantities, has an appreciable anti-knock action. Olefins and inert gases are known to have anti-knock effects, but only when added in comparatively large quantities. The effect of formaldehyde means that a considerable self-inhibition of the reactions leading to knock occurs and, together with the facts concerning organic peroxides, shows that the two products whose actions particularly yield keys to an understanding of knock reactions are formaldehyde and organic peroxides. It is for this reason that the sampling investigation has been largely concentrated on their estimation.

5. Sampling tests for peroxides and aldehydes

5·1. *Methods of analysis of the sampled gas*

The cylinder charge consists of carburetted fuel/air mixture plus a variable amount of unscavenged exhaust gas. This latter will be responsible for the presence of CO, CO_2; NO, NO_2; H_2O, SO_2, SO_3 (if the fuel contains sulphur, as it usually does); and, in some cases, HCHO and H_2. Of these gases only NO_2 and SO_2 would be expected to affect analytical methods. Formaldehyde from this source would be in very small amounts compared with those present due to the pre-flame oxidations themselves.

The carburetted mixture, by the time the compression pressure and temperature of around t.d.c. are reached, has undergone oxidation reactions and perhaps cracking reactions, so that, besides unchanged fuel and air, there will also be present peroxides, aldehydes, olefins, ketones, alcohols and carboxylic acids, in approximate order of importance, unless the fuel is of a special variety such as pure benzene or acetylene, when the pre-flame products will be less varied.

The possible interactions of these substances, their interference with the peroxide and aldehyde analyses and methods of combating such interference are described below.

NO_2 is by far the most reactive of these and is able to destroy peroxides readily, particularly in aqueous solution:

$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2,$$

$$HNO_2 + R\mathrm{OOH} \rightarrow R\mathrm{OH} + HNO_3.$$

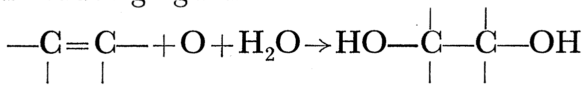
Thus it is essential to remove NO_2 from the sample for analysis. This is easily effected by the use of sulphamic acid in the solution used to scrub the sample gases, the reaction being very rapid:

$$HNO_2 + HSO_3NH_2 \rightarrow H_2SO_4 + N_2 + H_2O.$$

Tests have shown that this procedure effectively protects the peroxide from attack in the sample solution. Thus a series of samples were collected at the same angle in the cycle but using progressively stronger sulphamic acid solutions. It was found that the peroxide concentration in the samples rose steadily up to $3\frac{1}{2}\%$ acid, after which it remained constant. Also to confirm this, a solution of H_2O_2 in $3\frac{1}{2}\%$ sulphamic acid was divided and one-half treated with about ten times the amount of NO_2 vapour in air required to decompose the peroxide completely. On analysis the solution gave the same result as the untreated half. However, there is a possibility of gas-phase decomposition in the sample gases before they are scrubbed, but there is evidence that the effect, if it occurs, is not large (§5·2).

NO_2 has no effect on the chief methods of aldehyde analysis, those of Lea (1943) and of Schiff. SO_2 is a reducing agent, and although SO_2 and H_2O_2 do not react rapidly in the very dilute solutions with which we are concerned, it can affect reagents used in the peroxide analyses. Here again removal is easily effected by the addition of dilute bromine water which oxidizes it to sulphuric acid.

Olefins can also act as reducing agents



$$-\underset{|}{C}=\underset{|}{C}-+O+H_2O\rightarrow HO-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-OH$$

and are known to react with peroxides; but more serious is the reaction with iodine, the liberation of which from KI is the chief method for estimating peroxides. It has been found, however, that the bromine treatment for SO_2 removes olefins at the same time, and, if the treatment is carried out rapidly, no loss of peroxide is observed.

These above are the only serious interferences with possible analytical methods from minor constituents of the cylinder gases. Bearing in mind the above facts two satisfactory procedures were developed for peroxide analysis.

(1) *The potassium iodide method*

The gas passing from the sampling valve was taken to the scrubbing trap by as short a length of synthetic rubber tubing as possible. In the trap it was scrubbed by passage up a glass bead-packed column 20 in. high containing 40 ml. of $3\frac{1}{2}\%$ sulphamic acid solution. At the end of the sampling run the solution was transferred to a glass-stoppered bottle and immediately scrubbed with CO_2 for 2 min. to remove air. Bromine water (*c.* 50 % saturated) was then added rapidly until a faint persistent yellow colour was obtained, indicating the removal of SO_2 and olefins. Excess bromine was removed by the addition of 10 drops of a saturated phenol solution.

In order to speed the reaction of the peroxide with hydriodic acid a catalyst, consisting of one drop of 0·01 % ferrous ammonium sulphate solution, was added followed by 0·2 g. of potassium iodide. A further scrubbing with CO_2 completed the preparation of the solution, the bottle was stoppered and left overnight.

The iodine liberated by the peroxide was titrated with N/200 sodium thiosulphate solution using starch indicator. A blank run was carried out as above but using an identical volume of pure sulphamic acid solution. This method gave results slightly lower than the theoretical on known H_2O_2 solutions, perhaps due to side reactions. It was, however, very consistent.

(2) *The methylene-blue method*

This method was used on engine samples in the hope that, being a colorimetric method, it could be used to follow the rate of reaction of the peroxide and, therefore, give information as to the type of peroxide present by comparison with known peroxides.

The technique was to follow the preparation of the solution as for the iodine method up to the addition of phenol when 5 ml. of a 1 % methylene-blue solution in N-HCl, and reduced over cadmium amalgam, were added to the peroxide solution in a colorimeter cell. The oxidation of the dyestuff leuco-base was easily followed by the reduction in light transmission.

In general, the results were very similar to those obtained by the iodine method, but difficulty was experienced with very high 'blanks', the cause of which was not explained.

The rate of reaction of the engine samples was approximately the same as for H_2O_2, but hydrolysis of organic peroxides to H_2O_2 by the highly acid reagents is quite likely.

Other methods investigated include the thiocyanate method of Yule & Wilson (1931) and the stannous chloride method of Hoch & Schrader (1937), but these and other methods failed to yield consistent results with *c.* N/2000 solutions of peroxide (which is the concentration found in the engine condensates).

Aldehyde analysis

This is a much simpler problem as the concentrations are much higher (*c.* 30x) than in the case of peroxides. The bisulphite method of Lea (1943) was selected as most suitable for the rapid analysis of a large number of samples.

The sample was collected in a trap filled with a solution of sodium bisulphite freshly prepared by saturating a solution of sodium carbonate with SO_2 gas and diluting until it contained 25 g./l. of sodium bisulphite.

The solution of aldehyde bisulphite with excess sodium bisulphite was titrated with N-iodine solution using starch indicator until the sodium bisulphite was just destroyed. The aldehyde-bisulphite compound remained unaffected by iodine in acid solution and was decomposed by the addition of excess sodium bicarbonate, with the liberation of sodium bisulphite equivalent to the aldehyde present. A simple iodine titration with N/100-iodine then gave a measure of the aldehyde concentration. The end-point tended to be a little difficult to assess owing to fading.

This method was checked against a gravimetric method in which the aldehyde was precipitated as an insoluble 'dimedone' compound, filtered and weighed. This latter method was very accurate but too elaborate for routine engine sampling work.

Method of sampling

Using the potassium iodide method of analysis satisfactory results were obtained by sampling 6 l. of expanded cylinder gas in the case of peroxides and 3 l. for aldehyde, which, at a sampling rate of 200 ml. of gas/min., involved 30 and 15 min. runs respectively, thus enabling about 14 crank angles to be examined in a day.

It was found to be very important to carry out a peroxide curve test in a straight run on one day, as the results were greatly affected by various surface effects in the engine and valve which were difficult to reproduce.

The solution in the scrubber was drained off at the end of the run and examined immediately in the case of peroxides; aldehyde solutions, on the other hand, were quite stable and were analyzed in a batch at the end of the test.

Types of peroxide and aldehyde present in the samples

There is very little direct evidence to offer on this subject. Owing to the necessity for using an acid trap solution, hydrolysis might account for the fact that the peroxide behaved in the analyses in exactly the same way as does H_2O_2.

The engine peroxide had more affinity for water than had *t*-butyl hydroperoxide. This was shown by the fact that a CO_2 scrubbing procedure left the former in the solution (as did H_2O_2), but easily removed the latter from solution.

Shtern & Pollyak (1943) have identified H_2O_2 in engine-gas condensates by a polarographic technique but failed to prove the presence of organic peroxides conclusively.

In the 'dimedone' tests for aldehydes the aldehyde-dimedone compounds were tested for melting-point, and in all cases gave exactly the same melting-point as a sample of pure formaldehyde-dimedone compound, i.e. 189° C. The mixed melting-point was also unchanged. This showed that over the span of the aldehyde curves formaldehyde was at least in vast preponderance.

5·2. *Results with* iso-*octane as fuel*

'Mixed *iso*-octanes' was chosen as the first fuel for investigation, because it is a typical branched-chain paraffinic fuel obtainable in fairly large quantities in a relatively high degree of purity. Figures 9 and 10 show peroxide and aldehyde curves for this fuel at a series of compression ratios starting well below the knock limit and rising to a figure giving a heavy knock intensity. On all these curves a rise in pre-flame peroxide concentration takes place before t.d.c., followed by a much higher peak value just before the arrival of the flame. With increase of compression ratio, there is an earlier rise in peroxide concentration and a much higher peak value. There is a point of inflexion just after t.d.c., suggesting that the curves are two-stage in nature. There seems no doubt about this, since the effect has been observed in a very large number of curves obtained under similar conditions.

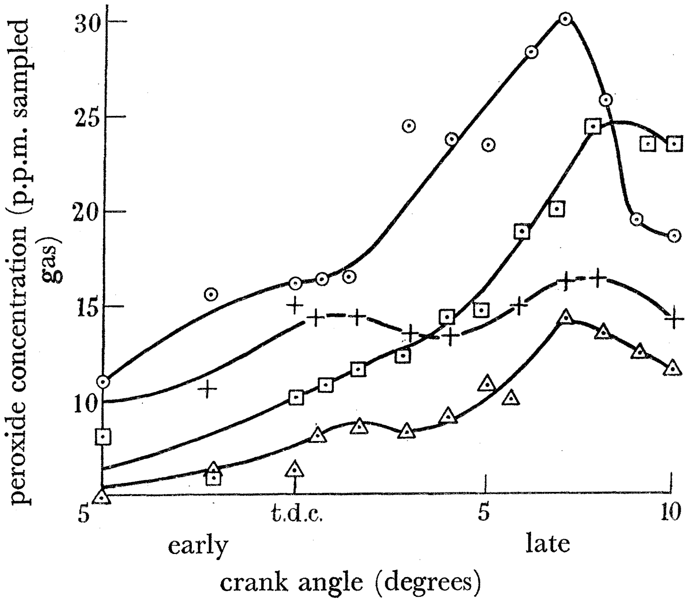


FIGURE 9. Peroxide concentration in gases sampled from the engine at various crank angles. Test conditions: Engine speed 1500 r.p.m.; mixture 12 % rich.; intake air temperature 70° C; engine coolant temperature 60° C; gas flow 200 ml./min.; ignition timing adjusted to give mean flame arrival 10° l.; Solex carburettor. Fuel: mixed octanes. △ c.r. 7·0 n.d.; ⊡ c.r. 8·0 n.d.; ⊙ c.r. 9·9 f.m.d.; + c.r. 9·9 mixed octanes + 3 ml. lead tetraethyl/imp. gal. n.d.

The effect (figure 9) of the addition of enough lead tetraethyl to suppress knock is to lower the concentration of peroxides very considerably. The effect is greater after t.d.c. than before, thus tending to confirm the two-stage nature of the curves. The parallel observation has been made in non-engine work that lead tetraethyl affects the second, much more than the first, stage of two-stage ignition (Chamberlain & Walsh 1950).

The aldehyde curves show a smooth rise up to the time of flame arrival, achieving a peak concentration some thirty times greater than the peak peroxide value. The effect of increasing compression ratio on the aldehyde concentration parallels the effect on the peroxide curve. Lead tetraethyl decreases the aldehyde concentration at all points.

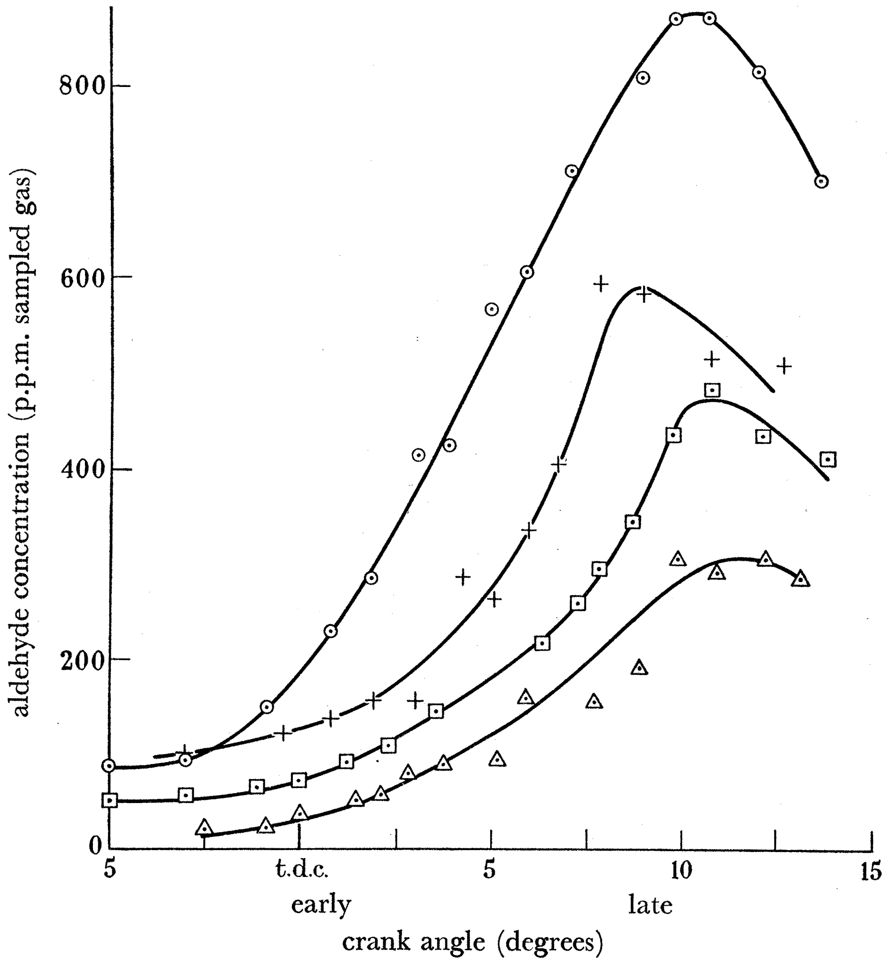


Figure 10. Aldehyde concentration in gases sampled from the engine at various crank angles. Test conditions: engine speed 1500 r.p.m.; mixture 12% rich; inlet air temperature 70° C; engine coolant temperature 60° C; gas flow rate 200 ml./min.; ignition timing adjusted to give mean flame arrival 10° l.; Solex carburettor. Fuel: mixed octanes. △ c.r. 7·0 n.d.; ⊡ c.r. 8·0 n.d.; ⊙ c.r. 9·9 'knocking'; + c.r. 9·9 mixed octanes + 3 ml. lead tetraethyl/imp. gal., n.d.

The effect of lead tetraethyl on the peroxide curve was explored still further by sampling at a fixed angle and varying the compression ratio from 7 to 14, i.e. from non-knocking to a fairly high knock intensity. The results for two separate sampling angles are shown in figures 11 and 12, from which it can be seen that, at 7° l., rise in compression ratio affects the peroxide but little, whereas at 1° l. there is a steady rise in peroxide with increase of compression ratio. This confirms that lead tetraethyl has little effect on the first stage of the knocking process, as this rise in peroxide concentration with compression ratio at 1° l. is very similar to the rise obtained with an unleaded fuel and is presumably a reflexion of the higher temperatures and pressures starting the reactions at an earlier stage in the cycle.

It will be noted that at 7° l. on the unleaded fuel, rise in compression ratio to the threshold of knock increases the peroxide concentration; thereafter increase in knock tendency does not increase the maximum peroxide concentration but the peak occurs earlier. This is understandable when we consider that a greater intensity of knock merely means that the volume of gas detonating is greater.

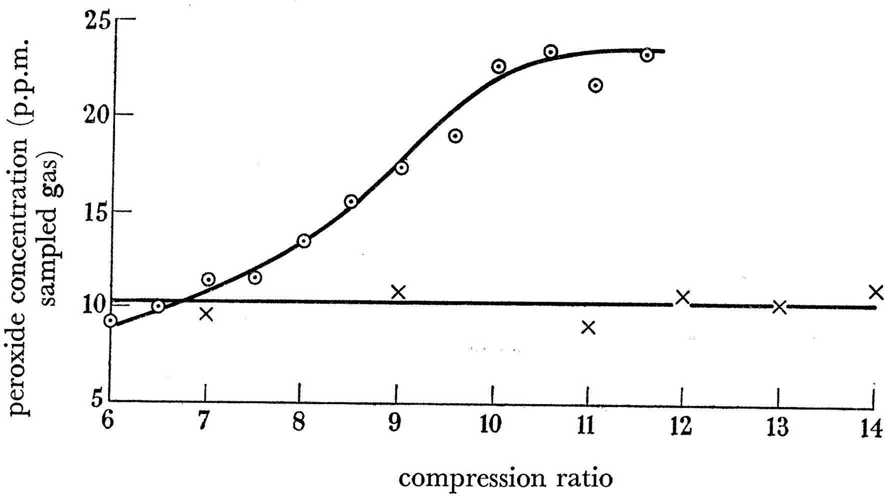


Figure 11. Peroxide concentration in gases sampled from the engine at a fixed crank angle of 7° l. The effect of compression ratio on clear and leaded mixed octanes. Test conditions: engine speed 1500 r.p.m.; mixture 12 % rich; engine coolant temperature 60° C; inlet air heat input 300 W; gas flow 200 ml./min.; ignition timing adjusted to give mean flame arrival 10° l.; Solex carburettor. × mixed octanes + 3 ml. pure lead tetraethyl/imp. gal.; ⊙ mixed octanes.

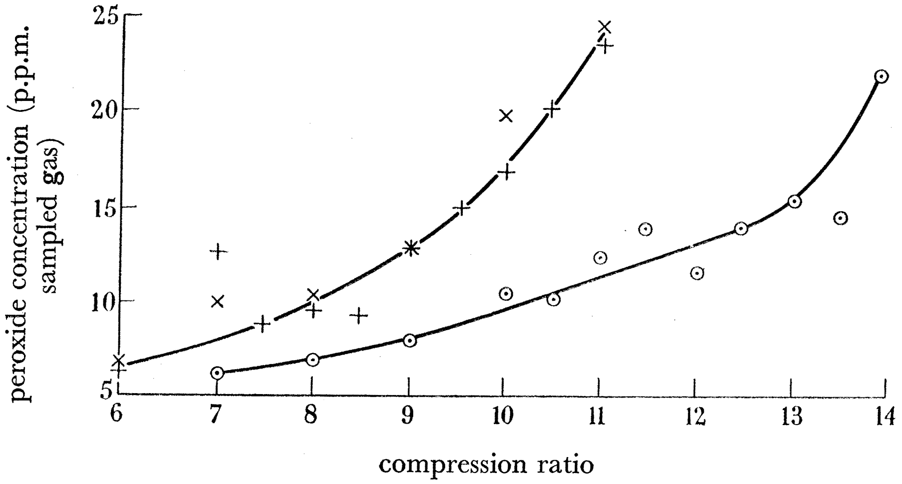


Figure 12. Peroxide concentration in gases sampled from the engine at a fixed angle of 1° l. The effect of compression ratio on clear and leaded mixed octanes. Test conditions: engine speed 1500 r.p.m.; mixture 12 % rich; engine coolant temperature 60° C; inlet air heat input 300 W; gas flow 200 ml./min.; ignition timing adjusted to give mean flame arrival 10° l.; Solex carburettor. ⊙ mixed octanes + 3 ml. lead tetraethyl/imp. gal.; × +mixed octanes.

Addition of N-methyl aniline to octanes to suppress knock has an effect on the peroxide curves similar to that of adding lead tetraethyl.

The effect of a pro-knock additive was shown by a test with amyl nitrate in the fuel. The result (figure 13) is a considerable increase in peroxide concentration. This is expected, since amyl nitrate undoubtedly acts as a source of free radicals which can start the chains

$$\begin{aligned} R+O_2 &\rightarrow ROO, \\ ROO+R_1H &\rightarrow ROOH+R_1. \end{aligned}$$

It would appear that the hydroperoxides formed in the presence of amyl nitrate include some that are more stable than those formed from the fuel itself, since the peak concentrations are very much higher than for the undoped fuel at the same knock intensity in spite of the lower compression ratio used with the doped fuel. This is not unexpected, since amyl nitrate contains all the likely isomers, and the hydroperoxides corresponding to the highly branched ones such as

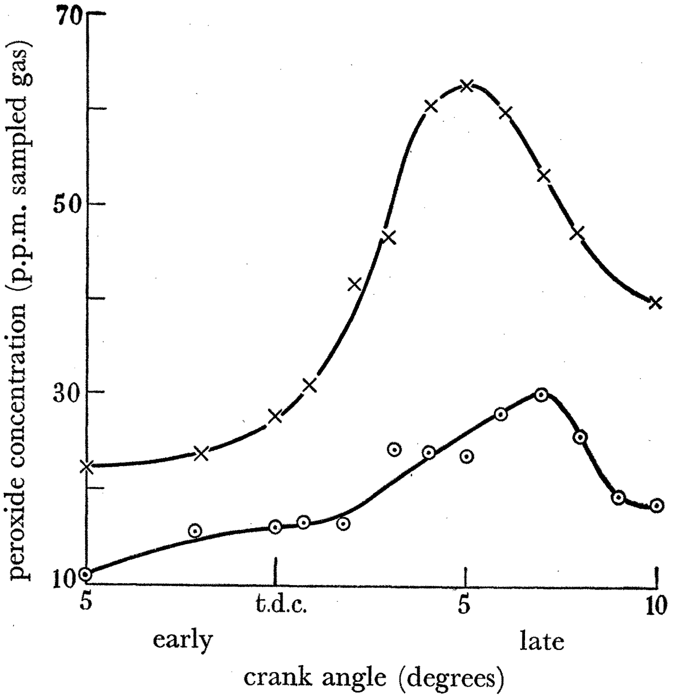
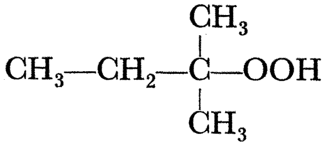


FIGURE 13. Peroxide concentration in gases sampled from the engine at various crank angles with amyl nitrate in the fuel. Test conditions: engine speed 1500 r.p.m.; mixture 12 % rich; engine coolant temperature 60° C; inlet air heat input 300 W; gas flow 200 ml./min.; ignition timing adjusted to give mean flame arrival 10° l.; Solex carburettor; frequent moderate detonation. Fuel: mixed octanes; × c.r. 8·2 mixed octanes + 20 ml. amyl nitrate/imp. gal.; ⊙ c.r. 9·9 clear mixed octanes.



$$CH_3-CH_2-\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{\underset{\displaystyle CH_3}{C}}}}-OOH$$

will be fairly stable.

A test with nitrogen peroxide was not so successful because, being a much less effective pro-knock than amyl nitrate, it was necessary to add a large quantity to the fuel to obtain a given effect, and this large quantity interfered with the analysis probably by reducing the peroxide on the way from the valve to the trap.

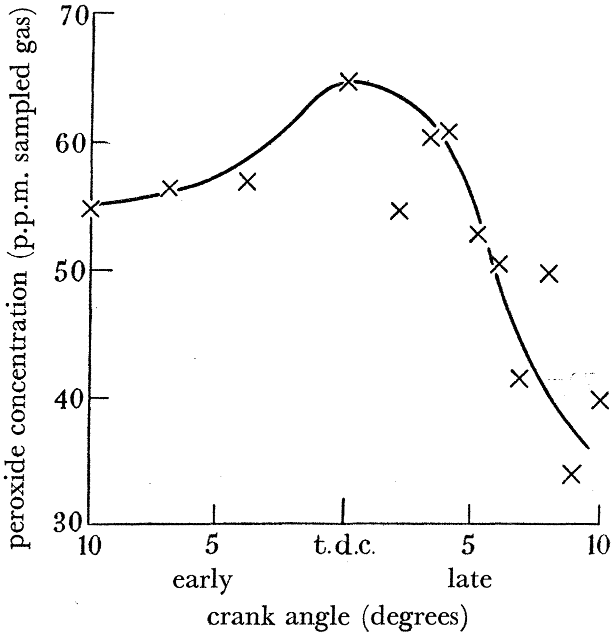


FIGURE 14. Peroxide concentration in gases sampled from the engine at various crank angles with *t*-butyl hydroperoxide in the fuel. Test conditions: engine speed 1500 r.p.m.; mixture 12 % rich, engine coolant temperature 60° C; inlet air heat input 300 W; gas flow 200 ml./min.; mean flame arrival 10° l.; ignition timing 17° e.; compression ratio 9·0; frequent moderate detonation. Solex carburettor. Fuel: mixed octanes + 0·5 % *t*-butyl hydroperoxide/imp. gal.

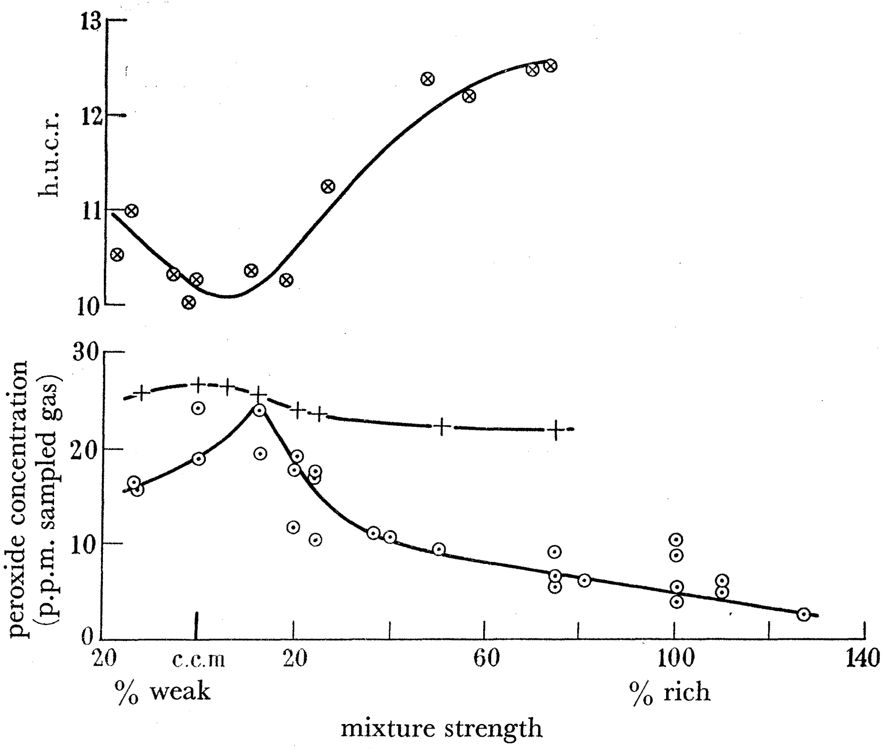


FIGURE 15. Variation of peroxide concentration in gases sampled from the engine at a fixed angle of 7° l. over the mixture range. Test conditions: engine speed 1500 r.p.m.; engine coolant temperature 60° C; engine oil temperature 60° C; inlet air heat input 300 W; gas flow 200 ml./min.; mean flame arrival 10° l.; Solex carburettor. Fuel: mixed octanes. ⊗ h.u.c.r.; + peroxide concentration with heavy knock; ⊙ peroxide concentration with no knock; c.r. 8·5.

A test was also carried out with 0·5% *t*-butyl hydroperoxide added to the fuel. The curve (figure 14) obtained at a compression ratio of 9·0 was very much as expected, the peroxide surviving in large part at early angles but decomposing as conditions became severe. The peak value was 65 p.p.m. (parts per million) at t.d.c., dropping to 35 p.p.m. just before the flame. Assuming the additive to be undecomposed, 0·5% in the fuel represents 84 p.p.m. in the sampled gas. The high recovery of peroxide in the sampled gas gives good confirmation of the validity of the sampling and analytical methods despite the known stability of this peroxide which, however, is probably only a little higher than that of some of the peroxides which might be expected from pre-reactions in highly branched octanes.

The effect of mixture strength on peroxide production was examined (*a*) at a constant compression ratio well below the knock limit, and (*b*) with the compression ratio raised in each case to a figure giving heavy knock. Under non-knocking conditions the peak peroxide concentration was found to occur at a mixture strength between 5 and 10% richer than chemically correct, i.e. approximately at the maximum knock mixture strength (figure 15). In fact, the curve of peroxide concentration against mixture strength was a close reflexion of the curve of h.u.c.r. against mixture strength. When the compression ratio was raised to the knock limit at each mixture strength on the other hand, it was found that the peak peroxide concentration was sensibly constant over the mixture range (the curve shown is the average of a large number of determinations). The slight drop in concentration with increasing mixture strength may be due to after-effects on the peroxides while they are in transit from the valve to the trap; such effects might be caused by the increased proportion of fuel residues at richer mixtures.

The curve of peroxide concentration over the mixture range obtained at 1° l. (figure 16) shows a pronounced drop at rich mixtures which is unlikely to be explained by the same effects as might account for the much smaller drop at 7° l.

Very rich mixtures may display peculiarities, as witness the work of Sokolik, Gen & Yantovskii (1947) on the two-stage ignition of benzene at rich mixtures, the work of Muhlner (1942) on motored engines and the peculiar reversals in the knock-limited power observed at mixtures around 100% rich on some boosted engines (see, for example, Biermann, Corrington & Harries 1942). It is interesting to note that there is no evidence of a change in the character of the peroxide curve at rich mixtures such as would account for these peculiarities.

The effect of speed was investigated by running at 2000 r.p.m. to compare with the figures already available at 1500 r.p.m. In both cases the compression ratio was adjusted to give the same knock intensity. At the higher speed this necessitated the use of a compression ratio 1·5 higher than at 1500 r.p.m., yet a similar peak peroxide value was obtained.

It is interesting to note from these results with varying compression ratio, mixture strength and engine speed that under knocking conditions, the peak peroxide concentration remains fairly constant. Whether or not knock occurs is related more immediately to the concentration of peroxide formed just before the arrival of the flame at the sampling point (7° l.) rather than to the concentration at the point of inflexion (1° l.). This is borne out by the effect of lead tetraethyl on the curve at the same compression ratio as for frequent moderate detonation (f.m.d.) on the unleaded fuel. The lead tetraethyl removes the peak at 7° l. but leaves the value at 1° l. relatively unaffected.

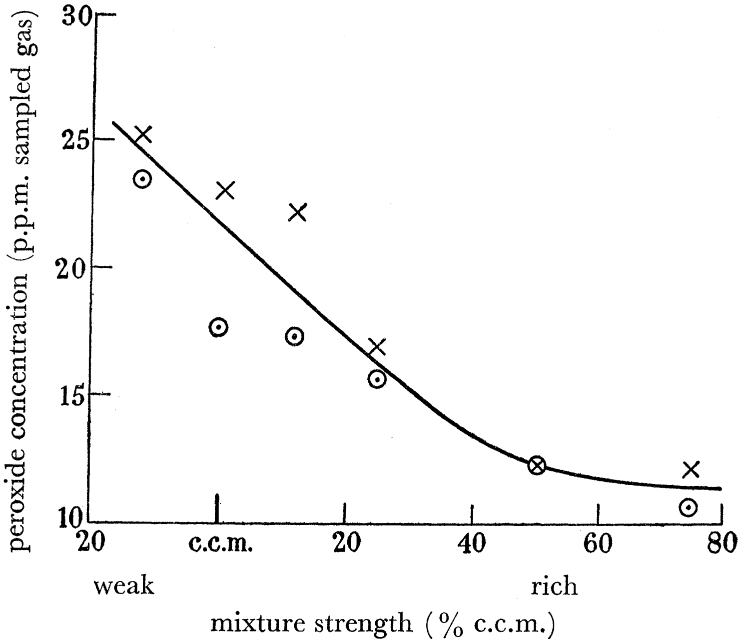
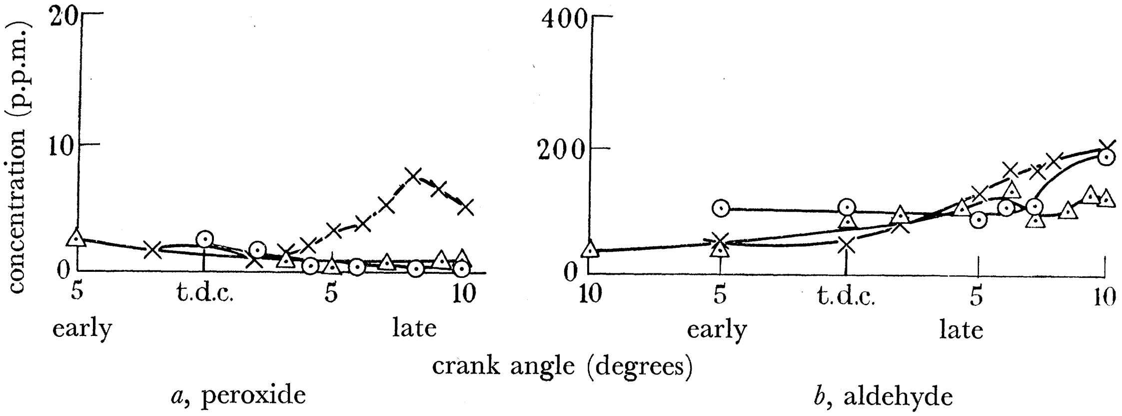


FIGURE 16. Variation of peroxide concentration in gases sampled from the engine at a fixed angle of 1° l. over the mixture range. Test conditions: engine speed 1500 r.p.m.; engine coolant temperature 60° C; inlet air heat input 300 W at 12 % rich and adjusted at other mixture strengths in proportion to the fuel flow; gas flow 200 ml./min.; mean flame arrival 10° l.; Solex carburettor; compression ratio set for heavy detonation. Fuel: mixed octanes.

5·3. *Results with other fuels*

Methane (*figure* 17)

Peroxide and aldehyde curves were obtained on methane at compression ratios of 15·0 and 18·8, the latter giving detonation of frequent moderate intensity. Curves were also obtained at a compression ratio of 18·8 with the addition of sufficient lead tetraethyl to suppress the knock. The lead was aspirated into the induction system as a vapour.



a, peroxide *b*, aldehyde

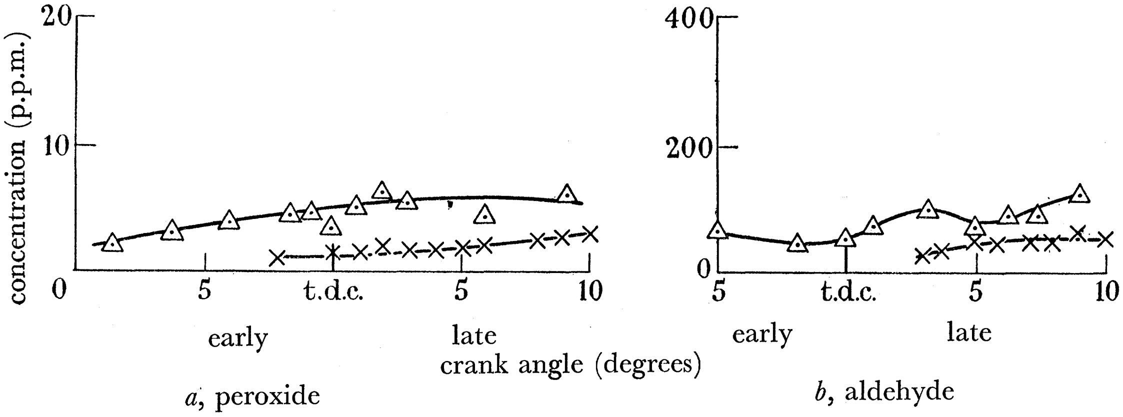
FIGURE 17. Peroxide and aldehyde concentrations in gases sampled from the engine at various crank angles on methane. Test conditions: engine speed 1500 r.p.m.; engine coolant temperature 60° C; inlet air heat input 300 W; mixture 12 % rich; mean flame arrival 10° l.; gas flow 300 to 400 ml./min. Solex carburettor. Fuel: methane. Peroxide curve: × c.r. 18·8 knocking; ⊙ c.r. 15·0; △ c.r. 18·8, methane + 0·55 ml. lead tetraethyl/hr. Aldehyde curve: × c.r. 18·85 knocking; ⊙ c.r. 15·0; △ c.r. 18·5 + 0·38 ml. lead tetraethyl/hr.

It can be seen that, in the case of the peroxide curves, raising the compression ratio to cause knock results in the formation of a peak in the peroxide curve between 3 and 10° l. This peak is eliminated by the addition of lead tetraethyl. In the case of the aldehyde curves, there is not such a big difference between the knocking and the non-knocking curves on clear methane, but the addition of lead tetraethyl does result in a reduction in concentration.

In all cases the peroxide and aldehyde concentrations are well below those obtained with *iso*-octane under comparable conditions. That some peroxide is obtained is in accord with the work of Everett & Minkoff (1949) who have detected peroxides in the combustion of methane in glass apparatus.

Benzene (*figure* 18)

Peroxide and aldehyde curves were obtained on clear benzene at a compression ratio (varying between 19·1 and 19·7) giving frequent slight detonation (f.s.d.). It can be seen that the concentrations of both peroxides and aldehydes were negligible. Experiments in which lubricating oil was added to the fuel suggested that even the very small peroxide concentration observed may, all or in part, be due to the combustion of oil which escapes past the piston.



a, peroxide *b*, aldehyde

FIGURE 18. Peroxide and aldehyde concentrations in gases sampled from the engine at various crank angles on benzene. Test conditions: engine speed 1500 r.p.m.; engine coolant temperature 60° C; inlet air heat input 300 W; mixture 12 % rich; mean flame arrival 10° l.; gas flow 300 ml./min.; Solex carburettor. Fuel: benzene. Peroxide curve: × c.r. 19·7, frequent slight detonation; △ c.r. 18·0, occasional moderate detonation, benzene + 3 ml. lead tetraethyl/imp. gal. Aldehyde curve: × c.r. 19·1, frequent slight detonation; △ c.r. 17·3, frequent moderate detonation, benzene + 3 ml. lead tetraethyl/imp. gal.

Lead tetraethyl was a pro-knock under these conditions, and its addition necessitated a lowering of the compression ratio by nearly two numbers in order to obtain the same intensity of knock. Both curves show increases over their unleaded counterparts although all the values are very low.

Alkyl benzenes (*figure* 19)

Peroxide curves were obtained on toluene, ethyl benzene, cumene, pseudo-cumene and mesitylene, each fuel being tested at the compression ratio giving f.m.d., to see whether with the addition of side chains to the molecule there was any transition to a more paraffinic type of curve. It can be seen that in no case was any appreciable quantity of peroxide obtained, even with the fuel with the longest side chain.

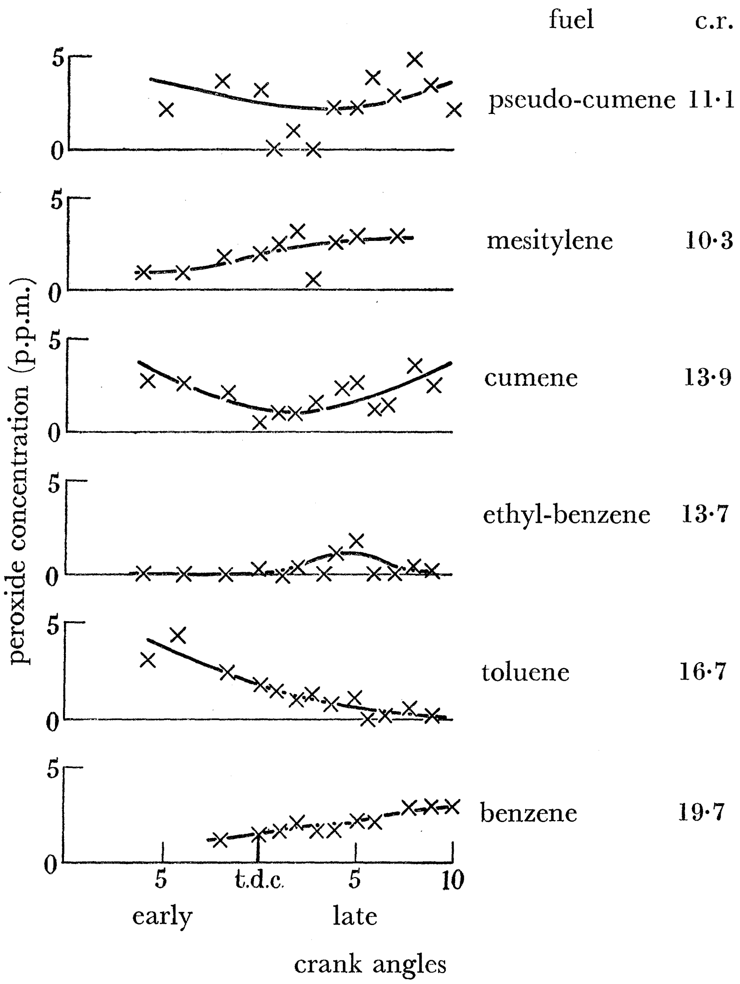


FIGURE 19. Peroxide concentration in gases sampled from the engine at various crank angles on fuels of the benzene group. Test conditions: engine speed 1500 r.p.m.; engine coolant temperature 60° C; inlet air heat input 300 W; mixture 12 % rich; mean flame arrival 10° l.; gas flow 200 ml./min.; frequent moderate detonation; Solex carburettor.

In order to form some idea of the effect of the aromatic nucleus on the pre-flame reactions, a test was carried out using a 50/50 mixture of benzene and *iso*-octane (figure 20). The compression ratio used was that giving f.m.d. on *iso*-octane alone and, with the addition of benzene, no knock occurred. It can be seen that the maximum peroxide concentration has been reduced to between one-half and one-third of that obtained on *iso*-octane alone at the same compression ratio.

A special test was carried out on benzene at a mixture strength 65 % richer than chemically correct (compression ratio 15·7 f.s.d.) to see whether at a mixture claimed by Sokolik, Gen. & Yantovski (1947) to give cool flames in laboratory tests, peroxides were formed in the engine. No peroxides were detected under this condition.

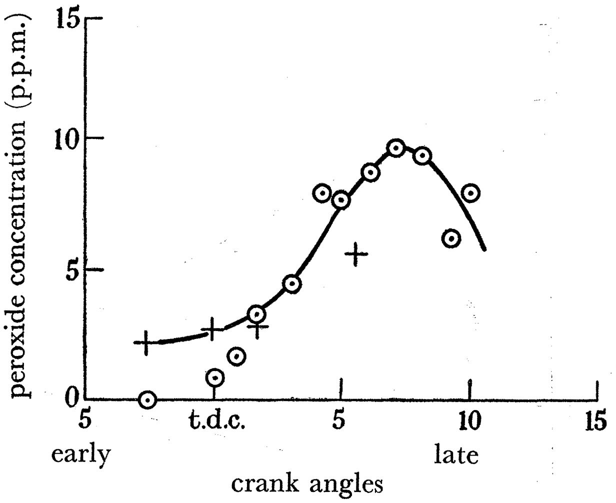


FIGURE 20. Peroxide concentration in gases sampled from the engine at various crank angles on 50/50 benzene/octanes. Test conditions: engine speed 1500 r.p.m.; engine coolant temperature 60° C; inlet air heat input 300 W; mixture 12 % rich; mean flame arrival 10° l.; gas flow 200 ml./min.; non-detonating; Solex carburettor. Fuel: 50/50 benzene/mixed octanes.

6. 'HIGH'- AND 'LOW'-TEMPERATURE IGNITION

A large number of additives were tested in benzene and methane as well as in fuels of the higher paraffinic and naphthenic types, such as *iso*-octane, neohexane, cyclohexane, etc. It was found that the effect of additives on the knock tendencies of benzene and methane was often very different from their effect on the higher paraffinic fuels.

Thus formaldehyde was an anti-knock in the latter class and a pro-knock in the former class (figure 21). Acetaldehyde was ineffective in the latter class but strongly pro-knock in the former class (figure 22). Nitrogen peroxide had only a slight pro-knock effect on the higher paraffinic fuels, but it was a strong pro-knock in benzene and methane (figure 23). Benzaldehyde was ineffective in *iso*-octane but was a pro-knock with benzene (figure 24).

It is well known (Townend 1937) that the pressure-temperature ignition diagrams for paraffinic fuels show two main regions, a so-called 'high'-temperature region and a so-called 'low'-temperature ignition peninsula. The formation of alkyl hydroperoxides is associated only with the 'low'-temperature region. Ignition in the 'low'-temperature region is by a two-stage process, involving a first time interval to the appearance of a so-called cool flame and a second from the appearance of a cool flame to the appearance of a normal flame. Ignition in the 'high'-temperature region is by a continuous, one-stage process. The ignition diagrams for methane and benzene show only the 'high'-temperature type of curve. Formaldehyde has an accelerating effect on the reactions leading to the 'high'-temperature type of ignition, but increases the first of the two time intervals involved in 'low'-temperature ignition. Nitrogen peroxide strongly promotes ignition in the 'high'-temperature region, but has opposing effects on the two stages involved in 'low'-temperature ignition; it may therefore have only a small overall effect on ignition by the low-temperature mechanism. Lead tetraethyl has little effect on the first time interval involved in 'low'-temperature ignition, but a profound effect on the second. At least with di-*iso*propyl ether (Chamberlain & Walsh 1949*a*), acetaldehyde has only a slight effect on 'low'-temperature

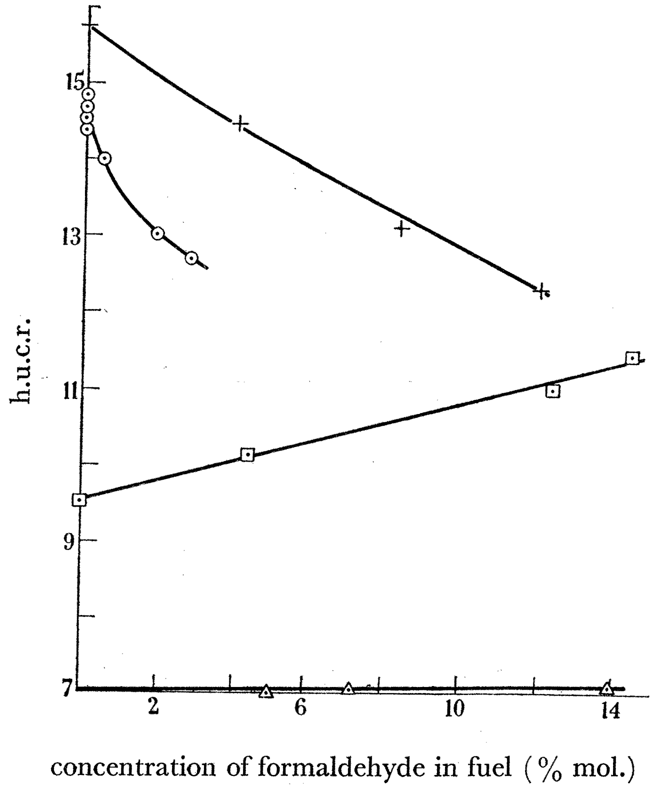


Figure 21. Effect of formaldehyde on the h.u.c.r.'s of various fuels. Test conditions: engine speed 1500 r.p.m.; inlet air temperature 120° C; engine coolant temperature 90° C; Solex carburettor; additive admitted with air. Fuels: + benzene; ⊙ methane; ⊡ *iso*-octane; △ cyclohexane.

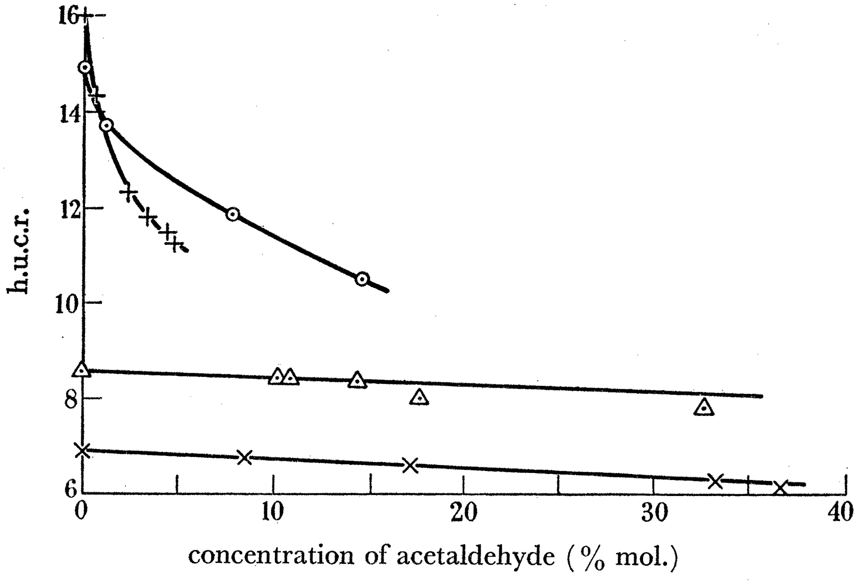


Figure 22. Effect of acetaldehyde on the h.u.c.r.'s of various fuels. Test conditions: engine speed 1500 r.p.m.; inlet air temperature 120° C; engine coolant temperature 90° C; Solex carburettor; additive admitted with air. Fuels: ⊙ benzene; + methane; △ *iso*-octane; × cyclohexane.

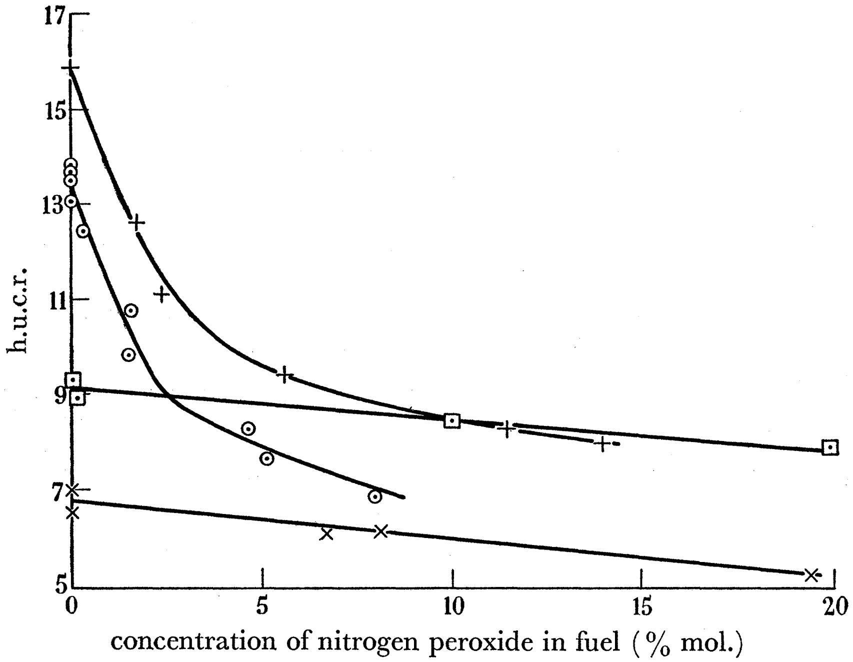


FIGURE 23. Effect of nitrogen peroxide on the h.u.c.r.'s of various fuels. Test conditions: engine speed 1500 r.p.m.; inlet air temperature 120° C; engine coolant temperature 90° C; Solex carburettor; additive admitted with air. Fuels: + benzene; ⊙ methane; ⊡ *iso*-octane; × cyclohexane.

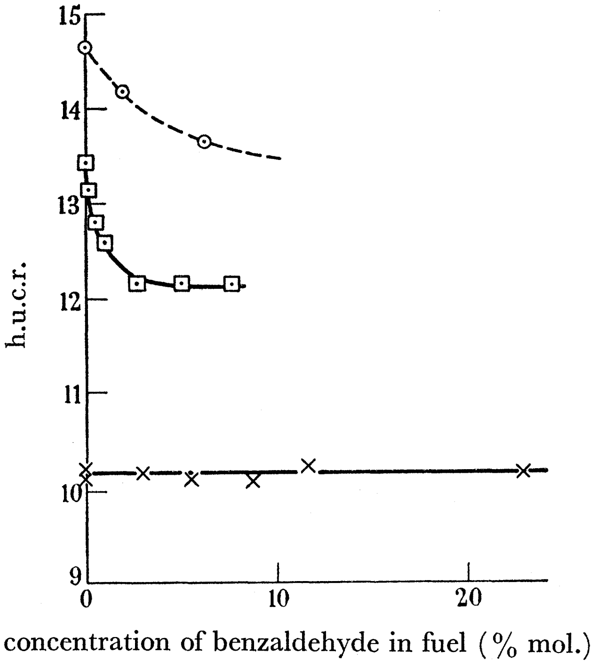


FIGURE 24. Effect of benzaldehyde on the h.u.c.r.'s of various fuels. Test conditions: Engine speed 2500 r.p.m.; inlet air temperature 70° C; engine coolant temperature 70° C; Solex carburettor; additive admitted with fuel. Fuels: ⊙ benzene; ⊡ benzene + 3 % volume acetaldehyde; × *iso*-octane.

combustion in comparison with a very marked promoting effect on 'high'-temperature ignition. Benzaldehyde is without effect on 'low'- but has an anti-oxidant effect on 'high'-temperature combustion.

It can be seen, therefore, that there is a close parallel between the effect of formaldehyde, acetaldehyde and nitrogen peroxide on knock with the higher paraffins and naphthenes in the engine and on oxidation by the 'low'-temperature process in the laboratory. Conversely, there is a similar parallel between the effect of these additives on knock with benzene and methane in the engine and on oxidation by the 'high'-temperature process in the laboratory. The lack of agreement with benzaldehyde is perhaps explained by the early decomposition of the additive under engine conditions.

Tests on further additives have borne out these conclusions. Thus methyl iodide has an anti-knock effect in *iso*-octane and cyclohexane but a marked pro-knock effect in benzene and methane (figure 25). The pro-knock effect in benzene and methane is in accord with the observation (Chamberlain & Walsh, unpublished) of the pro-oxidant effect of methyl iodide on the slow oxidation of di-*iso*propyl ether at 360° C (i.e. in the high-temperature region). In contrast to the engine observation on *iso*-octane, methyl iodide was found to have no effect in the 'low'-temperature region of di-*iso*propyl ether oxidation. Smaller quantities were, however, used in the non-engine tests, and this may account for the difference of observed effect.

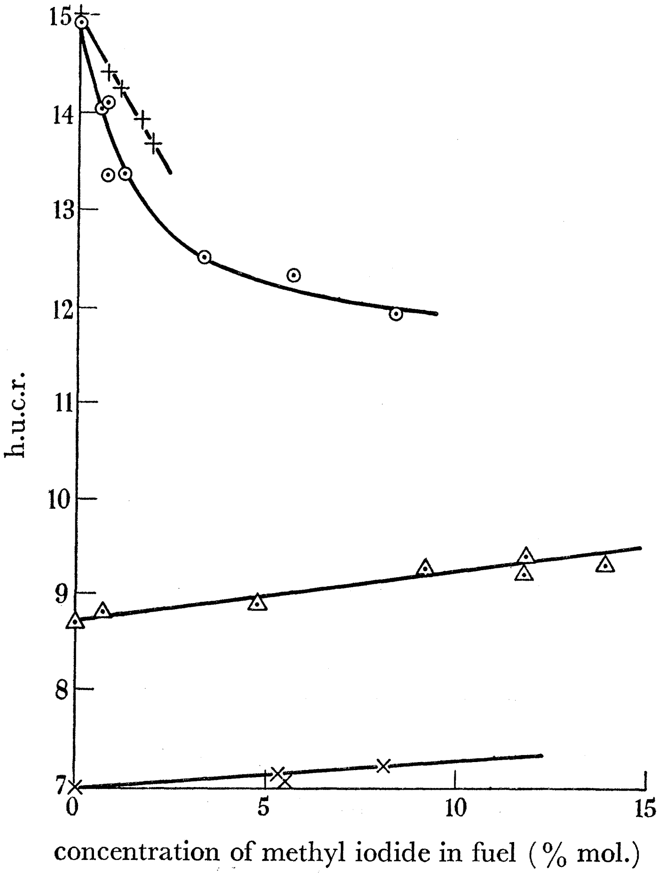


FIGURE 25. Effect of methyl iodide on the h.u.c.r.'s of various fuels. Test conditions: engine speed 1500 r.p.m.; inlet air temperature 120° C; engine coolant temperature 90° C; Solex carburettor; additive admitted with air. Fuels: ⊙ benzene; + methane; △ *iso*-octane; × cyclohexane.

Similar tests (table 5) have shown ethyl, *n*-propyl, *i*-propyl and *n*-butyl iodides to be anti-knocks in clear but pro-knocks in leaded fuel. This anti-knock effect may be due to the action of the liberated iodine. An alternative suggestion is that the iodides act as undecomposed molecules (perhaps by deactivating energy rich molecules engaged in propagating the combustion chains). This suggestion has the advantage that it might explain why the substances become pro-knocks in the higher h.u.c.r. fuels such as benzene and methane, where decomposition is likely. In a leaded fuel, the iodides, like iodine itself, have a pro-knock effect, due, presumably, to the formation of some compound containing lead and iodine.

TABLE 5. TESTS ON ALKYL IODIDES

engine speed 2500 r.p.m.
coolant temperature 70° C
maximum knock mixture
517 W heat input to induction air
ignition advance—optimum for maximum power mixture at each c.r.
Fuels: standard no. 1 and standard no. 1 + 4·7 ml. lead tetraethyl/imp. gal.

	change in h.u.c.r.	
	std. no. 1	std. no. 1 + 4·7 ml. lead tetraethyl/imp. gal
methyl iodide	+0·10	—
ethyl iodide	+0·11	—
n-propyl iodide	+0·04 +0·13	−1·39
i-propyl iodide	+0·04	−1·41
n-butyl iodide	+0·12	—

Organic peroxides (figure 26) are, as expected, strong pro-knocks in all classes of fuel.

The effect of lead tetraethyl, introduced into the intake air as a vapour, on the h.u.c.r. of various fuels is shown in figure 27. The very great lead response of methane is noteworthy. The low lead response of benzene is understandable, since benzene is itself an inhibitor of oxidation and the chains by which benzene oxidizes are known to be consequently short (Fort & Hinshelwood 1930). Under such circumstances no added inhibitor could be expected to be very effective.

The effect of aniline and N-methyl aniline on a variety of fuels is shown in figure 28. Both the amines, though anti-knocks in Standard no. 4 and cyclohexane, are pro-knocks in methane and benzene. The aromatic amines are thought to exert their anti-knock action as undecomposed molecules (Walsh 1949). The pro-knock effect in fuels of higher h.u.c.r. is, therefore, presumably due to the breakdown under the higher temperature condition of the additives to yield free radicals; and the greater pro-knock effect of *n*-methyl aniline than of aniline is presumably due to the former yielding more (and perhaps more potent) free radicals than the latter.

In order to make sure that the difference in effect of amines in methane and benzene on the one hand, and Standard no. 4 and cyclohexane on the other, was due to the different temperatures prevailing, rather than to the difference in nature of the combustion reactions involved, experiments were carried out as follows. Tests were performed on N-methyl

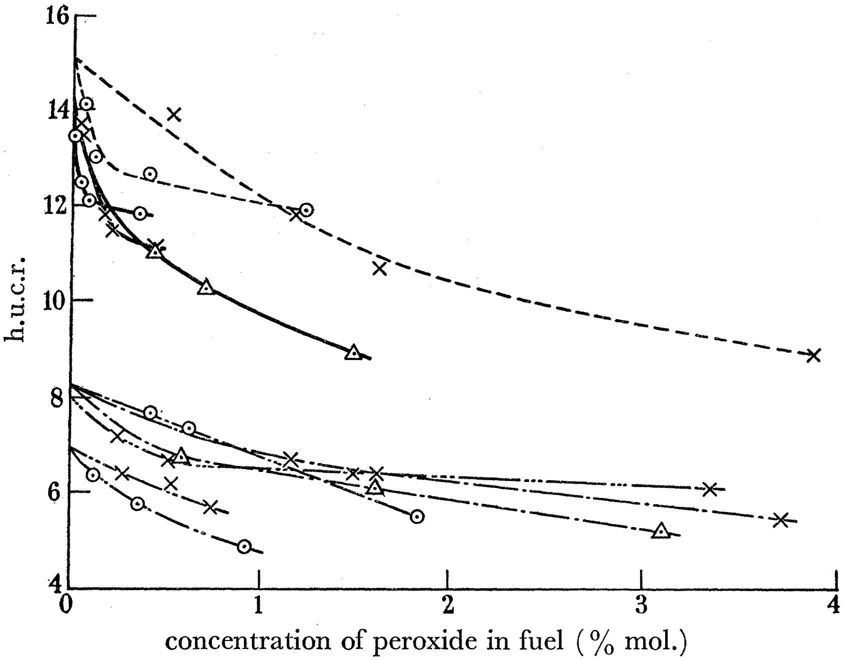


FIGURE 26. Effect of organic peroxides on the h.u.c.r.'s of various fuels. Test conditions: engine speed 1500 r.p.m.; inlet air temperature 120° C; engine coolant temperature 90° C; Solex carburettor; additive admitted with air. Fuels: —— methane; ---- benzene; —·— standard no. 4; —··— cyclohexane; —···— standard no. 1. Additives: ⊙, hydroxy methyl *t*-butyl peroxide; × *t*-butyl hydrogen peroxide; △ di-*t*-butyl peroxide.

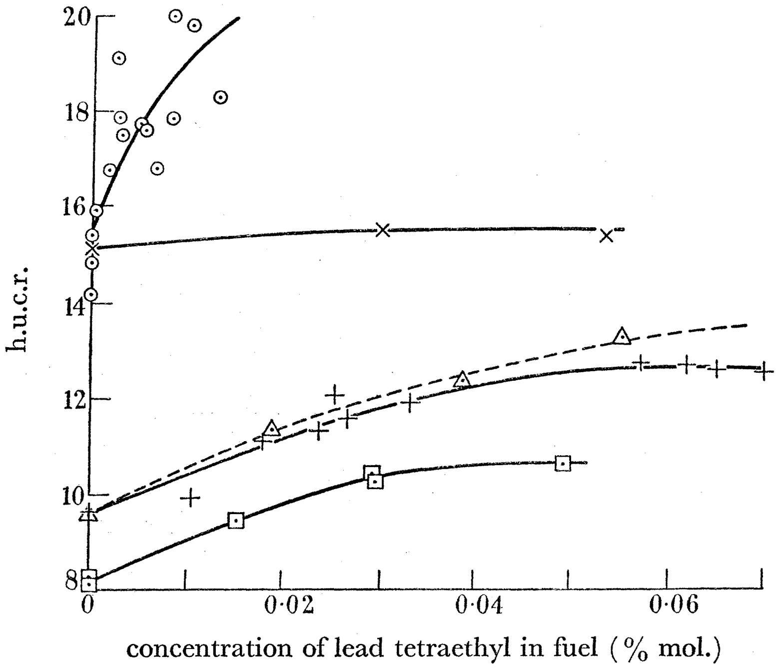


FIGURE 27. Effect of lead tetraethyl on the h.u.c.r.'s of various fuels. Test conditions: engine speed 1500 r.p.m.; inlet air temperature 120° C; engine coolant temperature 90° C; Solex carburettor; additive admitted with air. Fuels: ⊙ methane; ⊡ standard no. 1; + *iso*-octane; △ *iso*-octane (lead tetraethyl introduced with the fuel); × benzene.

aniline in blends of Standard no. 4 fuel and DTD 230 base in benzene. Figure 29 shows that with blends containing Standard no. 4 a content of only 25% benzene is sufficient to depreciate considerably the N-methyl aniline response. With DTD 230 base, on the other hand, a content of up to 50% benzene can be used without causing any loss in N-methyl aniline response; in fact, there is a slight increase in response in terms of h.u.c.r. A characteristic of the curves is that they appear to flatten off in the region of an h.u.c.r. of 10·0 to 10·5 regardless of the composition of the fuel. It seems probable, therefore, that above an h.u.c.r. of about 10·3 the pressure-temperature conditions inside the combustion chamber are such that most of the N-methyl aniline is destroyed before it can exert its anti-knock effect. At h.u.c.r.'s greater than *c.* 10·3 the pro-knock effect of the products of premature destruction of the N-methyl aniline is outweighing the anti-knock effect of the unchanged molecules. The efficacy of N-methyl aniline as an anti-knock thus appears to depend primarily on the pressure-temperature conditions at which it operates and only to a secondary extent on the chemical nature of the fuel. The addition of benzene does not of itself lower the N-methyl aniline response, but has a depreciating effect only in so far as its addition enables the pressure-temperature level of the engine to be raised above that necessary to cause extensive destruction of the N-methyl aniline molecules. An h.u.c.r. test carried out on pure N-methyl aniline resulted in a value of 10·1, i.e. approximately the same as the h.u.c.r. of transition from anti- to pro-knock when N-methyl aniline is added to the fuel. A test on B.A.M. 100 reference fuel at the same time gave a value of 10·0.

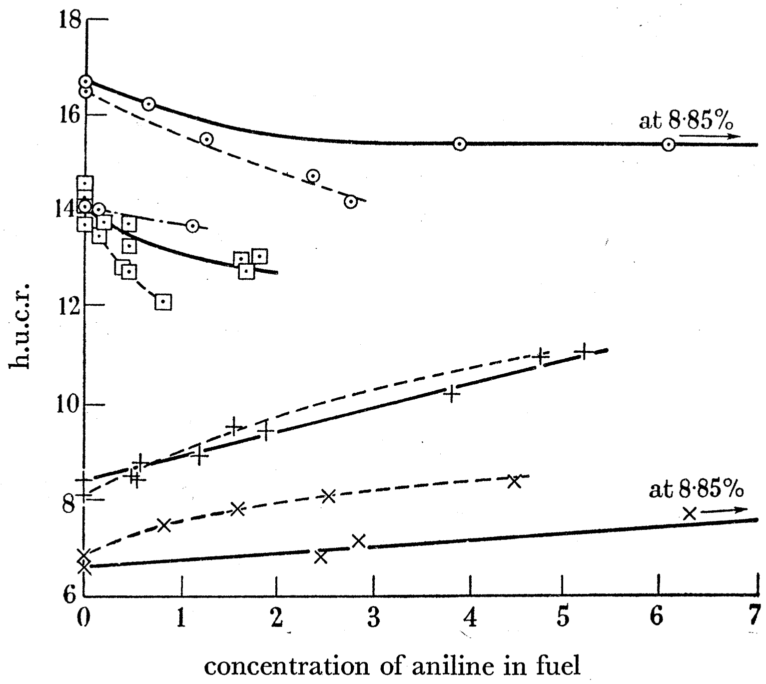


FIGURE 28. Effect of aniline and *n*-methyl aniline on the h.u.c.r.'s of various fuels. Test conditions: engine speed 1500 r.p.m.; inlet air temperature 120° C; engine coolant temperature 90° C; Solex carburettor; additive admitted with air. Fuels: ⊙ benzene; ⊡ methane; + standard no. 4; × cyclohexane. Additives: —·— clear fuel; —— aniline; ---- N-methyl aniline.

Although experiments in glass apparatus have never shown a 'low'-temperature peninsula with methane, a rudimentary 'low'-temperature peninsula has been found with the next member of the paraffin series, ethane (Townend 1937). Engine tests were, therefore, carried out with ethane to see whether it is the member of the paraffin series which marks the transition from the 'high'- to the 'low'-temperature knocking mechanism in the engine.

In ethane, as in methane, formaldehyde was found to be a pro-knock and nitrogen peroxide a strong pro-knock (figure 30). Hydrogen was ineffective in ethane but a pro-

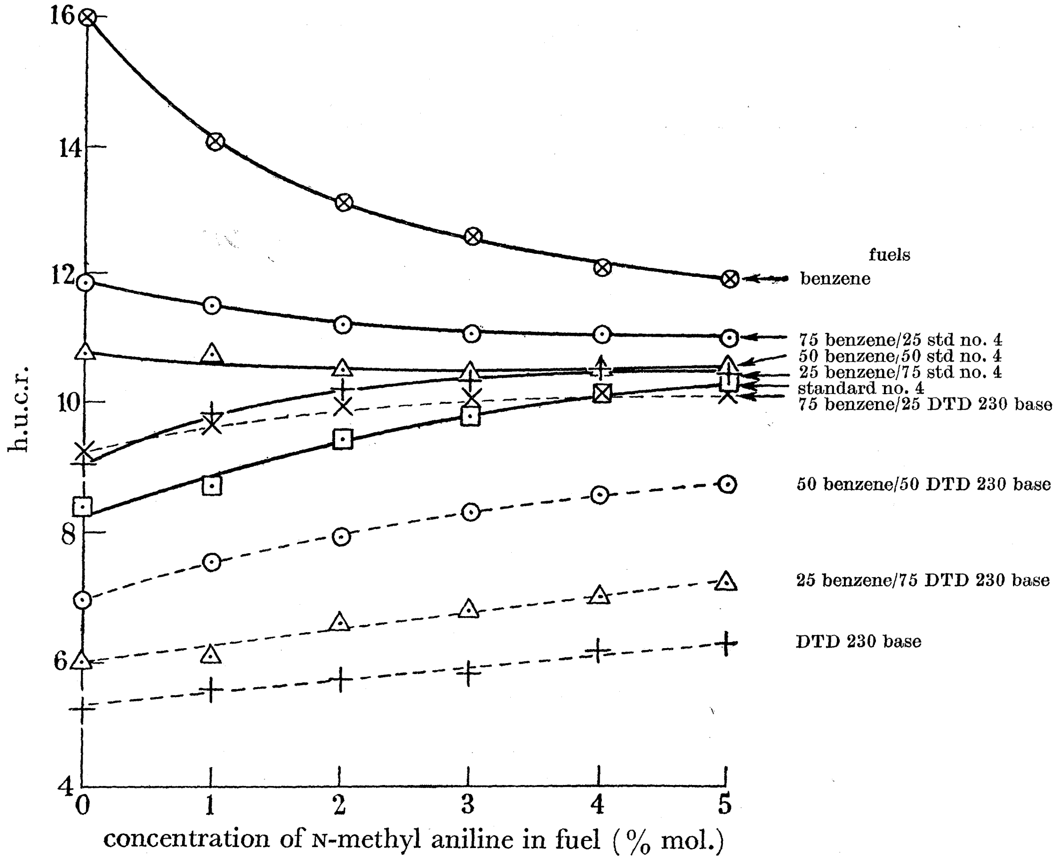


FIGURE 29. Effect of *n*-methyl aniline on the h.u.c.r.'s of blends of standard no. 4 and DTD 230 base with benzene. Test conditions: engine speed 1500 r.p.m.; inlet air temperature 120° C; engine coolant temperature 90° C; Solex carburettor; additive admitted with the fuel.

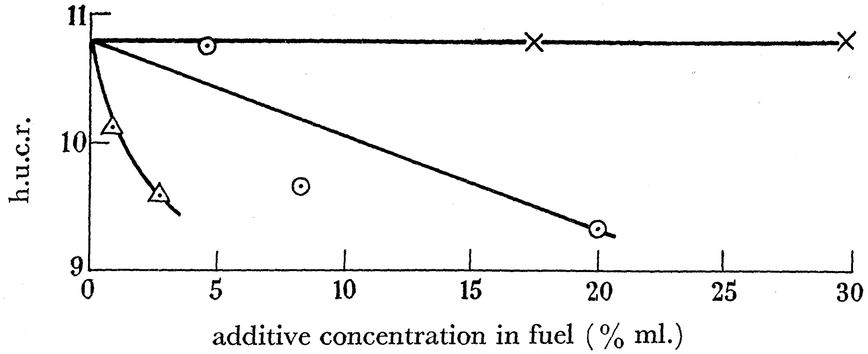


FIGURE 30. Effect of various additives on the h.u.c.r. of ethane. Test conditions: engine speed 1500 r.p.m.; inlet air temperature 120° C; engine coolant temperature 90° C; maximum knock mixture strength; ignition advance optimum for maximum power mixture at each compression ratio. Additives: × hydrogen; ⊙ formaldehyde; △ nitrogen peroxide.

knock in methane. The effects of the first two additives support the idea that ethane, like methane, knocks by a 'high'-temperature mechanism. The result with hydrogen suggests, however, that in the case of ethane there may be a certain 'low'-temperature component. As expected lead tetraethyl was found to be a strong anti-knock with ethane.

7. Pressure and temperature measurements

Figure 31 shows cylinder pressure diagrams obtained on the E. 6 engine, using a balanced disk pressure pick-up, under the principal sampling conditions. Figure 32 shows the corresponding temperature of the unburnt 'end-gas' calculated from these pressures and from the measured fuel and air consumptions using the method of Taylor, Leary & Diver (1941) with the thermodynamic charts of Hottel, Williams & Satterfield (1949). Locally, the 'end-gas' temperatures may be much higher than are indicated by these overall figures, and, in fact, it seems probable that a cool flame must pass in the 'end-gas' of the engine prior to the occurrence of knock in the case of those fuels which oxidize by a two-stage mechanism. Both Jost (1946) and Mühlner (1942) have claimed to have seen a cool flame in the combustion chamber of an engine motored under conditions of high-compression

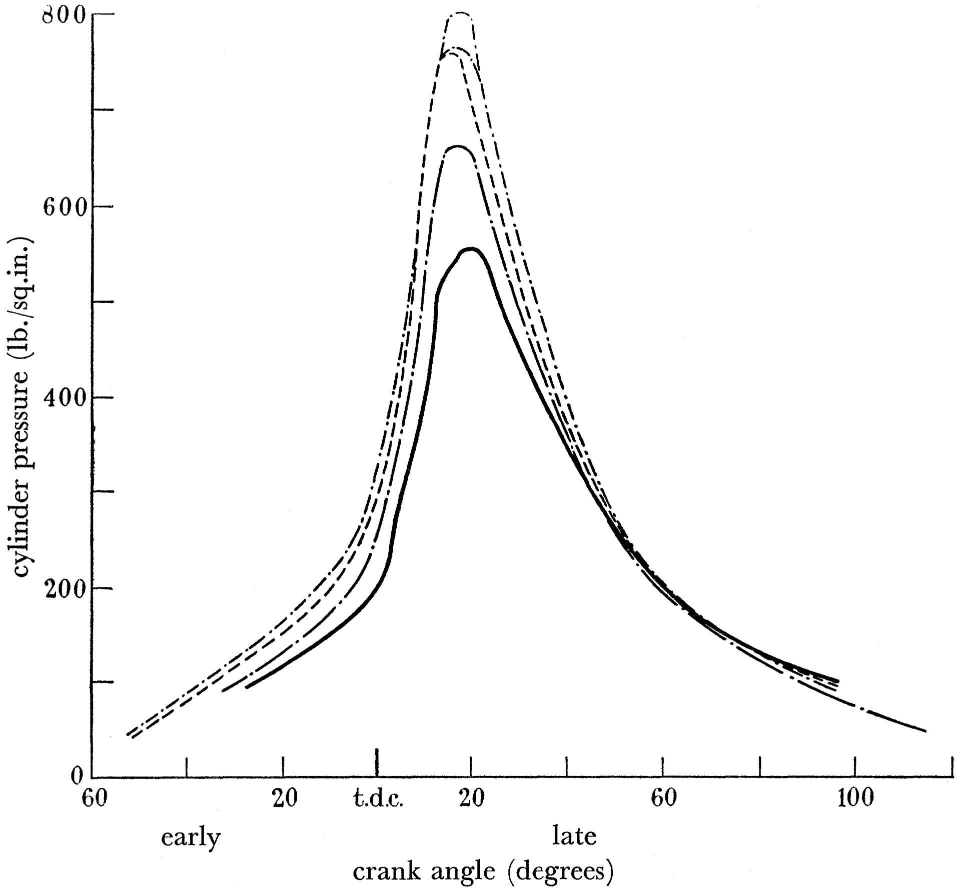


Figure 31. Cylinder pressure diagrams under sampling conditions. Test conditions: engine speed 1500 r.p.m.; engine coolant temperature 60° C; inlet air heat input 300 W; mixture 12 % rich; optimum ignition advance; Solex carburettor. Fuel: mixed octanes. —— c.r. 7·0; —·— c.r. 8·0; ---- c.r. 9·0; —·—·— c.r. 10·0, frequent slight detonation.

ratio and temperature, and Taylor, Taylor, Livengood, Russell & Leary (1950) and Levedahl & Sargent (1948) have obtained evidence of two-stage ignition in motored engines. In addition, there is a striking parallel between the engine peroxide curves (figure 9) and those obtained by Burgoyne (1940) in continuous-flow experiments. He found a steady rise in peroxide concentration as the reaction proceeded, and then, on the passage of the cool flame, the peroxide curve flattened off, later rising again in a manner similar to the engine peroxide curves. Some work has, therefore, been done to establish the time of passage of the cool flame with more certainty and link it with the engine peroxide curves.

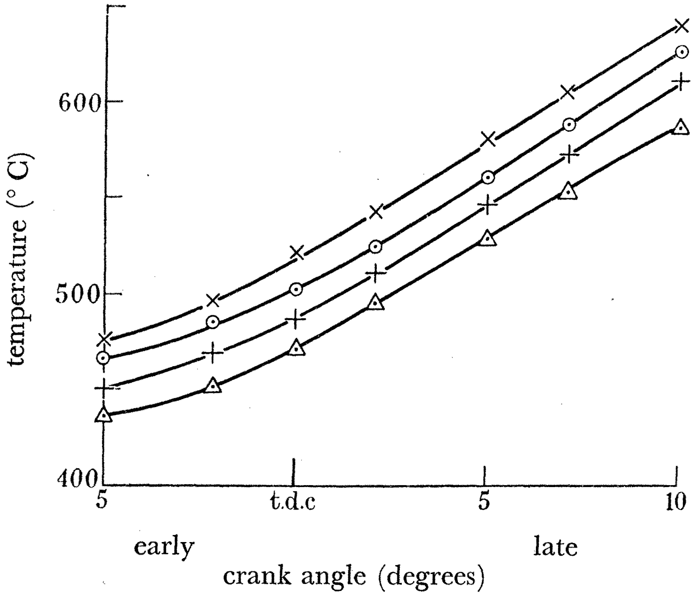


FIGURE 32. Calculated end gas temperatures under sampling conditions. Test conditions: engine speed 1500 r.p.m.; engine coolant temperature 60° C; inlet air heat input 300 W; mixture 12 % rich. × c.r. 10·0; ⊙ c.r. 9·0; + c.r. 8·0; △ c.r. 7·0.

7·1. *Ignition experiments on a motored engine*

Some tests were first carried out on a motored engine fitted with a glass observation window in the combustion chamber to establish the limits of cool- and hot-flame formation. The window had an optical system which turned the light through a right angle, thus protecting the observer from the consequences of a possible fracture of the glass window. The engine was motored at a constant speed of 1500 r.p.m. under the following conditions:

jacket temperature 60° C,
heat to intake air 300 W,
crankcase oil temperature 50 to 60° C,
shrouded inlet valve,

and with the fuel/air mixture passing through the carburettor in the normal way. The compression ratio was gradually raised until the sound of explosion was heard, and simultaneously a brilliant white flash was observed through the window. The critical compression ratio used as a standard in these tests was that which gave an explosion, on an average, once every 3 sec. Under certain conditions, in addition to brilliant white flames, bright blue flames, similar to those observed in the combustion of carbon monoxide, were seen. Sometimes a noise in the exhaust pipe accompanied these blue flames and at other times it did not. If the compression ratio was lowered sufficiently to avoid combustion, and a very close observation was maintained through the window until the eye became accustomed to the change in light intensity, a blue glow of a very low order of intensity and flashing at engine frequencies could sometimes be seen. On occasion a bright blue flame, with or without an audible sound, was intermittently superimposed upon the blue glow. The intensity of the blue glow varied according to the particular fuel being used, the fuel/air ratio and the compression ratio. At each mixture strength, therefore, if luminosity was observed, an attempt was made to adjust the compression ratio to give an intensity which was distinctly visible, but of a low order. However, it sometimes happened that a strong glow disappeared entirely when the compression ratio was lowered only a small amount (e.g. the glow at the rich side of the di-*iso*propyl ether curve, figure 40), and conversely, it was sometimes found that a fainter glow persisted to a compression ratio well below the critical (e.g. 35% rich mixture with *iso*-octane). It follows, therefore, that the distance of the blue-glow limit curve below the critical compression ratio curve does not denote its intensity but is a reliable estimate of its persistence.

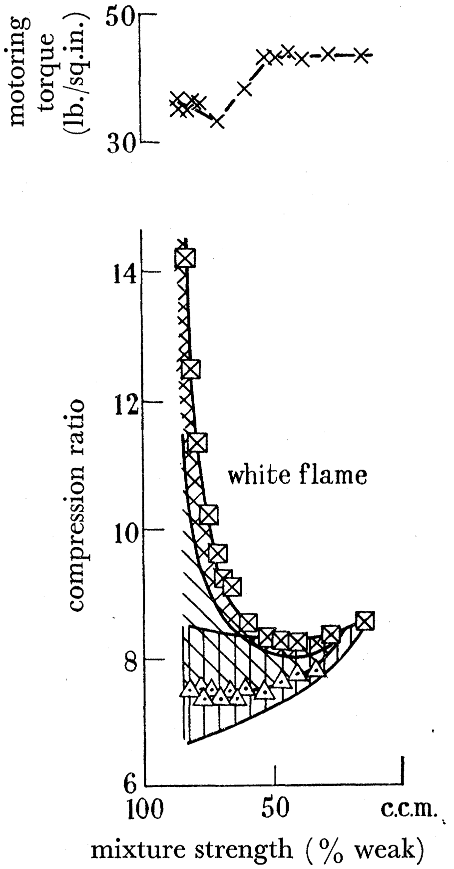


FIGURE 33. Ignition characteristics over the mixture range under motoring conditions. Fuel: N-heptane. Test conditions: engine speed (motoring) 1500 r.p.m.; engine coolant temperature 60° C; inlet air heat input 300 W; oil temperature 50 to 60° C; full throttle; shrouded inlet valve. ⊠ critical compression ratio; △ lower limit of blue glow; \\\ blue glow; /// bright blue flames; ||| black smoke.

Finally, the compression ratio was lowered by 0·8 from the critical, and a reading was taken of the torque required to maintain the engine speed at 1500 r.p.m. The reduction in this torque compared with that necessary under normal conditions was a measure of the intensity of the reactions occurring before ignition. The reduction of compression ratio by 0·8 was, in most cases, sufficient to eliminate entirely auto-ignition of the charge.

Figure 33 shows the ignition curve for *n*-heptane. Proceeding from a weak mixture, in addition to a combustion noise in the exhaust pipe, occasionally a heavy knock in the combustion chamber would accompany ignition. The knock progressively increased until at 26% weak, only violent combustion was recorded. Considerable quantities of black smoke were emitted from the exhaust test-cock at compression ratios below the critical.

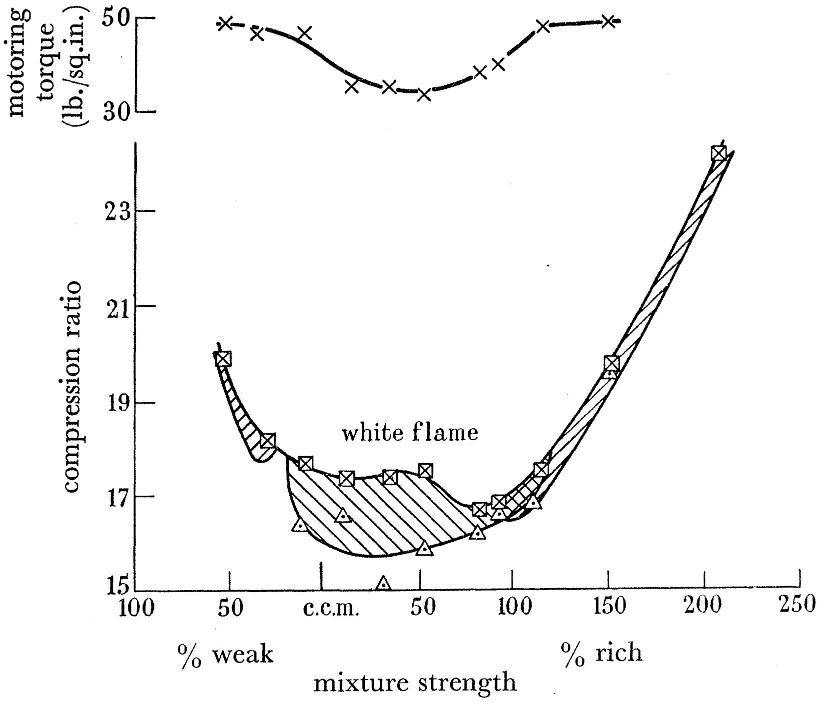


FIGURE 34. Ignition characteristics over the mixture range under motoring conditions. Fuel: *iso*-octane. Test conditions: engine speed (motoring) 1500 r.p.m.; engine coolant temperature 60° C; inlet air heat input 300 W; oil temperature 50 to 60° C; full throttle; shrouded inlet valve. ⊠ critical compression ratio; △ lower limit of blue glow; \\\ blue glow; /// bright blue flames.

As the mixture was richened the range of compression ratio giving black smoke became narrower until at mixtures richer than 50% weak the smoke limit merged with the ignition limit. The black smoke was also accompanied by a strong characteristic odour. The mixture strength requiring the lowest compression ratio for auto-ignition occurred at 45% weak, and the power required to motor the engine was lowest at about 70% weak.

With *iso*-octane (figure 34) at the weak end white flecks and white flames (unaccompanied by noise) could be seen through the observation window at compression ratios of 18·0 and over, and these persisted even when all fuel was entirely cut off from the engine. It seems likely that this is due to the combustion of lubricating oil entering the cylinder from the crankcase. The white flecks were never observed at rich mixtures with any of the fuels tested, even when the compression ratio was considerably higher than 18·0. It is interesting to speculate whether these white flecks could be misinterpreted as point auto-ignitions in high-speed photographs of engine combustion.

The ignition curve for *iso*-octane exhibits two minimum values, one occurring at about the correct mixture strength and the other at about 75 % rich. There seems no doubt about this, as it has been observed in six separate tests on this fuel. The blue glow was less intense than that produced by *n*-heptane and was most persistent at about 35 % rich. The lowest motoring torque was also recorded in this region. Combustion was often violent at mixtures 150 % richer than chemically correct, and was occasionally violent at other mixture strengths.

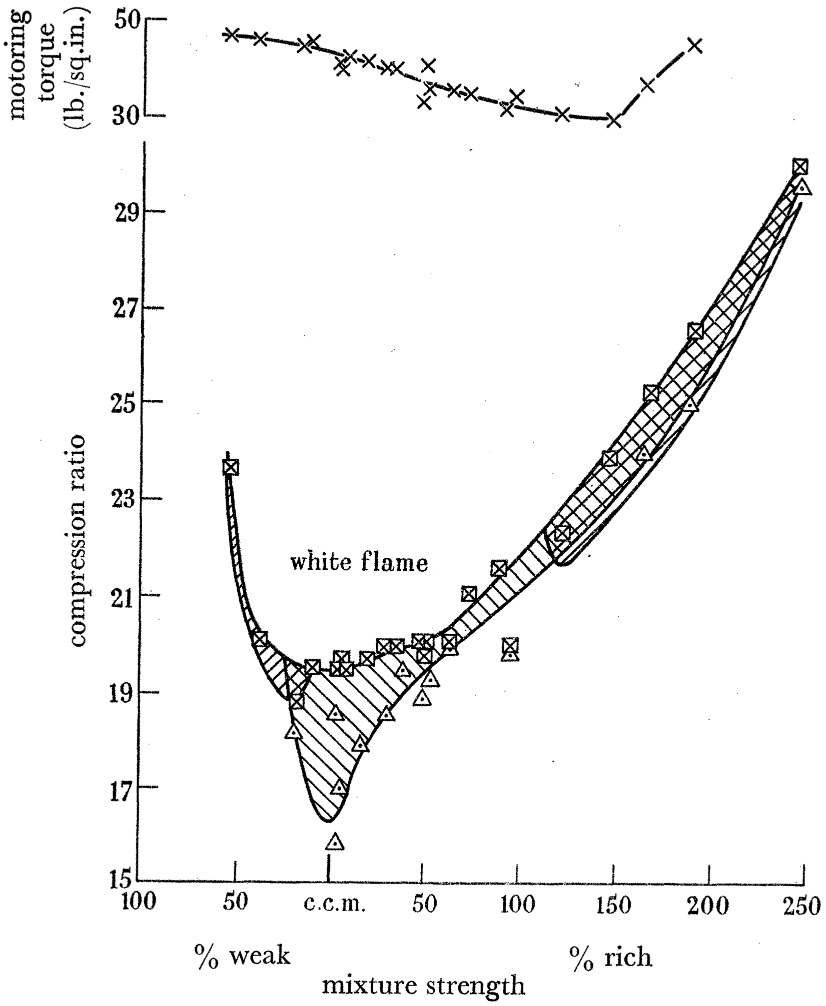


FIGURE 35. Ignition characteristics over the mixture range under motoring conditions. Fuel: *iso*-octane + 4 ml. lead tetraethyl/imp. gal. Test conditions: engine speed (motoring) 1500 r.p.m.; engine coolant temperature 60° C; inlet air heat imput 300 W; oil temperature 50 to 60° C; full throttle; shrouded inlet valve. ⊠ critical compression ratio; △ lower limit of blue glow; \\\ blue glow; /// bright blue flames.

The effect of lead tetraethyl on the *iso*-octane curve is shown on figure 35. The minimum compression ratio for auto-ignition occurs at chemically correct mixture in this case and has been increased by more than two ratios by the addition of 4 ml./gal. of lead tetraethyl

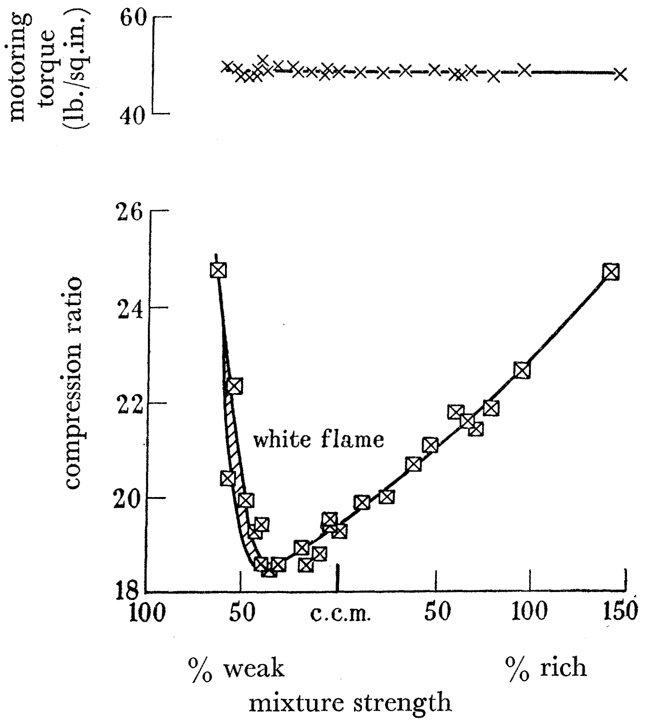


FIGURE 36. Ignition characteristics over the mixture range under motoring conditions. Fuel: benzene. Test conditions: engine speed (motoring) 1500 r.p.m.; engine coolant temperature 60° C; inlet air heat input 300 W; oil temperature 50 to 60° C; full throttle; shrouded inlet valve. ⊠ critical compression ratio; /// bright blue flames.

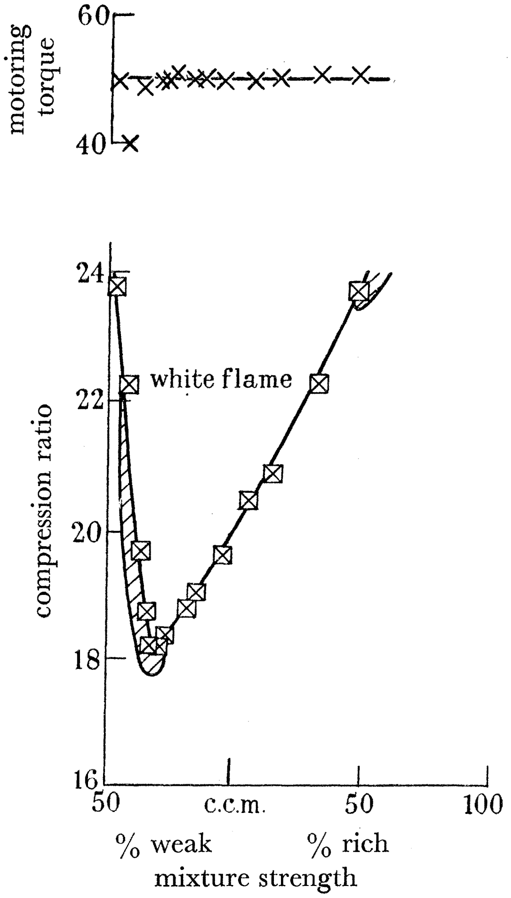


FIGURE 37. Ignition characteristics over the mixture range under motoring conditions. Fuel: methane. Test conditions: engine speed (motoring) 1500 r.p.m.; engine coolant temperature 60° C; inlet air heat input 300 W; oil temperature 50 to 60° C; full throttle; shrouded inlet valve. ⊠ critical compression ratio; /// bright blue flames.

to the fuel. The second minimum, which was at 75% rich with the clear fuel, is almost entirely eliminated. A blue glow persisted at a rather low intensity up to a mixture 90% rich and then became progressively stronger, but more intermittent. There was no violent combustion weaker than 170% rich, but beyond this, auto-ignition was sometimes violent. A strong odour, similar to that observed with clear *iso*-octane, coincided with the appearance of the blue glow at a weak mixture and persisted to the richest mixture explored. The pre-flame reactions generated the greatest amount of power at a mixture 150% rich.

A test with clear *iso*-octane carried out immediately after the leaded run was a good check on the first curve, thus demonstrating the absence of 'carry-over' in these tests.

The curves for benzene and methane (figures 36 and 37) are similar. No blue glow was observed with these fuels. The minimum compression ratio for ignition is sharply defined at about 35% weak in both cases. Bright blue flames were sometimes observed, in addition to the usual white flames. A blue flame, similar to that of carbon monoxide, has been observed by Prettre (1938) in continuous-flow experiments with benzene and toluene at temperatures only some 10° below the ignition limit. No exhaust smell preceded the onset of ignition, and the motoring torque remained constant throughout the tests. The combustion was never violent.

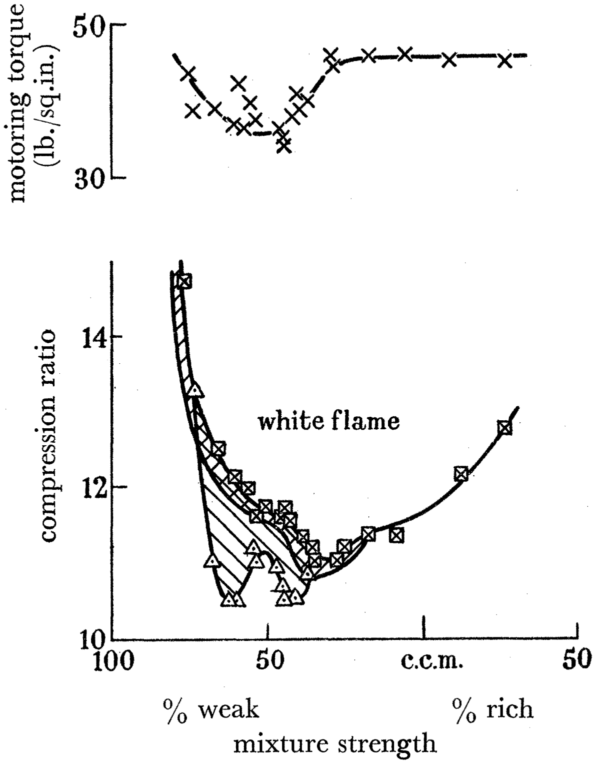


FIGURE 38. Ignition characteristics over the mixture range under motoring conditions. Fuel: N-heptene. Test conditions: engine speed (motoring) 1500 r.p.m.; engine coolant temperature 60° C; inlet air heat input 300 W; oil temperature 50 to 60° C; full throttle; shrouded inlet valve. ⊠ critical compression ratio; △ lower limit of blue glow; \\\ blue glow. /// bright blue flames.

With *n*-heptene (figure 38) the minimum compression ratio for ignition occurred at a mixture 35% weak. The blue glow was visible over a range of mixture from 75 to 39%

weak. Although very strong blue glows were seen in the region of 50% weak, they rapidly disappeared as the compression ratio was lowered below the critical value. The glow appeared to be more persistent on either side of this region, however. Combustion was usually violent, expecially at mixtures richer than 30% weak. An odour similar to that observed with *n*-heptane was detected but became much fainter as the mixture was richened beyond 7% weak. Black smoke issued from the exhaust test-cock as the critical compression ratio was approached. This first became apparent at 66% weak and continued to be visible up to a mixture 25% rich. The test was discontinued at this point because of the extremely violent nature of the combustion.

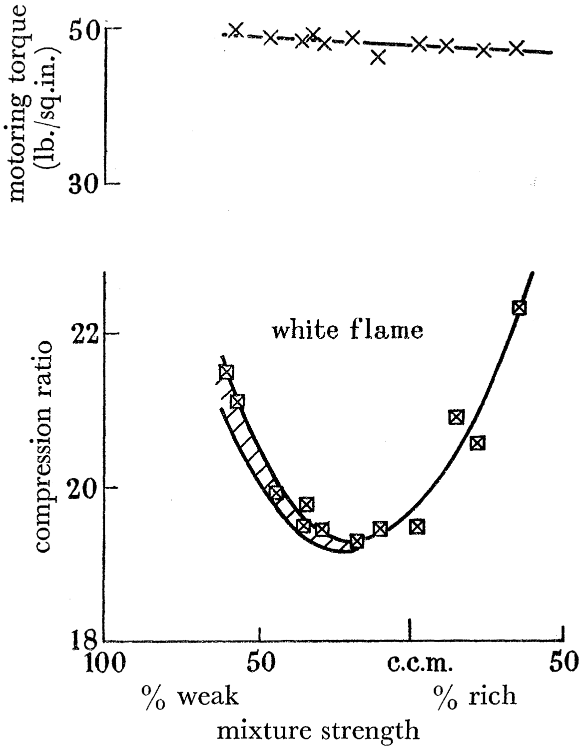


Figure 39. Ignition characteristics over the mixture range under motoring conditions. Fuel: di-*iso*butylene. Test conditions: engine speed (motoring) 1500 r.p.m.; engine coolant temperature 60° C; inlet air heat input 300 W; oil temperature 50 to 60° C; full throttle; shrouded inlet valve. ☒ critical compression ratio; /// bright blue flames.

The behaviour of di-*iso*butylene (figure 39) was quite different from that of *n*-heptene. The minimum of the ignition curve was at a mixture 20% weak. The combustion was never violent at mixtures richer than 56% weak, but weaker than this the ignition suddenly changed from explosions resembling those with benzene to the type of combustion exhibited by *n*-heptene. A blue glow was not observed. Neither was there any smell or smoke from the exhaust at compression ratios below the critical. There was no reduction in motoring torque due to preliminary reactions. As with benzene and methane, bright blue flames intermingled with the white flames on the weak side of the curves.

Tests were also carried out with di-*iso*propyl ether and diethyl ether (figures 40 and 41), as they have been so often used for investigations into cool-flame formation in glass apparatus. The curve for di-*iso*propyl ether exhibited a characteristic not shown by any of the other fuels. The ignition curve descended in the normal way to a mixture strength about 108 % rich, whereupon the limiting compression ratio suddenly dropped from 17·4 to 14·8. Coincident with this change in limiting compression ratio, the motoring torque altered by 10 lb./sq.in. m.e.p., and the blue-glow characteristic changed abruptly from a continuous bright glow to a somewhat brighter but intermittent glow. The blue glow observed with di-*iso*propyl ether was stronger than that seen with the fuels described previously,

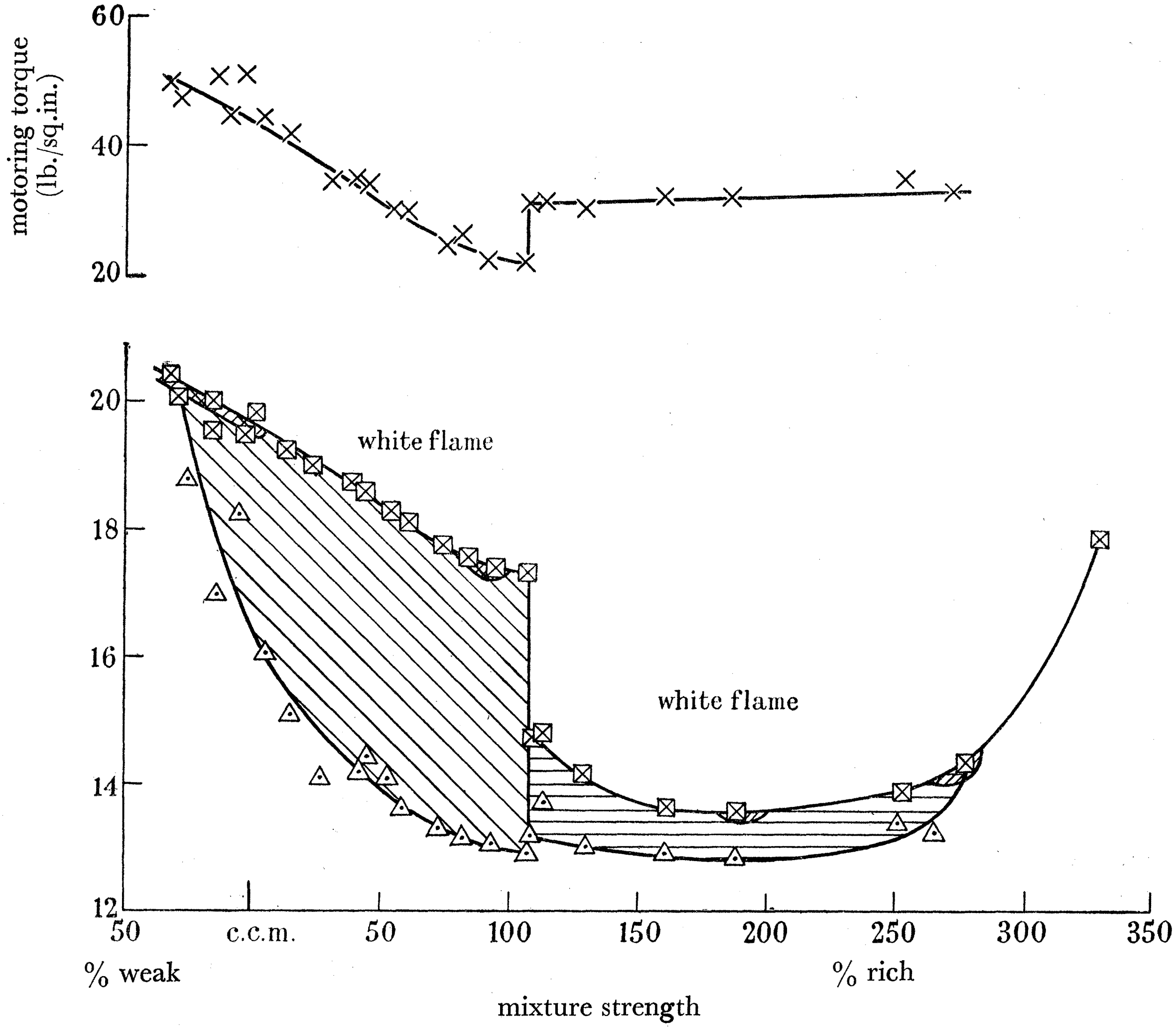


FIGURE 40. Ignition characteristics over the mixture range under motoring conditions. Fuel: di-*iso*propyl ether. Test conditions: engine speed (motoring) 1500 r.p.m.; engine coolant temperature 60° C; inlet air heat input 300 W; oil temperature 50 to 60° C; full throttle; shrouded inlet valve. ⊠ critical compression ratio; △ lower limit of blue glow; \\\ continuous blue glow; /// bright blue flames; ≡ flickering blue glow.

and it persisted over a wide range of mixture strengths. The combustion was usually not violent, but sometimes a loud noise accompanied spontaneous ignition, particularly at mixtures beyond 100 % rich. Just the weak side of chemically correct mixture, a faint odour preceded combustion. This became progressively stronger as the mixture was enriched to 275 % rich. No smoke was observed from the exhaust pipe prior to combustion. The torque required to motor the engine was reduced by more than 50 % at a mixture 105 % rich.

Owing to the violent nature of the auto-ignition, it was not possible to obtain a torque reading at the richest mixture.

The curve for diethyl ether (figure 41) resembled that for *n*-heptane in general characteristics. A blue glow was seen of intensity about equal to that observed with di-*iso*propyl ether, but it occurred over a more limited range of mixture strength. The luminosity was sometimes very strong at a compression ratio of 4·5, the lowest available with the standard E. 6 engine. The minimum compression ratio for auto-ignition occurred at about 35% weak. The combustion was often violent, and the curve had to be discontinued at 42% rich for this reason. An exhaust odour prior to auto-ignition was first detected at a mixture 77% weak and disappeared at 4% weak. No smoke was produced. The motoring torque reached a minimum value at about 70% weak.

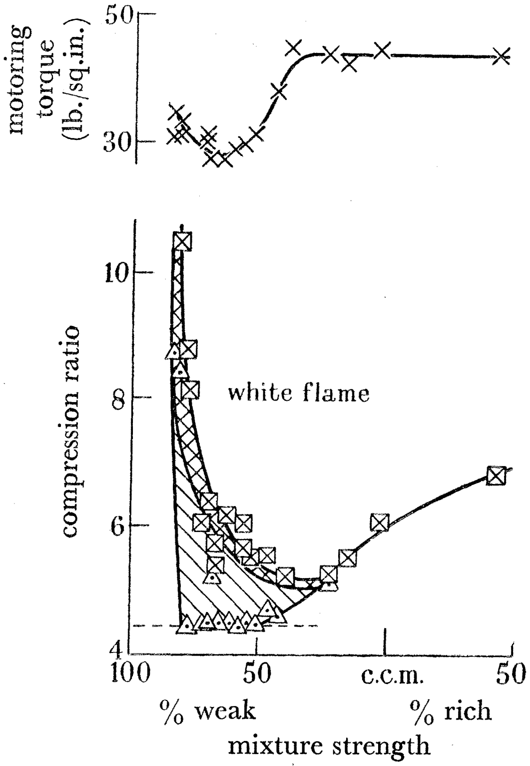


FIGURE 41. Ignition characteristics over the mixture range under motoring conditions. Fuel: di-ethyl ether. Test conditions: engine speed (motoring) 1500 r.p.m.; engine coolant temperature 60° C; inlet air heat input 300 W; oil temperature 50 to 60° C; full throttle; shrouded inlet valve. ☒ critical compression ratio; △ lower limit of blue glow; \\\ blue glow; /// bright blue flames.

7·2. *Experiments with a fine wire thermometer*

In the tests described above, three separate phenomena have been observed, a white flame, a bright blue flame and a low-intensity blue glow, and the limits of their formation have been established for a series of fuels over a wide range of mixture strength. The appearance of the bright blue flame appeared to be associated on certain occasions with a noise in the exhaust pipe, and they always appeared in the same range of compression ratio as the white flames or a little below. The blue glow, on the other hand, was of a very much lower order of intensity and started to appear at a compression ratio considerably below the hot-flame limit. Over the range where a blue glow appeared, reactions in the combustion chamber were sufficient to develop some power output. These considerations suggested that it was the low-intensity blue glow which corresponded with the 'cool' flame previously observed in both engine and non-engine experiments. In order to provide confirmation of this some further experiments were carried out with the object of measuring the temperature rise, etc., associated with the blue glow and determining the time in the cycle at which it passed so that this could be linked with the peroxide sampling curves.

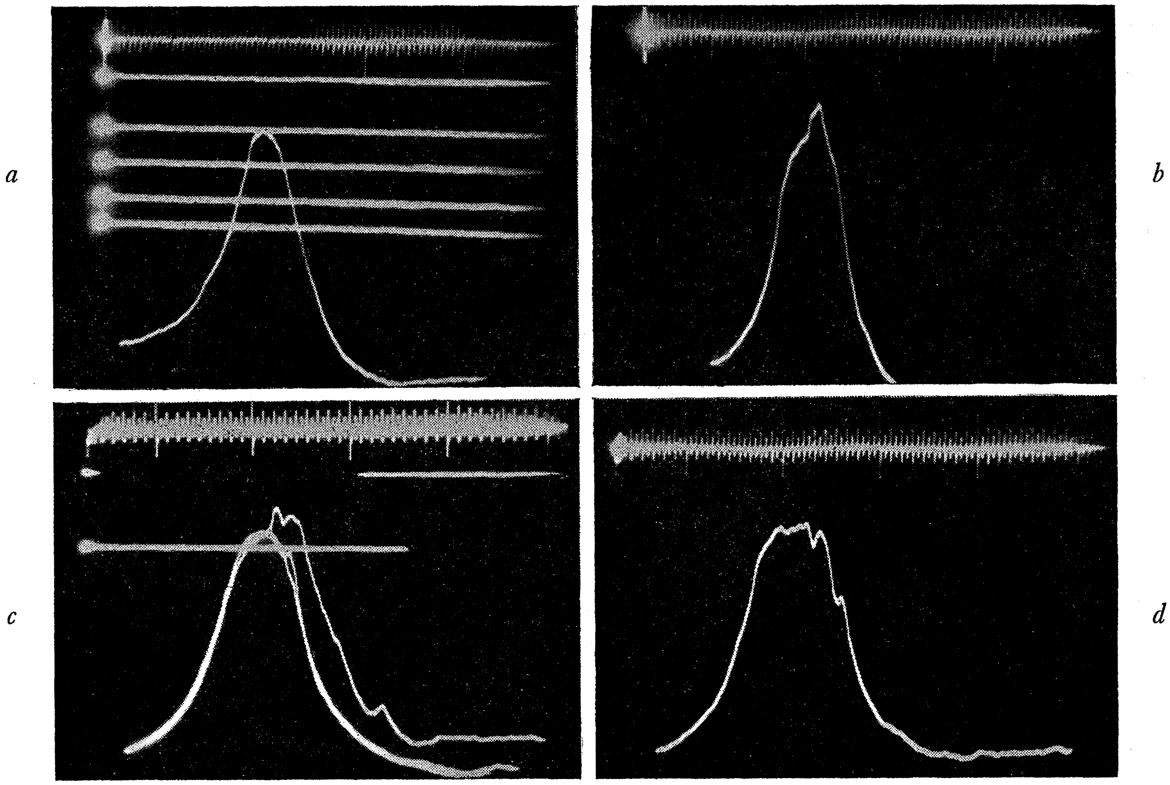


FIGURE 42. Temperature *v.* crank angle curves showing cool flames. *a*, air c.r. 7·0; *b*, *iso*-octane c.r. 17·2 74 % rich mixture; *c*, N-heptane c.r. 7·8 46 % weak mixture; *d*, N-heptane c.r. 8·0 69 % weak mixture.

An extremely sensitive resistance thermometer, the element of which consisted of nickel wire 0·0003 in. in diameter, was inserted in the spark-plug hole normally filled by the sampling valve. The thermal capacity of this wire was sufficiently small to enable it to follow the cyclic changes of temperature occurring in the 'end-gas'. By means of suitable electronic amplification, the small changes in the resistance of the wire element were transferred into a diagram on the screen of a c.r.o. A scale of crankshaft degrees was also projected on to the oscilloscope screen.

The resistance thermometer was found to work well under motoring conditions. A typical oscilloscope diagram obtained on air at 7·0 compression ratio is shown in figure 42*a*. The elongated division near the centre of the degree scale represents the t.d.c. position. To the left of this line is the compression stroke and to the right is the expansion stroke. Each small division of the degree scale is 5 degrees of crankshaft angle. The diagram for an air/fuel mixture at a low compression ratio is substantially the same, but, with certain fuels, on raising the compression ratio to the region between the blue-glow and white-flame limit curves, a sharp temperature rise was observed on the diagram. Figure 42*b* is an example of the type of diagram produced with *iso*-octane at a compression ratio in the region of the white-flame limit and in a region where a blue glow was observed in the engine cylinder. The temperature rise observed in this case is *c.* 50° C. Owing to the thermal lag in the response of the wire, and the steep rate of temperature rise on the passage of the blue glow the observed rise is certainly less than the true temperature rise due to the blue glow. The cool-flame temperature rise has been reported as about 100° C by Neumann (1938). This provides further evidence that the blue glow observed in these engine experiments corresponds with the cool flame observed in experiments in glass apparatus.

It can be seen from figure 42*b* that the cool flame passes shortly after t.d.c. This is in good agreement with the point of inflexion of the peroxide curves shown in figure 9.

No similar temperature rise has been observed with benzene.

The temperature peaks did not occur on every cycle, and for purposes of comparison, a composite photograph, figure 42*c*, was taken with *n*-heptane at a mixture strength 46% weaker than chemically correct. By using a slower shutter speed, two consecutive cycles were recorded, and the considerable difference in peak thermometer temperature is clearly demonstrated. On one curve there is evidence of two temperature peaks, and this is also shown by figure 42*d*. Experiments with diethyl ether in glass apparatus have shown the existence of multiple cool flames under certain conditions (Newitt & Thornes 1937) and explanations have been put forward to account for them (Frank-Kamenetskii 1940).

An attempt was made to obtain an indication of the passage of the cool flame through the 'end-gas' of the engine under firing conditions by motoring the engine, firing once and then observing the temperature trace of a fine wire placed in the knocking zone. No definite evidence of cool-flame formation could be obtained by this method.

8. Formaldehyde as a fuel

Sampling experiments have shown that formaldehyde is present in the pre-flame reactions in the engine cylinder in amounts dependent upon the engine conditions. By using formaldehyde itself as fuel in the engine and observing the effects of various significant additives on its knock tendency, it was hoped to obtain information on the stage in the pre-flame reactions at which the additives exert their knock action, i.e. whether it is before or after the formaldehyde-formation stage. Further, since the oxidation of formaldehyde has been extensively studied in non-engine apparatus (for example, Bone & Gardner, 1936; Kane, Chamberlain & Townend 1937; Axford & Norrish 1948), observations on its behaviour in the engine might be expected to serve as an additional help in interpreting engine data.

Owing to the readiness with which it polymerizes, it would be difficult to devise a system for metering formaldehyde as a gas. It was decided, therefore, to meter the solid polymer, *para*formaldehyde, and to generate the formaldehyde gas after the metering stage. Powdered *para*formaldehyde was made into a slurry with a low vapour-pressure oil and was fed into the generating tank through a variable-speed Archimedean screw. The heat for depolymerization was supplied to the oil in the generating tank, which was maintained at a temperature of about 240° C and was continuously stirred by mechanical means. It was found to be necessary to heat the delivery pipe to the engine electrically to prevent the formaldehyde gas repolymerizing on the walls. The quantity of formaldehyde supplied to the engine was controlled by variation in the speed of rotation of the Archimedean screw.

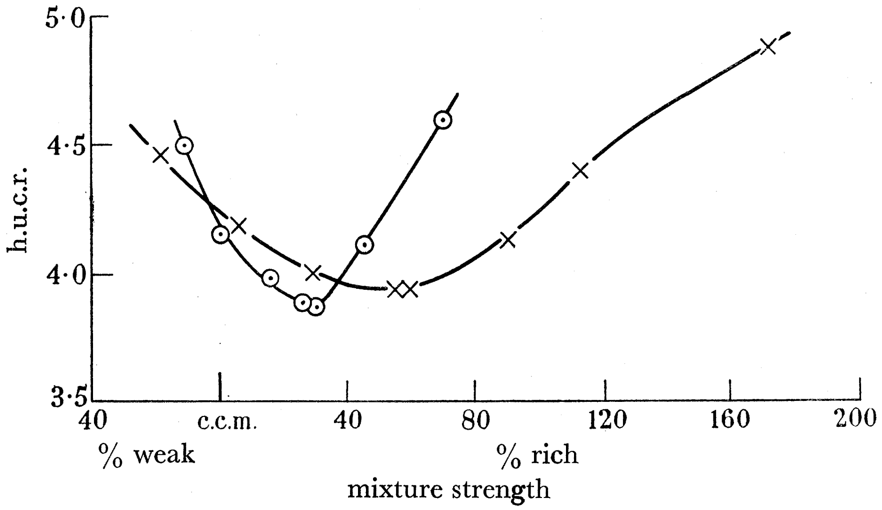


Figure 43. H.u.c.r.-mixture strength curve on formaldehyde compared with one one octane/heptane blend. Test conditions: engine speed 1500 r.p.m.; inlet air temperature 120° C; engine coolant temperature 90° C; ignition advance optimum for maximum power at each compression ratio; Solex carburettor. Fuels: ⊙ 75 n-heptane/25 *iso*-octane; × formaldehyde.

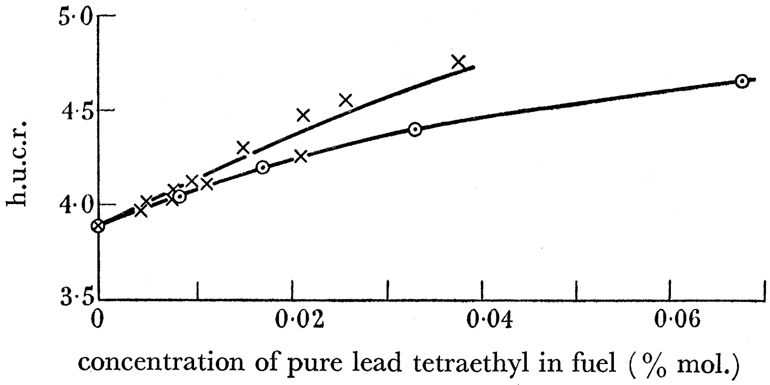


Figure 44. Effect of pure lead tetraethyl on formaldehyde and on octane/heptane blend. Test conditions: engine speed 1500 r.p.m.; inlet air temperature 120° C; engine coolant temperature 90° C; ignition advance optimum for maximum power mixture at each compression ratio; maximum knock mixture strength; Solex carburettor. Fuels: ⊙ 75 n-heptane/25 *iso*-octane; × formaldehyde.

A special piston, enabling compression ratios down to 3·0 to be reached, was used.

Figure 43 shows an h.u.c.r.-mixture strength curve on formaldehyde compared with one on an octane/heptane blend of about the same minimum h.u.c.r. It can be seen that the knock resistance of formaldehyde is very low—approximately equivalent to 25 octane numbers under these conditions. This is perhaps not surprising in view of the ready oxidation characteristic of this substance (Bone & Gardner 1936; Axford & Norrish 1948).

Figure 44 shows a lead response curve on formaldehyde compared with a similar curve for the octane/heptane blend. The response with formaldehyde is positive and not less than that with the octane/heptane blend. The significance of this to the mechanism of inhibition by lead tetraethyl is that it implies that the latter is able to destroy one of the limited number of species of chain carrier present in the oxidation of formaldehyde. The implication is analyzed in detail elsewhere (Chamberlain & Walsh 1950). N-Methyl aniline also has an anti-knock effect in formaldehyde not less than in the octane/heptane blend.

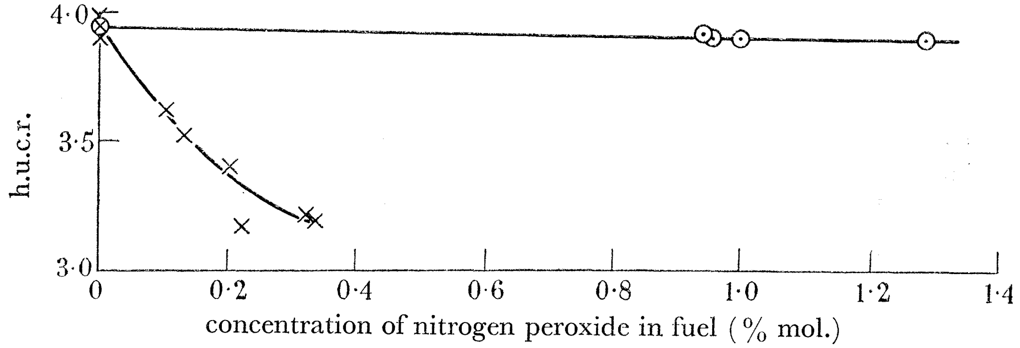


FIGURE 45. Effect of nitrogen peroxide on formaldehyde and on octane/heptane blend. Test conditions: engine speed 1500 r.p.m.; inlet air temperature 120° C; engine coolant temperature 90° C; ignition advance optimum for maximum power at each compression ratio; maximum knock mixture strength; Solex carburettor. Fuels: ⊙ 75 N-heptane/25 *iso*-octane; × formaldehyde.

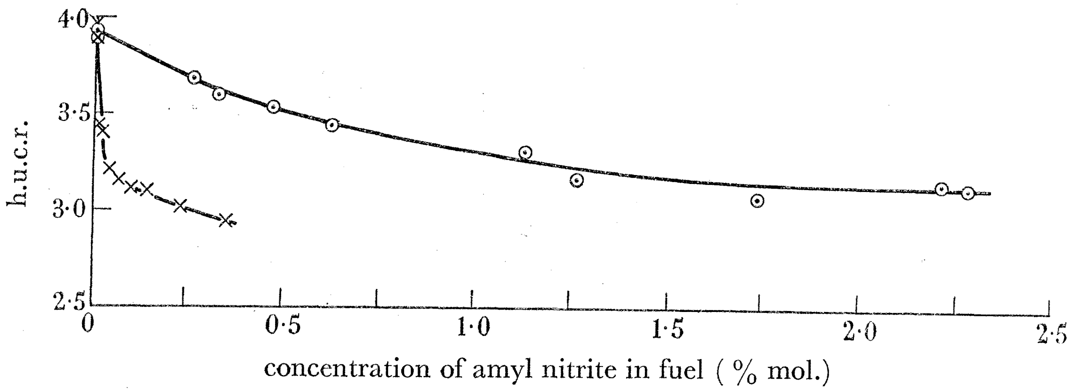


FIGURE 46. Effect of amyl nitrite on formaldehyde and on octane/heptane blend. Test conditions: engine speed 1500 r.p.m.; inlet air temperature 120° C; engine coolant temperature 90° C; ignition advance optimum for maximum power at each compression ratio; maximum knock mixture strength; Solex carburettor. Fuels: ⊙ 75 N-heptane/25 *iso*-octane; × formaldehyde.

Nitrogen peroxide has a strong pro-knock effect in formaldehyde as compared with its negligible effect in the octane/heptane blend (figure 45). Although the effect of nitrogen peroxide on the oxidation of formaldehyde in non-engine experiments does not appear to have been studied, its strong pro-knock effect in the engine is in accord with the observation that formaldehyde has no 'low'-temperature peninsula and does not form cool flames (Kane *et al.* 1937). Amyl nitrite has an even greater effect on the h.u.c.r. of formaldehyde than has nitrogen peroxide (figure 46). This supports the belief that the nitrite has a twofold effect, (*a*) because it produces organic free radicals and (*b*) because it produces NO$_2$. Since only (*a*) affects the paraffinic blend, the smaller effect of amyl nitrite in this fuel is explained. For a particular concentration of nitrogen peroxide, the difference between the h.u.c.r.'s of the blend and of formaldehyde in figure 45 is close to the difference, for the same concentration of amyl nitrite, of the h.u.c.r.'s of the blend and of formaldehyde in figure 46.

The above additive tests with formaldehyde show that its oxidation is best classified as of the 'high'-temperature type. Figure 10 (§5·2) shows that the formation of formaldehyde (and, therefore, presumably the oxidation) takes place particularly in the second of the two time intervals shown by figure 9 to characterize the reactions leading to knock. One can, therefore, understand why the reactions of the second stage of two-stage ignition should resemble those of 'high'-temperature oxidation (Chamberlain & Walsh 1948, 1949).

9. Hydrogen as a fuel

Hydrogen behaves somewhat differently from the other fuels. In most cases, owing to the extreme ease with which it ignites, a mixture strength richer than about 25 to 30% weaker than chemically correct cannot be used. If the attempt is made to run with a richer mixture, self-ignition occurs so early on the compression stroke that the mixture is eventually ignited in the induction manifold. This means that in general a true maximum knock mixture strength cannot be obtained, and accordingly a mixture a little on the weak side of the richest at which it is possible to operate has been selected for the additive tests with hydrogen.

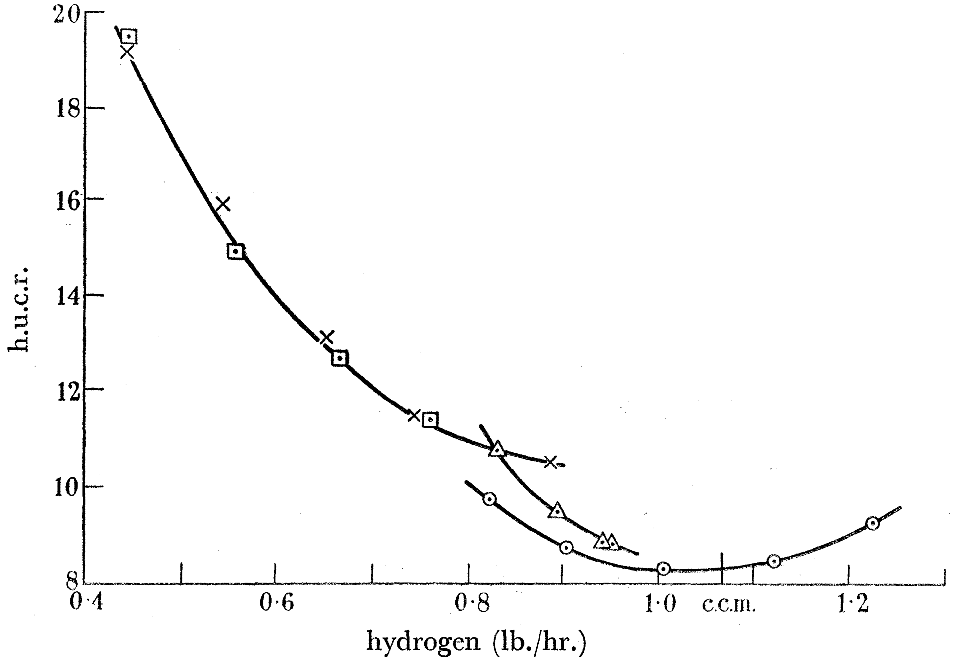


Figure 47. H.u.c.r.-mixture strength curves on hydrogen. Test conditions: engine speed 1500 r.p.m.; engine coolant temperature 60° C; engine oil temperature 60° C. ⊡ × ignition 25° e.; ⊙ ignition optimum at each compression ratio; △ ignition 8° e.

King, Wallace & Mahapatra (1948) have recently found that, by thoroughly removing all traces of carbonaceous deposit from the combustion chamber and keeping the chamber as clean as possible whilst running, it was possible to operate over the whole mixture range without backfiring. A similar experiment with hydrogen using the Ricardo E. 6 engine confirmed this observation. In addition, a full h.u.c.r.-mixture strength curve (figure 47) was plotted, and it was found that, under conditions where the whole mixture range could be explored, a curve similar in shape to that obtained with other fuels and having its minimum at about the same mixture strength was obtained.

Both Ricardo (1924) and Egerton *et al.* (1935) have recorded the anti-knock action of hydrogen when added to petrol. More extensive tests with methane, benzene and leaded petrol (figure 48) show that (*a*) in methane and benzene hydrogen has a pro-knock effect,

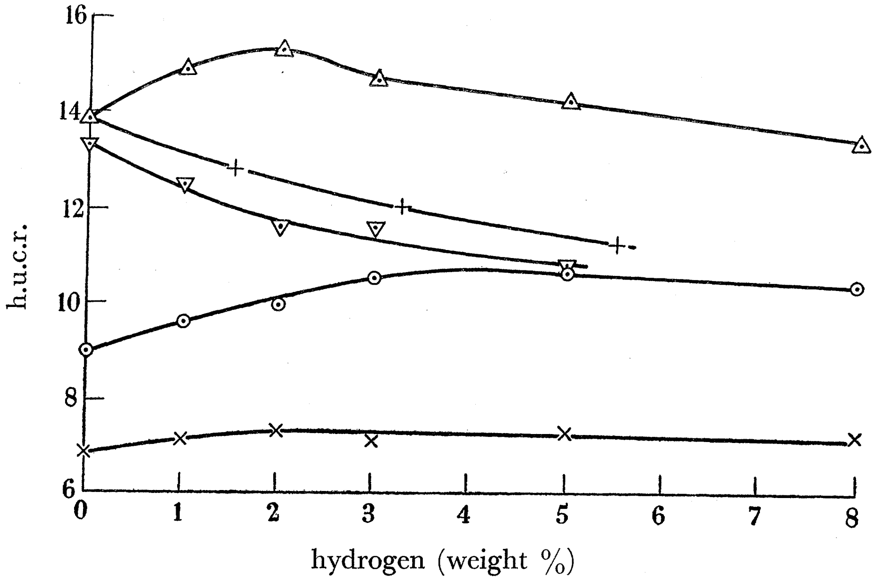


Figure 48. Effect of hydrogen on the h.u.c.r.'s of various fuels. Test conditions: engine speed 1500 r.p.m.; inlet air temperature 120° C; engine coolant temperature 90° C; Solex carburettor; additive admitted with air. Fuels: ▽ benzene; + methane; ⊙ *iso*-octane; △ *iso*-octane + 4 ml. lead tetraethyl/imp. gal.; × cyclohexane.

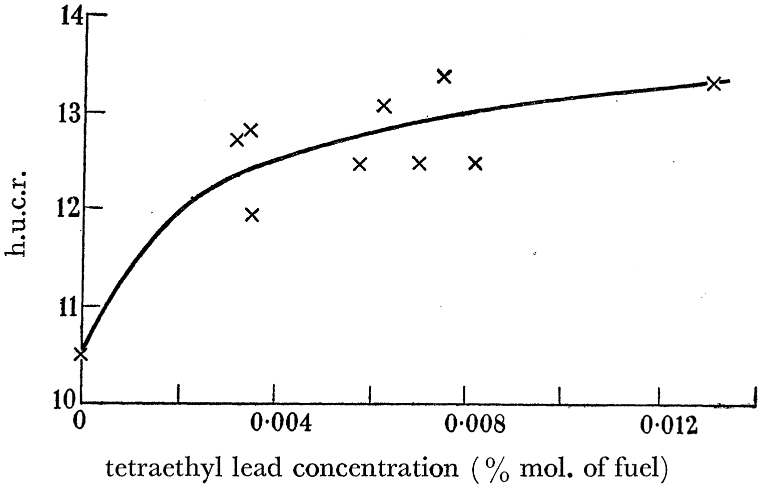


Figure 49. Effect of lead tetraethyl on the knock tendency of hydrogen. Test conditions: engine speed 1500 r.p.m.; inlet air temperature 120° C; engine coolant temperature 90° C; ignition advance 10° e.; hydrogen consumption 0·65 lb./hr. All results corrected to an h.u.c.r. of 10·5 on hydrogen.

(*b*) in cyclohexane and both clear and leaded *iso*-octane, the first small additions of hydrogen have an anti-knock effect and subsequent additions a pro-knock effect. The anti-knock action in certain fuels can be explained as being due to the accelerating effect which hydrogen has on the flame velocity. This reduces the time available for knock to occur in the 'end-gas'. If so, in the case of benzene and methane, and other fuels, when the addition of hydrogen is large, this effect must be swamped by an accelerating action of hydrogen on the 'end-gas' reactions themselves.

Lead tetraethyl has a profound anti-knock effect in hydrogen (figure 49). This is directly contrary to the result reported by Egerton *et al.* (1935). It seems likely that their failure to detect the anti-knock effect of lead tetraethyl is due to the fact that they were not able entirely to eliminate pre-ignition when running on hydrogen (Egerton & Moore 1949).

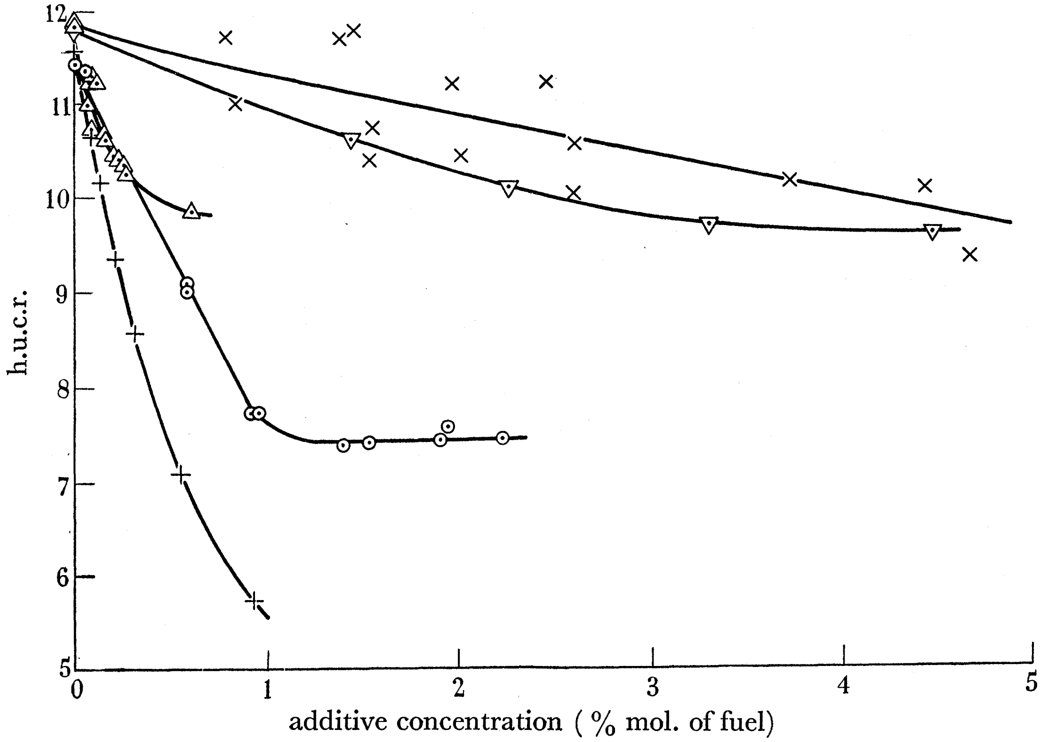


FIGURE 50. Effect of various additives on the knock tendency of hydrogen. Test conditions: engine speed 1500 r.p.m.; inlet air temperature 120° C; engine coolant temperature 90° C; ignition advance 10° e.; hydrogen consumption 0·65 lb./hr. Additives: × formaldehyde; △ *t*-butyl hydroperoxide; + amyl nitrite; ⊙ nitrogen peroxide; ▽ acetaldehyde.

The importance of the observation that lead tetraethyl exerts a strong anti-knock effect with hydrogen as fuel is that it implies that the inhibitor is able to destroy a species of chain carrier which does not contain carbon at all (Chamberlain & Walsh 1950 and in course of publication).

Amyl nitrite, nitrogen peroxide and *t*-butyl hydrogen peroxide are all strong pro-knocks (figure 50). The result on nitrogen peroxide is in accord with the observations of Egerton *et al.* (1935), but they say 'diethyl peroxide did not give rise to "knock" and amyl nitrite only in a very minor degree'.

Formaldehyde and acetaldehyde are both pro-knocks, but not so powerful in this respect as the peroxides and amyl nitrite. Acetaldehyde is slightly more effective than formaldehyde.

The effects of aniline and *n*-methyl aniline on the h.u.c.r. of hydrogen are shown in figure 51. These curves exhibit the curious characteristic of a strong anti-knock effect for the first small amounts of additive, with subsequent additions having little further effect. This phenomenon has not been observed with any of the other fuels in which the anilines have been tested.

Peroxide curves at various mixture strengths and with hydrogen as fuel are shown in figure 52. In all cases the peroxide concentrations obtained were negligible.

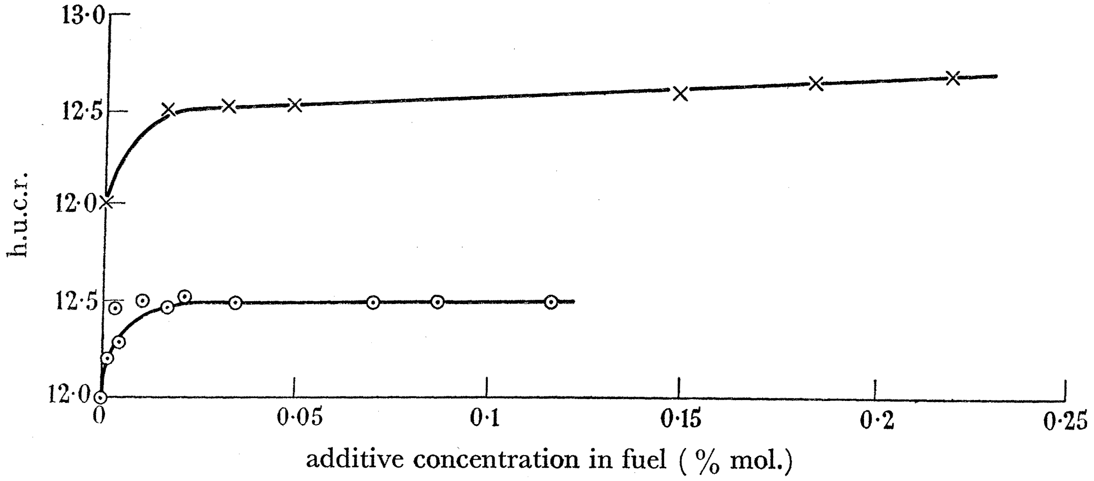


FIGURE 51. Effect of aniline and *n*-methyl aniline on the knock tendency of hydrogen. Test conditions: engine speed 1500 r.p.m.; inlet air temperature 120° C; engine coolant temperature 90° C; ignition advance 10° e.; hydrogen consumption 0·65 lb./hr. Additives: × aniline. ⊙ N-methyl aniline.

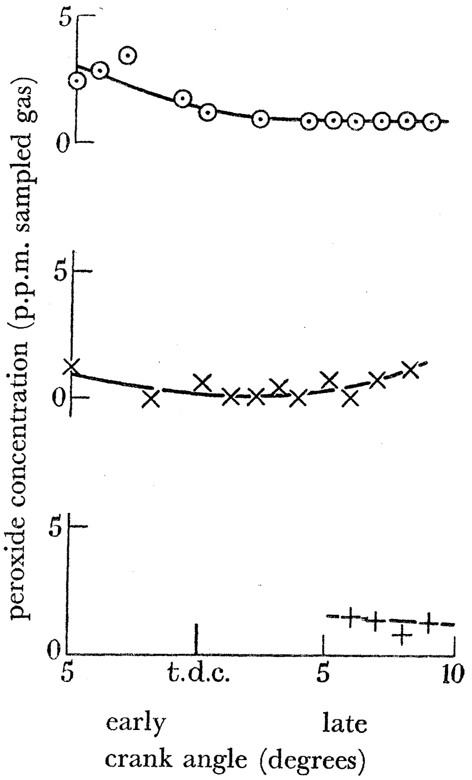


FIGURE 52. Peroxide curves with hydrogen. Test conditions: engine speed 1500 r.p.m.; engine coolant temperature 60° C; mean flame arrival 10° l.; gas flow 300 ml./min. ⊙ c.r. 16·2, frequent slight detonation, mixture 60 % weak; × c.r. 12·1, frequent moderate detonation, mixture 38 % weak; + c.r. 7·0, no detonation, mixture 12 % rich.

10. General discussion and conclusions

Recent studies using high-speed photography (Miller 1947; Male 1948) make it appear that knock involves the setting up in the 'end-gas' of a detonation wave, initiated either in the normal flame or from a centre of auto-ignition. It used to be said that engine knock could not be the same as detonation in long tubes because (*a*) the dimensions of the engine cylinder were not sufficient to enable a true detonation wave to 'get up speed', (*b*) the fuels which knock most readily in engines are not specially prone to detonation in tubes, (*c*) Rifkin & Sokolik (1938 *a*, *b*) showed that pentane/air mixtures, such as might be drawn into an engine running on pentane, will not detonate although they will knock, (*d*) additives that do not delay the onset of detonation in a tube act as engine anti-knocks. These arguments would be valid if no pre-flame reactions were taking place in the 'end-gas'. That such pre-flame reactions do occur has been amply demonstrated both by photographic and spectrographic means as well as by sampling experiments, and it seems possible that it is this pre-sensitization of the 'end-gas' which would enable it to support a detonation wave (Egerton *et al.* 1935). Anti-knocks, which do not delay the onset of detonation in a tube, would, therefore, inhibit not so much the detonation wave as the pre-detonation reactions, reducing the latter to such an extent as to make the mixture incapable of supporting a detonation wave.

It is clear, therefore, that whether we adopt the old view of knock being simply a spontaneous ignition of the 'end-gas' or the newer one, that it involves the passage of a detonation wave, it is the pre-flame reactions in the 'end-gas' which control its occurrence. There is no doubt that these pre-flame reactions are of a chain type and that they take place within the volume of the 'end-gas', i.e. are independent of the nature of the cylinder walls. In order to specify further the nature of the pre-flame reactions, we must refer to the work of Townend on spontaneous ignition.

Townend and his school showed that the pressure-temperature ignition diagrams for most combustibles have two main regions, a so-called 'high'-temperature region and a so-called 'low'-temperature region. At low pressures, with paraffins, the latter lies below 450° C. Ignition in the 'low'-temperature region is by a two-stage process involving the formation of cool flames and peroxides, probably alkyl hydrogen peroxides. Ignition in the 'high'-temperature region, on the other hand, is by a continuous one-stage process. We now have much evidence that with most normal fuels the reactions leading to knock in the 'end-gas' of an engine correspond to those involved in 'low'- rather than 'high'-temperature oxidation. This evidence may be summarized as follows:

(*a*) The effect of additives such as formaldehyde, acetaldehyde and nitrogen peroxide on the knock tendency of fuels in the engine generally accords with their effect on 'low'- but not on 'high'-temperature ignition (§ 6).

(*b*) A cool flame has been detected in the engine cylinder shortly after t.d.c. under conditions simulating those obtaining in the 'end-gas' prior to knock (§ 7).

(*c*) Peroxides are formed in the 'end-gas' of the engine cylinder, and the occurrence of knock appears to depend upon their concentration. The effect of changing engine variables, such as mixture strength and speed, support this (§ 5).

(*d*) The peroxide curves appear to be two-stage in nature with a point of inflexion occurring some 7° before knock under our particular conditions of test. The occurrence of this point of inflexion in the sampling curve appears to coincide with the passage of a cool flame in the 'end-gas'. Lead tetraethyl has a bigger effect on the second half of the peroxide curve than on the first, in agreement with its known greater effect on the second of the two stages involved in 'low'-temperature ignition (§5). Similarly, Jost (1946) has observed that, under conditions of adiabatic compression simulating those of the pre-flame gases of spark-ignition engine, ignition is of a two-stage type.

(*e*) There is a parallel (Maccormac & Townend 1938; Day & Pease 1941) between the order of the minimum pressures required for ignition in the 'low'-temperature region and the order of knock ratings in the engine.

(*f*) There is a correlation between the knock ratings of fuels and the temperature coefficient of the variation of the time lag for ignition in the 'low'-temperature zone; but there is no correlation with the temperature coefficients for the high-temperature region (Sokolik 1939).

Though it therefore seems certain that the reactions leading to knock with ordinary paraffinic fuels are, in the main, of the 'low'-temperature type, the question arises: How can a mechanism of ignition that at low pressures is only found below 450° C be important in the pre-flame gases of an engine where the temperature rises to well over 600° C? The answer is that the upper temperature boundary of the 'low'-temperature system on a pressure/temperature graph has a positive slope, so that the temperature to which the system persists increases continuously with pressure. The fundamental reasons for this are suggested elsewhere (Chamberlain & Walsh 1949; Walsh, results to be published). Briefly, they are that 'low'-temperature ignition depends upon the formation of alkyl hydroperoxides by the reactions

$$\left.\begin{aligned} R+\mathrm{O_2} &= R\mathrm{O_2}, \\ R\mathrm{O_2}+R\mathrm{H} &= R\mathrm{OOH}+\mathrm{R}, \end{aligned}\right\} \tag{1}$$

and that these die away as the temperature rises because the radical R decomposes to a radical unable to join with O_2 in a two-body collision; increase of pressure favours the bimolecular reaction (1) at the expense of the unimolecular decomposition of R. There is therefore no difficulty in understanding how the 'low'-temperature system of ignition persists at the high temperatures reached in the pre-flame gases of an engine. The crux of the matter lies in the high pressures at which the engine pre-flame reactions occur.

Fuels, such as benzene and methane, which were found by Townend and his school to possess no 'low'-temperature ignition peninsula, must knock in the engine by reactions corresponding to the 'high'-temperature ignition process. In agreement:

(*a*) The effect of additives on the knock tendency of these fuels in the engine is in accord with their effect on 'high'-temperature ignition.

(*b*) There is an absence of peroxides in gases sampled from the combustion chamber of the engine in the case of benzene and only a small concentration in the case of methane.

(*c*) No cool flames have been detected in the engine when running with benzene or methane.

With normal fuels, the reactions leading to knock are: (i) auto-catalytic, in that they form peroxides and are catalyzed by the addition of organic peroxides (though not greatly influenced by the formation of nitrogen peroxide in the engine cylinder); (ii) subject to a considerable self-inhibition in that they produce formaldehyde which has been shown to have an appreciable anti-knock effect. With fuels such as benzene and methane, however, the reactions leading to knock, so far from being subject to such self-inhibition, are autocatalytic not via peroxides but via aldehydes; in addition, they are presumably strongly catalyzed by any nitrogen peroxide formed in the engine.

Judging from the effect of additives on its knock tendency, ethane, like methane, knocks by a 'high'-temperature mechanism.

Formaldehyde has no 'low'-temperature ignition peninsula, although its ignition curve occurs at low temperatures. Thus its low h.u.c.r. in the engine is not very surprising. The effect of additives on its h.u.c.r. suggests that the reactions leading to knock with formaldehyde resemble those of the 'high'-temperature ignition process.

The lack of effect of lead tetraethyl on the first of the two stages characterizing 'low'-temperature ignition suggests that its action is specific to a particular species, *Y*, of chain carrier which is not important in that first stage. In such a case, the use of formaldehyde as an engine fuel is particularly important because it helps to reduce the number of possibilities for *Y*. The use of hydrogen has a similar importance. Assuming that in all the cases where lead tetraethyl is an effective anti-knock it destroys one and the same species of chain carrier, this latter must be present in methane combustion, in the second stage of 'low'-temperature ignition of a higher paraffin, in formaldehyde combustion and in hydrogen combustion. The deductions from this are dealt with elsewhere (Chamberlain & Walsh 1950 and in course of publication). We wish here only to point out that to determine the effect of an additive in such a series of fuels and on each of the two stages preceding 'low'-temperature ignition is a very powerful method of gaining an understanding of the mode of action of an additive.

The investigation described in this paper was carried out in the Laboratory of Ricardo and Co., Engineers (1927) Ltd., on behalf of the Shell Petroleum Co. The authors are indebted to both these Companies for permission to publish this paper. They also desire to express their gratitude to Mr J. G. G. Hempson who designed the electromagnetic sampling valve and the fine-wire resistance thermometer, and to Messrs J. H. Pignéguy, G. Marden and J. A. Stanier for assistance with the experimental work.

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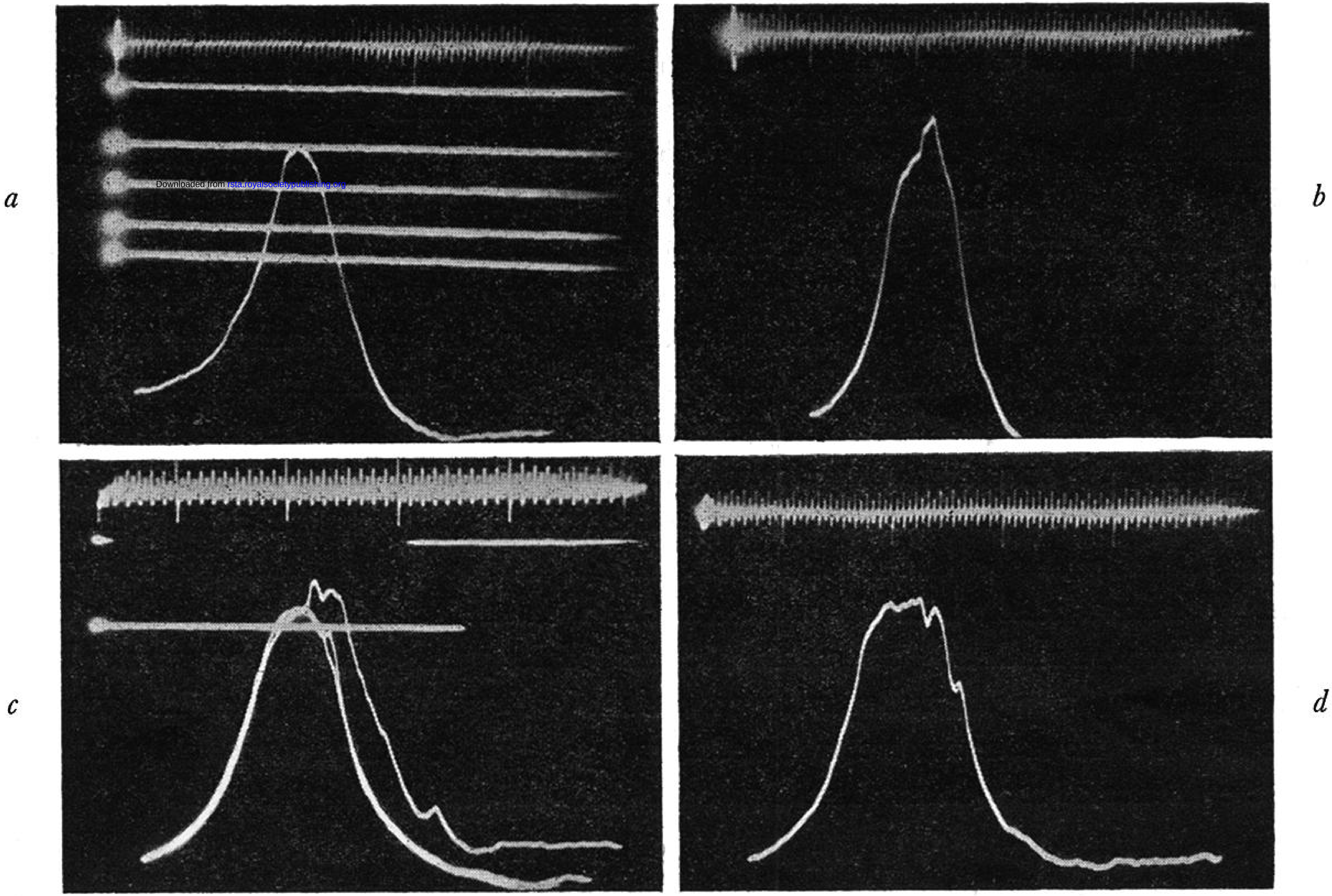

IGURE 42. Temperature *v.* crank angle curves showing cool flames. *a*, air c.r. 7·0; *b*, *iso*-octane c.r. 17·2 74 % rich mixture; *c*, N-heptane c.r. 7·8 46 % weak mixture; *d*, N-heptane c.r. 8·0 69 % weak mixture.