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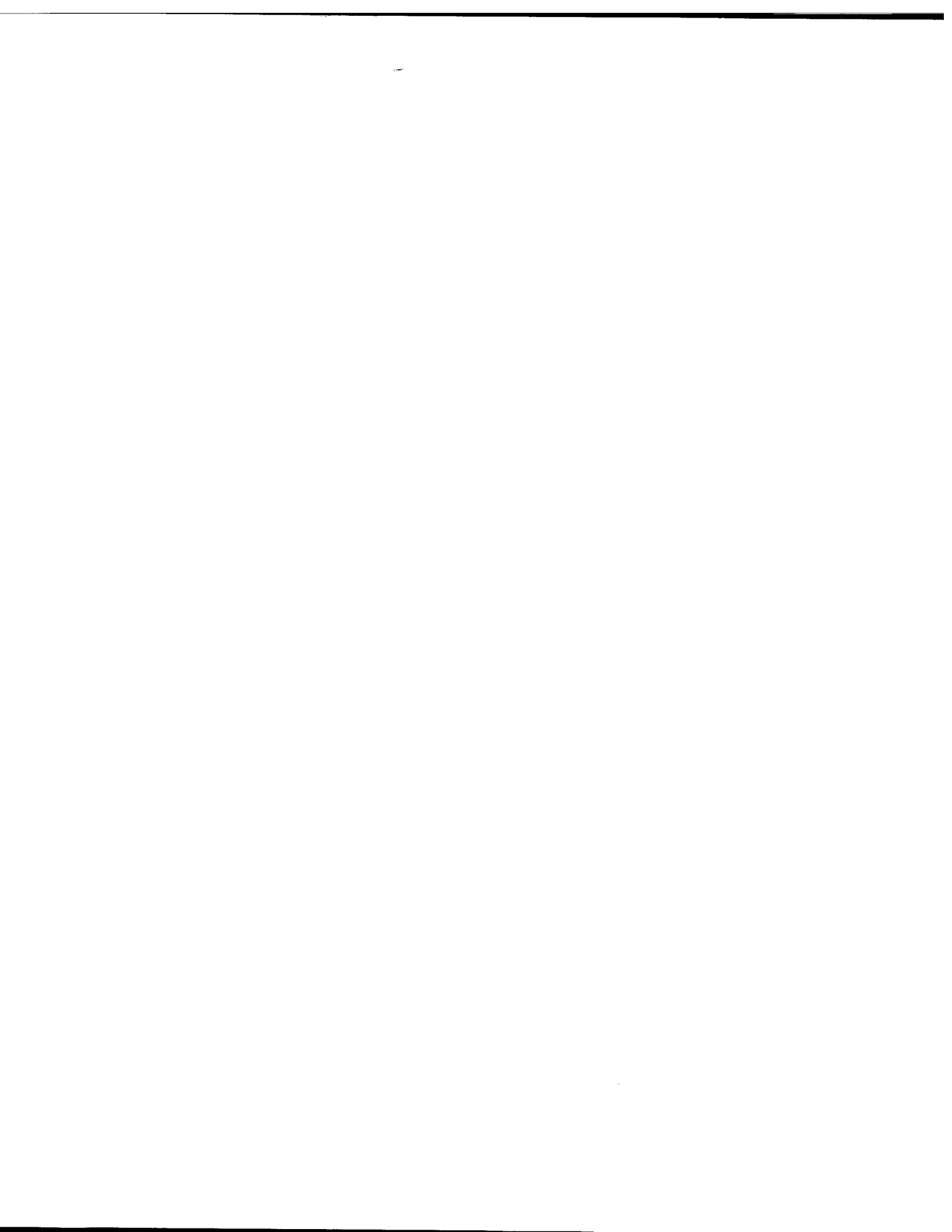
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XXX. THE HYDROGEN ENGINE AND DETONATION OF THE END GAS, BY
THE IGNITING EFFECT OF CARBON NUCLEI FORMED BY PYROLYSIS OF
LUBRICATING OIL VAPOR

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By R. O. KING³ AND S. V. HAYES²

ABSTRACT

Experiments with a C.F.R. spark ignition engine were carried out at compression ratios of 13 : 1 and lower. It was found that ignition and detonation of the mixture ahead of the flame front was due to its impregnation with finely divided carbon produced by the pyrolysis of the vapor of lubricating oil. The carbon accumulated on surfaces until in part dispersed into the hydrogen-air mixture by the entering turbulence. The carbon in the aerosol thus formed ignited at the relatively high temperature and pressure attained by the end gas in the conditions of the experiments. The onset of the consequent detonation and its severity at a particular engine speed was found to be dependent upon the factors of compression ratio, mixture strength, the initial compression temperature and that of the jacket coolant, the nature of the lubricating oil, and the rate at which it passed the piston into the combustion chamber or was supplied as an additive. Thus in the final experiment for which pre-vaporized cetane was used as an additive the shock of the accompanying detonation pressure waves was so great that the cylinder broke loose from the crank case because of the failure of the retaining casting.

INTRODUCTION

It was shown by experiments with hydrogen as the fuel for a C.F.R. Otto cycle engine (Part XXVII (1)), that preignition did not occur at a compression ratio of 10 : 1 when the exhaust valve was sodium-cooled and the spark plug was a cool running type. These experiments were carried out at engine speeds ranging from 900 to 1800 r.p.m. The jacket coolant was maintained at 100°F. and the air supply at 65°F. Mixtures ranging from 70% weak to 60% rich were used without the occurrence of detonation.

When the compression ratio was raised to 12 : 1, the top piston ring overlapped the three spark plug holes in the cylinder wall and lubricating oil passed into the combustion chamber at the positions of the holes at a rate greater than normal, as shown by the accumulation of soot on adjacent surfaces of the piston crown. Slight preignition then occurred infrequently when the engine was operated at 1800 r.p.m., although the jacket coolant had been reduced to 65°F. as a precautionary measure. When lower speeds at 1500 and 1200 r.p.m. were used, the frequency of preignition increased and backfiring as well as what appeared to be detonation occurred occasionally as mixture strength was increased to the correct value. These effects were avoided by allowing the engine to run for a few minutes on a weak

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mixture before using a correct or rich mixture in order to burn off excess carbon.

The experiments of this Part were carried out for the purpose of determining the operating conditions responsible for the occurrence of preignition and for detonation of the end gas by the igniting effect of carbon nuclei arising from pyrolysis of the vapor of lubricating oil passing the piston or supplied as an additive.

EXPERIMENTAL ARRANGEMENTS

The experiments were carried out with the C.F.R.-F4 engine that had been used for those described in Part XXVII (1). The exhaust valve was sodium-cooled. The cast iron piston was fitted with four pressure rings and one oil scraper ring. Ignition was by a cool variety of spark plug in the standard position but spark was not required after the exhaust valve had attained the requisite temperature. The temperature of the oil in the crank case was maintained at 140°F. The methods of regulating engine and mixture temperature and of metering rates of supply of air and hydrogen were as used for the experiments described in Part XXVII. Engine speed was maintained at 1200 r.p.m. except for the experiments described in Section IV. Mixtures are described as per cent weak or rich according to the percentage by which the hydrogen to air volume ratio is less or more than that required for a chemically correct mixture.

Oils Used as Lubricants or as Additives

Oils described as P.30 and P.10 were from a paraffin base crude and were graded by the supplier as S.A.E. 30 and S.A.E. 10 respectively. They were free of oxidation inhibitors or detergents. A synthetic oil, L.B. 300 X, is described as S.300. Cetane, C₁₆H₃₄, as obtained from the Eastman Kodak Co., was used as an additive only.

The terms "compression ratio" and "mixture strength" are abbreviated in subsequent text, as convenient, to C.R. and M.S. respectively, and compression ratios are stated as single numbers.

I. PRELIMINARY EXPERIMENTS

Compression ratios of 13.0 and 12.3 were used. Lubricating oil therefore passed the piston at a greater than normal rate at the positions of the three spark plug holes in the cylinder wall as was shown by the experiments of Part XXVII. Oils S.300 and P.10 were used when the C.R. was 13.0 and the jacket coolant maintained at 55°F. Oil S.300 only was used when the C.R. was 12.3 and the jacket coolant was raised to a temperature of 140°F.

Experimental Results, C.R. 13.0

Jacket Coolant 55° F., Mixture Supplied at 70° F., Speed 1200 r.p.m.

The experiment was started with a mixture 20% weak and the engine operated for 15 min. with spark timing adjusted to the optimum value. M.S. was then gradually increased and spark timing always adjusted to the

corresponding optimum until the engine continued to run without spark ignition. The crank case was always cleared of used oil and washed before it was filled to the standard level with a different variety. It appeared however that considerable "blow by" occurred at compression ratios used for the experiments. Thus after an oil had been used for 15 hr. running time it was found to have become blackened, presumably by impregnation with the carbon that had been formed in the combustion chamber and not retained in the standard oil filter of the engine; as a matter of some interest an experiment was carried out with oil S.300 that had been used for the running time mentioned. Experimental results are tabulated below.

TABLE I

Oil in crank case	M.S. required for detonation
S. 300 fresh	Correct
S. 300 used for 15 hr.	4.5% weak
P. 10 fresh	8.0% weak

The results indicate that the vapor of oil S.300 is more resistant to pyrolysis than that of the paraffin base oil P.10 and that resistance diminishes as the oil becomes impregnated with the finely divided carbon.

Experimental Results, C.R. 12.3

Jacket Coolant 140° F., Mixture Supply 60° F., Speed 1200 r.p.m.

The crank case was drained of used oil and washed before it was filled to the standard level with fresh oil, S.300. Vaporization of oil deposited on surfaces in the combustion chamber was promoted by raising the temperature of the jacket coolant to 140° F. The experiment was started, as before, with a mixture 20% weak, which after 15 min. running time, was gradually increased while spark timing was adjusted to corresponding optimum values. The engine continued to run without spark ignition when M.S. had been increased to the correct value. Four indicator diagrams were then taken by means of a Photocon capacitance type of pressure pickup, the associated amplifier, and a Dumont oscilloscope. The diagrams are reproduced as Fig. 1. They show that, although a spark was not used, detonation occurred whilst combustion pressure was rising. The initiation of combustion must therefore have been due to the attainment of an igniting temperature by the surface of maximum temperature. This was necessarily that of the exhaust valve because the spark plug was an exceptionally cool variety and the detonation must have occurred in the end gas. The timing of surface ignition could not be regulated in conditions of a fixed C.R. and engine speed and was therefore somewhat irregular. The diagrams show that detonation occurred before t.d.c. in the circumstances. The engine continued to run but with power output reduced by approximately 30%. However the shock of detonation pressure waves occurring before t.d.c. was so severe that the experiment was discontinued after indicator diagrams had been taken.

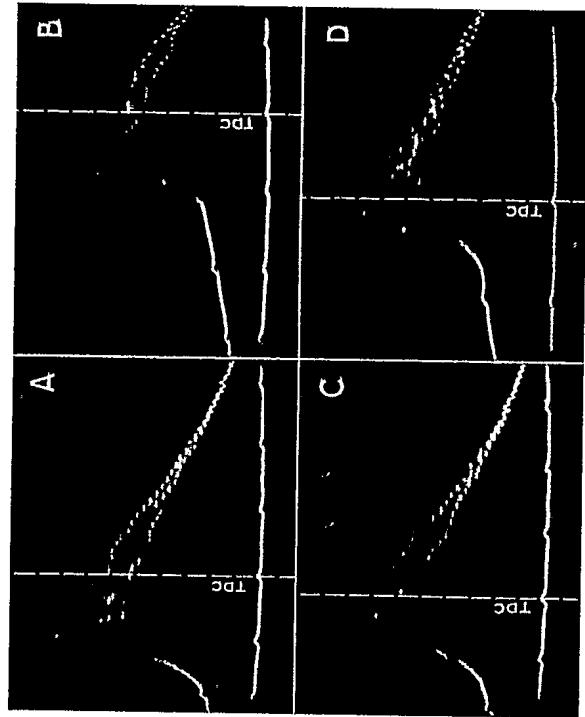


FIG. 1. Pressure-time diagrams, C.R. 12.3, 1200 r.p.m. Oil S.300 in crank case, jacket coolant 140° F., correct mixture supply at 60° F.

II. LUBRICATING OIL ADDED TO THE HYDROGEN-AIR MIXTURE AS A LIQUID

The experiments were carried out with a C.R. of 10.0 in order that the top piston ring should not lose its bearing on the cylinder wall at the spark plug holes. Lubricating oil from the crank case then passed the piston into the combustion chamber at the relatively low rate consequent on the cylinder and piston having been maintained in the conditions specified for the A.S.T.M.-C.F.R. method of knock rating.

Combustion of the vapor of oil added to the hydrogen-air mixture would be expected to yield an increase in power output. The rate of oil addition was therefore limited to 30 cc. per hr. This is equivalent to 1/70th of a drop of warm oil per cycle. A Bosch fuel injection system was tried but failed to operate until rate of oil supply was greater than 70 cc. per hr. It was then found that the Cox sampling device* could be adapted to deliver oil to the entering hydrogen-air mixture at suitable rates. This device is designed to take a sample of gas from any part of the engine cycle during a period of 1.0 millisecond. The direction of operation was reversed and lubricating oil injected into the cylinder during the induction stroke in order that it might be dispersed into the gaseous mixture by the random turbulence created at the inlet valve. It appeared however that the oil was deposited on the cylinder wall by the turbulence. Thus it was in the same state as that passing

*The device was supplied by Commercial Research Laboratory Inc., 20 Barlett Avenue, Detroit 3, Michigan.

into the combustion space from the crank case. Many experiments were carried out but results of special interest were not obtained.

The temperature of surfaces in the combustion chamber was then increased by raising that of the jacket coolant to 212° F. The rate of vaporization of oil deposits was thus increased and distribution of the vapor in the gaseous mixture was promoted by using a shrouded inlet valve to create a swirl in it. An experiment was carried out by the method described in Section I and when M.S. was increased to be 20% weak the engine ran without spark ignition but the timing of surface ignition as shown by the oscilloscope was extremely irregular. When nuclear ignition of the end gas occurred near t.d.c. the detonation shock wave was of great violence and the experiment ended when the Draper-Li pressure pickup, rated at 2000 lb. per sq. in., was crushed and the bronze bushing of the big end bearing was deformed.

III. THE DETONATION OF HYDROGEN-AIR MIXTURES BY CARBON NUCLEI DERIVED FROM LUBRICATING OIL AS SHOWN BY LIGHT INTENSITY DIAGRAMS

The light emitted by hydrogen burning in air is too low in intensity for photographic recording, irrespective of its concentration in the air. The light emitted by the burning of the vapor of lubricating oil in a homogeneous mixture with air is also too low in intensity for photographic recording when the concentration of air in the mixture is greater than required for complete combustion. The vapor of lubricating oil did not however form a homogeneous mixture with the gaseous mixture in the conditions of the experiments described in Section II and soot was deposited on surfaces in contact with flame even when the concentration of oxygen was in excess of that required for complete combustion. It was indicated by experiments described in Part XXVII (1) that the deposits built up as running continued until they were in part dispersed into the gaseous mixture by turbulence. Detonation would be caused by the soot becoming incandescent or pyrophoric at the temperature attained by the end gas, and light emission might be of sufficient intensity for photographic recording. Experiments carried out accordingly are described below.

Arrangements for Light Intensity Experiments

The viewing window, a short length of polished pyrex rod, occupied one of the spare holes in the cylinder wall. Light from the window was received by a photoelectric multiplier which provided a light intensity-time diagram on the screen of a dual-beam Dumont oscilloscope. The necessary spark ignition was by a cool plug in the standard position. The second spare hole was occupied by a "Sunbury" pressure pickup which provided a rate of pressure change-time diagram on the oscilloscope screen simultaneously with the light intensity-time diagram.

Conditions of Engine Operation

The hydrogen-air mixture was 55% weak. Engine speed was maintained at 900 r.p.m. by adjustment of load. The compression ratio was fixed at 10.0.

The temperature of the jacket was 212° F. and that of the mixture 70° F. A shrouded inlet valve was used to produce a swirl in the mixture. The crank case was cleared of used oil and then filled to the standard level with fresh S.300 oil. Oil P.30 as an additive was supplied by the Cox sampling device at the rate of 22.0 cc./hr.

Light Intensity and Rate of Pressure Change Diagrams

Photographs of diagrams which appeared simultaneously on the screen of the dual beam oscilloscope are reproduced as Fig. 2. The upper and lower horizontal traces on the diagrams are for part of the cycle in which there was no combustion. The lower trace is therefore for zero rate of pressure change

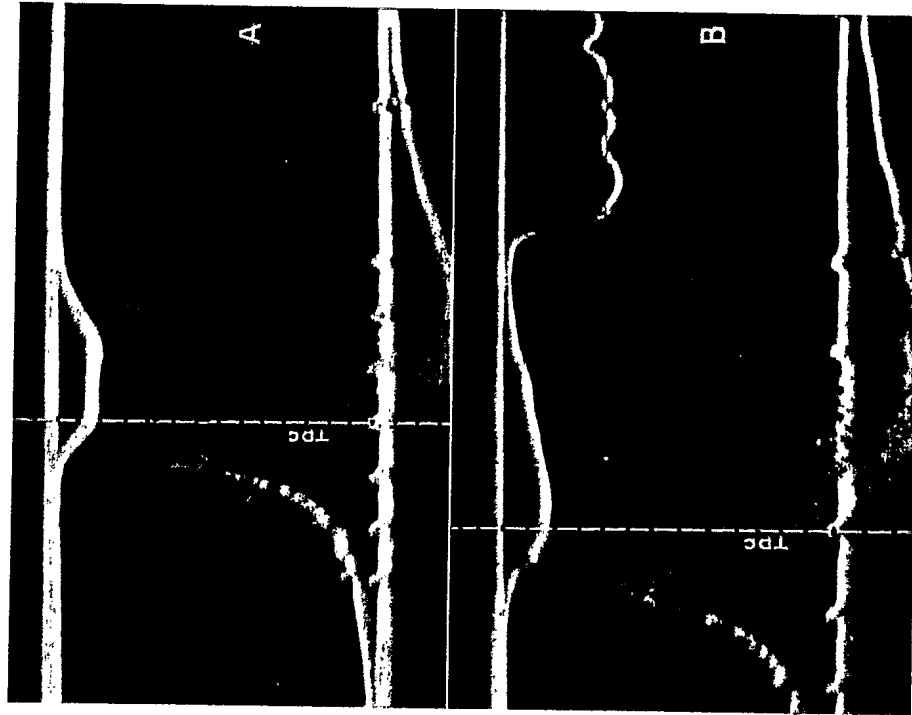


FIG. 2. Light intensity and rate of pressure change diagrams taken simultaneously C.R., 10.0. Oil S.300 in crank case, jacket coolant 212° F., speed 900 r.p.m., mixture 55% weak at 70° F.

A. No additive.

B. Oil P.30 added by Cox device at 22 cc./hr.

and the upper for zero light intensity. The light intensity trace extends down from the zero trace because a negative potential from the photoelectric multiplier was applied to the magnetizing coil of the related beam of the oscilloscope and the circuit to the multiplier completed through earth. The small "blips" on the lower trace are 10° of crank revolution apart and represent time intervals of 1.85 milliseconds at the engine speed 900 r.p.m., in respect of the upper as well as the lower horizontal trace. The blip at t.d.c. is marked by a broken vertical line. Combustion of the hydrogen is shown to be substantially complete at the time in degrees of crank revolution indicated by the intersection of the rate of pressure change trace with the horizontal trace for zero rate of pressure change. It is shown by both light intensity diagrams that the luminosity due to incandescent carbon particles appeared late in the combustion period and the rate of pressure change diagrams show that detonation then occurred.

Diagrams A.—These were taken before lubricating oil was supplied as an additive. The light intensity shown by the relevant diagram was then due to the incandescence of carbon particles that had been formed by pyrolysis of the vapor of oil S.300 that had passed the piston into the combustion chamber. The diagrams show luminosity beginning at 10° before t.d.c. with faint detonation pressure waves accompanying the igniting effect of the carbon particles. Combustion of the hydrogen was then well advanced and was substantially completed at approximately 5° after t.d.c. but luminosity due to the incandescence of free carbon continued until 15° after t.d.c. That is for 10° of crank revolution after combustion of the hydrogen had been completed.

Diagrams B.—These were taken while the paraffin base oil was supplied by the Cox sampling device as an additive, at the rate of 22 cc./hr. The diagrams show that luminosity appeared, as in the diagrams A, at approximately 10° before t.d.c. but the accompanying detonation pressure waves are more clearly defined. The pressure waves were not of sufficient energy to cause knock that was easily audible. Luminosity due to the incandescence of free carbon continued until it became zero at 45° after t.d.c., that is, for 40° of crank revolution after combustion of the hydrogen had been completed. Incandescence of free carbon then recurred with the emission of a relatively high level of light intensity which diminished slowly during the remaining time interval shown on the diagrams. The hydrogen-air mixture always contained some small proportion of oil vapor and the small pressure changes shown by the rate of pressure change diagrams before the occurrence of detonation and the later fuzziness of the diagrams are attributed to partial burning of the vapor.

The Recurrence of Luminosity

The finely divided carbon or soot formed by pyrolysis of the vapor of lubricating oil was of the nature of carbon black. It is known that the particle size in that material varies to an extent depending on the method of pyrolysis and the nature of the substance from which it was procured, and that the

freshly formed carbon possesses in a remarkable degree the power of absorbing gases. These characteristics may afford an explanation for the recurrence of luminosity during the expansion stroke of the engine, especially in view of the relatively large concentration of free oxygen then available because the hydrogen-air mixture supplied to the engine was 55% weak.

Oil S.300 passed the piston at the minimum practicable rate and it may be assumed that the carbon produced by pyrolysis was composed of extremely fine particles. Light was emitted for 15° of the expansion stroke only as shown by diagrams A and as there was no recurrence of luminosity it appears that all of the carbon was consumed by the oxygen then available.

The carbon produced by pyrolysis of hydrocarbons is known to contain both fine and coarse particles, thus when oil P.30 was used as an additive the burning of the fine particles and those produced by pyrolysis of oil S.300 passing the piston would account for the emission of light during 25° of the expansion stroke as shown by diagrams B. The subsequent occurrence of luminosity with a relatively high light intensity may be attributed to the burning of the coarser particles initiated by the adsorbed oxygen and sustained by the available free oxygen. The rate at which oil was vaporized was far from constant, when it was supplied as a liquid additive, and in some cases light emission was continuous although of variable intensity during the part of the expansion stroke shown on the diagrams.

IV. THE PREVAPORIZATION OF ADDITIVES AND EXPERIMENTS WITH CETANE

Experiments described in preceding sections demonstrated that the finely divided carbon responsible for detonation in the end gas was provided by the pyrolysis of the vapor of the lubricating oil. Vaporization involves a time factor, as represented by engine speed; thus whatever the rate at which oil passes the piston into the combustion chamber the proportion vaporized prior to spark ignition, at a particular speed, is not increased to a significant extent except by raising the temperature of surfaces to which the oil adheres as a liquid and thus inviting the occurrence of preignition due to the temperature attained by the exhaust valve. Thus it appeared that oil or cetane when used as an additive should be vaporized immediately prior to admission through the inlet valve, if results of an enhanced significance were to be obtained. A method of vaporization was therefore devised and used for experiments described in this Section.

The Methods of Vaporizing and Metering Small Rates of Supply of Liquid Additives

The vaporizing device and its arrangement for the discharge of vapor into the well of the inlet valve are shown by Fig. 3. The device comprises three concentric tubes. The outer one is of mild steel with an inside diameter of 0.30 in., and a perforation is provided in the blank lower end through which vapor of the additive is discharged. Within the outer tube is a concentric thin-walled steel tube having an outside diameter of 0.25 in. The annulus

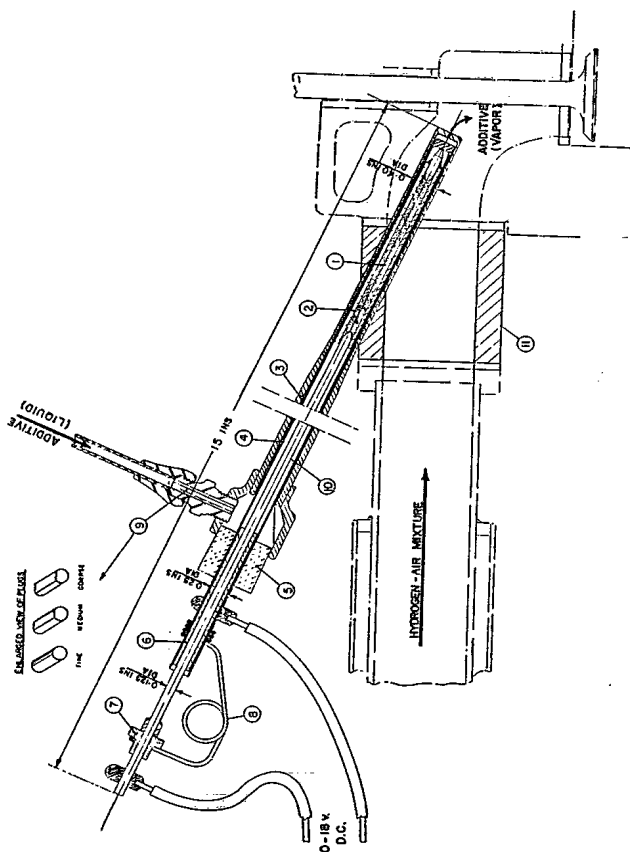


FIG. 3. Vaporizer for liquid additives.

1. Graphite powder
2. Silica tube
3. Outer steel tube
4. Inner steel tube
5. Vapor seal
6. Glass tube
7. Insulator
8. Spring
9. Flow restrictor
10. Steel electrode

formed by the two tubes is then 0.025 in. wide. The additive is supplied to the upper end of the annulus and is vaporized as it flows to the lower end by an electric heater enclosed in an inner concentric tube of silica. Powdered graphite is used as the resistor of the heater. The graphite forms part of an electric circuit completed in the device by a steel rod 0.125 in. in diameter projecting from the upper end and extending through the inner steel tube to make contact with the graphite. The rod is insulated by a length of glass tube from the inner steel tube. This tube connects with the lower end of the graphite resistor to complete the electrical circuit within the tube. The rate of heat supplied by the resistor is regulated by adjustment of the current supplied by a storage battery. The resistance of the graphite heater was 3.0 ohms, and 3.0 amp. were required to vaporize S.300 oil supplied at a rate of 30 cc./hr. If as much as 60% of the heat developed in the heater was radiated from the outer surface of the vaporizing device it would, if all absorbed by a correct hydrogen-air mixture supplied to the engine running at 900 r.p.m., raise its temperature by 2.5° F. only.

The device for the supply of additive to the vaporizing device at measured rates is shown by the diagram of Fig. 4. The rate of supply is controlled by adjustment of the air pressure in the receiver and further by the resistance plugs shown on Fig. 3. The rate is measured by timing the rate of fall of the

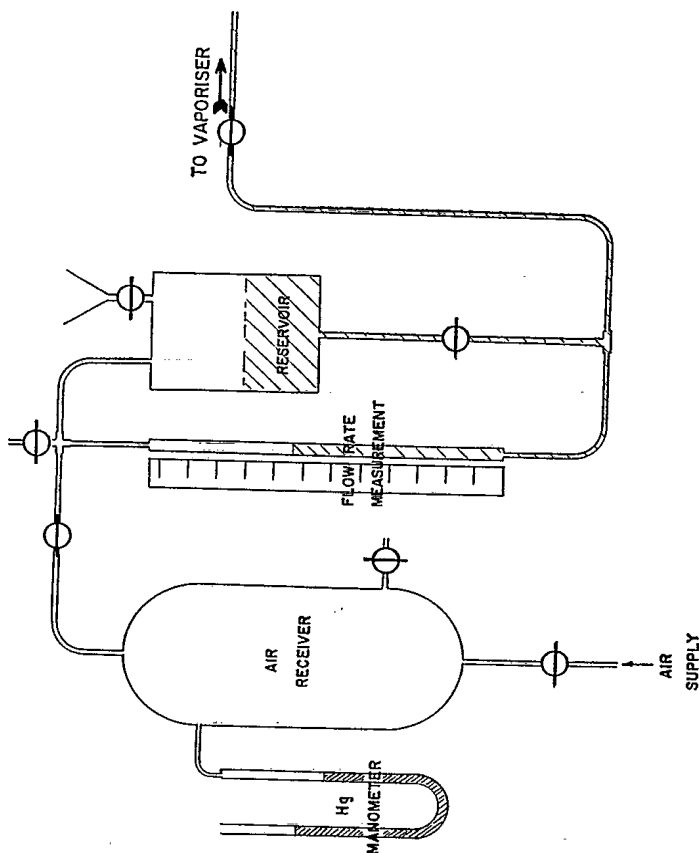


FIG. 4. Device for the supply of liquid additives to the vaporizer at measured rates.

additive in a graduated glass tube having an inside diameter at 4.0 mm. It was possible to measure accurately rates of additive supply as low as 3.0 cc./hr., and complete vaporization of the additive was obtainable with rates of supply greater than were required for experiment. The heating current was always regulated to be little greater than required for complete vaporization of the additive. The device was found to be suitable for the vaporization of lubricating oils as well as for additives with a unique boiling point. The results obtained when cetane was used are presently described. Those obtained when lubricating oils were prevaporized will be described in a subsequent paper.

Conditions Used for Experiments with Prevaporized Additives

Preliminary experiments with cetane demonstrated that detonation shock became extremely severe as mixture strength approached the correct value, and in consequence charge density was reduced by throttling to 64% of normal. Otherwise the conditions of experiment were as follows: compression ratio 10:0, engine speed 900 r.p.m., mixture temperature 110° F., and jacket coolant 212° F. Spark ignition, when used, was by a cool plug. Cetane was supplied to the vaporizer at the rate of 30 cc./hr. A Photocon pressure pickup with associated electronic equipment was used to obtain pressure-time diagrams.

Experimental Results with Cetane as an Additive

The engine was warmed up by running with spark ignition for 15 min. on a mixture 50% weak, with oil S.300 in the crank case. M.S. was then gradually increased and spark timing always adjusted to corresponding optimum values. A considerable degree of detonation was observed when M.S. had been increased to be 15% weak. Pressure-time diagrams were then taken at two-minute intervals for a period of eight minutes, and have been reproduced as Fig. 5 with t.d.c., marked by a vertical broken line. They show

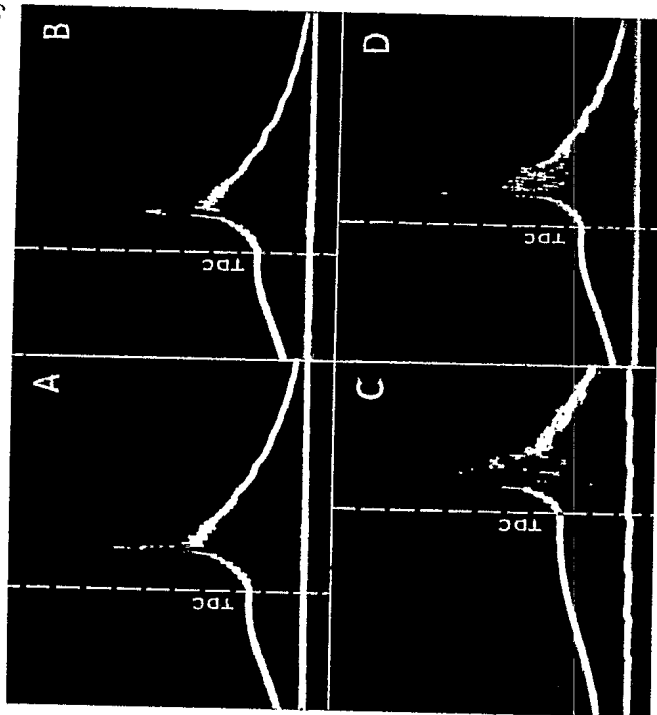


FIG. 5. Pressure-time diagrams taken at 2-min. intervals until spark ignition was replaced by surface ignition. C.R. 10, speed 900 r.p.m., jacket coolant 212° F., mixture 110° F. and 15% weak.

little variation in the time of occurrence of detonation, which always occurred after t.d.c., but show that the volume of end gas in which the effect occurred tended to increase. There was a corresponding increase in the amplitude of the gas vibrations which follow detonation, pressure waves, and the engine continued to run when the spark was switched off.

Cetane was then supplied to the vaporizer at the rate of 30 cc./hr., and the four pressure-time diagrams reproduced as Fig. 6 were taken at half-minute intervals. They show that nuclear ignition accompanied by detonation pressure waves continued to occur in the end gas, and as combustion was not initiated by a spark it must have been initiated on the attainment of the requisite temperature by the exhaust valve, which provided the surface of maximum temperature in the combustion chamber. Thus the diagrams show that ignition timing was much less regular than when combustion was initiated by a spark, as would be expected.

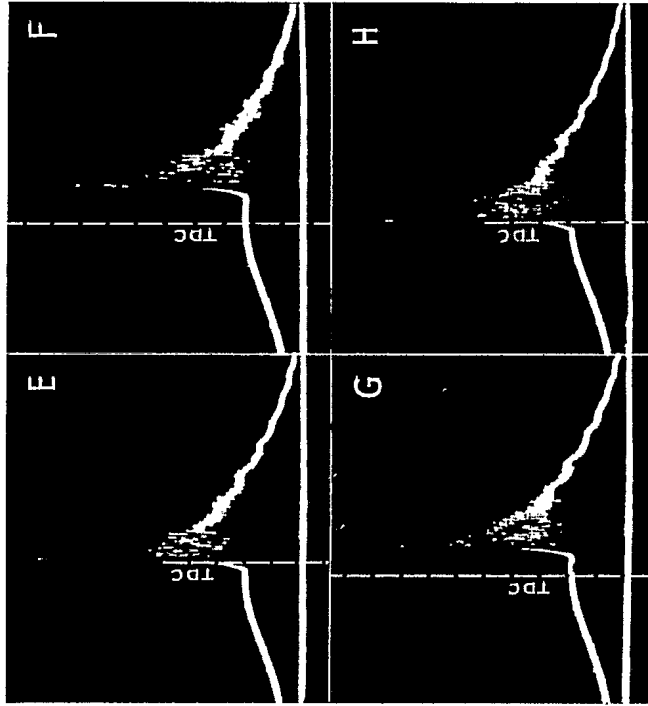


FIG. 6. Running continued with surface ignition and with addition of 30 cc./hr. of cetane prevaporized. Pressure-time diagrams taken at ½ min. intervals until cylinder broke loose from crank case.

It is shown by the last diagram taken that nuclear ignition accompanied by detonation pressure waves of large amplitude had occurred at t.d.c. The engine was unable to tolerate the consequent shock and the cylinder broke loose from the crank case because of the fracture of the retaining casting.

CONCLUSION

Experiments described in Part V (2) and Part XXVII (1) demonstrated that if an experiment were started with a clean combustion chamber, detonation did not occur until a deposit of soot arising from pyrolysis of lubricating oil vapor had built up on surfaces to such an extent that it was in part carried into the hydrogen-air mixture by turbulence. The consequent detonation occurred irregularly and a residue of soot always remained on surfaces in the combustion chamber.

It was concluded that detonation would not be dependent on a build-up of surface deposits of soot if the hydrogen-air mixture entering the cylinder carried the vapor of oil. The vaporizer described in Section IV *ante* was designed accordingly. Cetane, a standard fuel oil for the Diesel engine, was selected for experiments because of its unique boiling point, 549° F. The vapor was mixed with the hydrogen-air mixture by being ejected into the well of the inlet valve but it appeared that it formed a fog in the relatively cool gaseous mixture and that some might condense on surfaces before being dissipated by the heat of compression. The temperatures of surfaces were

therefore raised by maintaining the jacket coolant at 212° F. and the hydrogen-air mixture supply was maintained at 110° F. The mixture was 15% weak, engine speed 1200 r.p.m. Spark ignition was necessary and timing was adjusted to the optimum value, 3° in advance of t.d.c.

It is shown by the diagrams of Fig. 5 that combustion pressure rise began at t.d.c. approximately, and continued in the normal manner for about 5° of crank revolution. Detonation accompanied with large scale pressure waves then occurred in the end gas. The diagrams show that normal combustion and the subsequent detonation occurred with a high degree of regularity. They show also the small scale pressure waves known to follow spark ignition.

When the vapor of cetane was added to the mixture, running continued with spark ignition switched off. Thus it appeared that the temperature attained by the exhaust valve sufficed for the ignition. It is shown by the diagrams of Fig. 6 that combustion then proceeded in the normal manner for a brief and variable time interval before the occurrence of detonation in a corresponding volume of end gas. Thus it is shown by diagram E that detonation had occurred at t.d.c. in nearly the whole of the mixture, by diagrams F and G that detonation occurred after an appreciable interval of normal combustion, at from 5° to 10° after t.d.c., by diagram H, that detonation occurred again at t.d.c. in substantially the whole mixture. The diagrams of Fig. 6 were taken during a running period of two minutes. Thus combustion occurred 900 times while the hydrogen-air contained the vapor of cetane in the extremely small concentration provided by the supply of the liquid to the vaporizer at the rate of 30 cc./hr., i.e., 0.0011 cc. per cycle. The diagrams show that detonation may have occurred at t.d.c. in half of the combustion periods. It is not surprising therefore that the cylinder broke loose from the crank case after two minutes of running. The damage to the engine would have been regretted had it not provided a striking illustration of nuclear ignition of the end gas and its consequent detonation.

ACKNOWLEDGMENTS

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