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Pre-reactions in gasoline engines without ignition.

by Eernst Schmidt and Egon Mühlner

A. Introduction

It is known that before ignition, reactions take place in the mixture drawn into combustion engines which induce the combustion proper; at sufficiently high compression they can reach self-ignition. These reactions are very important for the combustion mechanism. First of all they control the ignition lag and the special type of self-ignition known as knocking. These pre-reactions have been studied by heating gas-air mixtures in a closed container and measuring the pressure increase at various initial temperatures. At initial temperatures of 200° to 300°C sometimes oxidations occur which can be accompanied by luminescence, whence they are also called "cold flames". In higher hydrocarbons these oxidations occur only after a finite time, the so-called induction time, which varies between fractions of seconds and hours. The resulting compounds accelerate the reaction. The reaction velocity reaches a maximum and then drops again to zero, unless it reaches self-ignition. Generally however only a fraction of the oxygen present is transformed and then the reaction quietens down again. Other tests were made on flowing mixtures, heated for a short time to a high temperature and rapidly cooled again. The chemical analysis of the combustion products shows the transformation. Beside CO_2 and CO, aldehydes and peroxides were also found.

If we are interested in engine combustion, a free-aspirating engine can be run in the usual way, with an outside drive and no ignition. As early as 1931 Mondain-Monval (1) carried out such tests with measurements on flowing mixtures in a small four-stroke engine; at 200 to 300°C he observed pre-reacting.

Peletier and co-workers (2) made similar tests on a C.F.R. test engine at 900 rpm., with a mixture of 70% iso-octane and 30% n-heptane, i.e. octane number 70. The pre-reactions were marked by a swelling of the indicator diagram during the expansion stroke. The effect grew with mixture enrichment and reached its maximum at a fuel ratio of 1.8, the latter being the ratio of actual fuel quantity to stoichiometric quantity. (We avoid the expression "air excess coefficient" which in the case of air deficiency is misleading and otherwise unsatisfactory; as known the air excess coefficient is $\lambda = 1$ in the stoichiometric combustion, i.e. when the air excess is exactly zero. It is better to call the air excess coefficient "Air ratio", the reciprocal value of which is the fuel ratio). Fig. 1 shows a graph recorded by Peletier with an optical indicator; it shows

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(1) P. Mondain-Monval: Comptes Rendus, Vol. 192 (1931) P. 1158, and Chemie et Industrie, Vol. 27 (1932) P. 770.

(2) L.A. Peletier, G.G. van Hoogstraten, J. Smittenberg and P.L. Kooyman: Chaleur et Industrie, Vol. 20 (1939) P. 120.

superimposed the working stroke of three fuels of different octane number. The left side corresponds to compression, the right to expansion. The swelling of the expansion curve due to pre-reactions has clearly a different amplitude for each fuel. This swelling of the diagram falls off with the isooctane content, i.e. as the octane number increases. An addition of TEL has the same effect. We made other tests on a small two-stroke engine at 1,500 rpm; instead of the usual indication, we measured the temperature increase of the mixture during its passage through the engine. The cylinder could be electrically pre-heated at different temperatures. At 150°C intake temperature and cylinder temperatures of 200° to 300°C, a 65% isooctane fuel (octane number 65) showed a 30°C temperature rise, whilst the temperature of a 43% isooctane fuel (octane number 43) rose by 50°C. The condensation products of the outgoing mixture showed that the fuel was unaltered but for about a 5% content of water-soluble elements, including 30% of peroxides.

Broeze reported on these tests in the May 1939 open session of the D.A.L. (1). As they were made only on a few isooctane and n-heptane mixtures and in a limited range of test conditions, it seemed worth extending them. New tests were therefore undertaken in the engine research section of the Institut für Motorenforschung der Luftfahrtforschungsanstalt Hermann Göring.

B. New tests on pre-reactions in gasoline engines without ignition.

1. Test arrangement.

In the design of the test equipment particular stress was laid on defined and reproducible test conditions, as far as this is at all possible in a running engine. A liquid cooled single-cylinder (101 mm. bore x 130 mm. stroke = 1.04 lt. cubic capacity) fuel-test engine built by the Forschungsinstitut für Kraftfahrzeuge und Fahrzeugmotoren der Technischen Hochschule Stuttgart (2), was used. Fig. 2 shows a cylinder head section. Cylinder jacket and head are of cast-iron with cast cooling ports, the piston of light alloy. Inlet and exhaust valves are of the same design placed vertically in the cylinder head. The exhaust valve opens 47° B.B.C. (before bottom dead centre) and closes 7° A.T.C. The inlet valve opens 7° B.T.C. and closes 47° A.B.C. The combustion chamber has the shape of a regular cylinder. The inlet and exhaust ducts have the usual 90° elbows. The compression ratio can be varied in wide limits between 5 and 25. Four sockets in all in the cylinder and cylinder head can be used for mounting quartz pressure gages, indicating thermocouples, quartz windows as shown in Fig. 2. The unused sockets are sealed by studs, filling almost completely the whole duct to the cylinder.

Fig. 3 shows the whole test assembly. Air is aspirated in a from pipes running under the test room at a constant temperature registered by thermometer b; it goes through an air meter c and enters the pressure equalizing tank d. From here it flows through a pipe 65 mm. bore and 700 mm. long, in which two electric resistances e are mounted, to the carburettor f (Model Sum), the rotary slide throttle of which was generally fully open. The fuel consumption is measured volumetrically in the usual way by a calibrated glass vessel g. The weight consumption is obtained from the fuel density determined

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(1) J.H. Broeze, H. van Driel and L.A. Peletier: Betrachtungen überden Klopfvorgang im Otto-Motor. Schriften der Deutschen Akademie der Luftfahrtforschung, Vol. 9, p. 187 (Berlin 1939)

(2) P. Schmidt, Neue Kraftfahr-Ztg. Vol. 13 (1938) p. 79.

by aerometric method. A thermometer h is cast in the gauge vessel to obtain the true fuel temperature at any moment.

From the carburettor the mixture flows to the engine in a well insulated pipe about 1 m. long and 68 mm. bore, in which are inserted shortly before the cylinder head, an ordinary thermometer i and one provided with fins k. Fuel droplets dragged behind are deflected by two 90° bends in the pipe. After going through engine m the mixture enters the likewise insulated exhaust pipe, which again has a ribbed thermometer l to measure the terminal temperature. The mixture is then aspirated by fan n, after an air addition of many times its quantity is made through pipe o. The mixture can be extracted for examination through stop valve p. The compression ratio of the engine can be varied by lifting and lowering the cylinder block by means of crank q. Elastic joints allow the connections to stretch. Fluid manometers r measure the mixture pressure before and after the engine. The coolant is circulated by pump s through tank t. Electric heater u and thermometers v before and after the cylinder are mounted in its circulation. Technical glycol was used. At 0.2 Kg/sec. the circulation was so fast that the difference between admission and exit temperature of the coolant did not exceed 0.2°C. The temperature of the whole cylinder block can thus be assumed to be uniform. Aeroshell medium was used as lubricant, its temperature was kept constant by a water-cooled spiral in the crank case. A 2,500 rpm. D.C. dynamometer w was used to drive the test engine; its moment was measured by counterweights.

Fig. 4 shows the fins used to measure the mixture temperature before and after the cylinder. They are turned in aluminium and their extensive contact surface with the mixture allows the accurate temperature determination over the whole cross-sectional area of the flow. The ribbed part is insulated from the pipe by fiber connections, its cavity containing the mercury bulb of the thermometer is filled with oil.

2. Test conduct.

Apart from the measurements specially taken to study the influence of varying working conditions, all tests were carried out in the following conditions: speed = 1,800 rpm., mixture temperature = 140°C, coolant temperature = 140°C, oil temperature = 75°C, oil pressure = 2.4 atm. The stable working condition of the engine was reached in about 2 hours, after which measurements could be started. Each single test stage required about 45 minutes run.

A test with pure air was made before each measurement with the mixture. For a constant 140°C admission temperature, the exit temperature of pure air at compression ratio $\varepsilon = 6$ was generally 145°C; this figure however varied by a few degrees from day to day, presumably owing to small changes in the engine conditions. At the beginning of the tests the exit temperature was even 2 to 3°C below the admission temperature. The effect of these variations was excluded by counting the temperature increase Δt of the mixture always from the immediately preceding exit temperature of pure air. After the air test, fuel was admitted by opening the carburettor jets; the mixture temperature before the cylinder was kept at 140°C by adjusting the inlet air heater. For each compression ratio a series of tests was carried out with gradually increasing fuel quantity. In this connection the compression ratio ε is expressed in the conventional manner, i.e. the ratio of the cubic capacities when the piston is at the two dead centres.

Some fuels with various octane numbers were tested in this way In supplementary tests on one fuel only the effect of variations of the working conditions was also investigated. Moerer the torque reduction of the motor due to pre-reactions was determined.

3. Accuracy of test results.

The working conditions of a running engine cannot be kept constant for a long time, even with the greatest care, as perhaps in a laboratory apparatus. During the operation, running-in and wear vary the friction conditions; these depend mainly on the lubricant, the state of which varies considerably with varying conditions, soiling, fuel absorption etc. These variables affect directly the torque measurement, as well as the temperature condition of the engine through the friction heat. Certainly cylinder and cylinder cover are kept at nearly constant temperature by the coolant; the non-cooled piston however is heated by friction and subsequently delivers heat to the air. This explains the changes in the exit temperatures of pure air. Fortunately however the difference used for the evaluation between mixture exit and air exit temperature in the preceding pure air test was considerably better to reproduce. In these circumstances, when the same test was repeated after many days, the possible error in this difference was as little as ± 1° to 2°C. The error within a series of tests without stopping and cooling the engine was only ± 0.4°C. The errors of the various thermometer readings were ± 0.2°C. The fuel quantity could be determined with an accuracy of about ± 0.5%. The accuracy of the torque measurement was ± 0.02 Kg referred to a lever arm of 716 mm.; the reproducibility of a measurement was possible only up to ± 0.1 Kg owing to the above variations of the friction conditions.

4. Aids for test evaluation.

In the following graphs covering all test results the compression ratio ε is always expressed as usual as the ratio of the cubic capacities when the piston is at the two dead centres. The real compression ratio is smaller, because the inlet valve closes 47° A.B.C. Table 1 shows the comparison of conventional compression-ratio ε and the corrected compression ratio ε_b corresponding to a sudden closing of the inlet valve 47° A.B.C. The final closing period of the valve increases the actual compression ratio beyond ε_b, whilst the heat exchange with the cylinder wall reduces the compression temperature. It is therefore convenient to calculate the latter with ε_b and adiabatic compression.

The compression temperatures for an initial mixture temperature of 140°C are plotted in Fig. 5 as a function of fuel ratio β and compression ratio ε. The curves are calculated on the assumption of adiabatic compression with the corrected compression ratio ε_b, though they are indicated with ε to simplify matters. Octane was taken as a typical fuel; its specific heat ratios were calculated according to G. Damköhler for a medium compression temperature of 500°C and are shown in Table 2 for various fuel ratios. The curves show the very considerable variation of the compression temperature with the mixture strength.

Table 1
Correction of compression ratios.

ε = Compression ratio determined in the usual way from the ratio of the cylinder capacities at the dead centres.
ε_b = Compression ratio corrected taking into account the delayed valve closing.

ε	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	10.0
ε_b	4.52	4.96	5.40	5.84	6.28	6.72	7.16	7.60	8.04	8.92

Table 2

Adiabatic exponent $\varkappa = c_p/c_v$ of an octane-air mixture as a function of the fuel ratio β.

β	0	0.5	1	1.5	2	2.5	3	3.5	4
$\varkappa$	1.360	1.322	1.298	1.274	1.252	1.239	1.225	1.211	1.200

Table 3

The test fuels.

Fuel No.	Fuel type	Octane number		Composition, Volume						Theoretical air requirement kg air/ kg fuel
		nominal	measured	Alcohol	Olefins	Paraffins	Aromatics	Naphthene	Lead tetraethyl	
1	Commercial basic gasoline	58	56.4	0	8	-	7.3	-	0	14.88
2	Lead-free aviation fuel	74	72.0	0	5	-	4.1	-	0	14.94
3	Aviat^{n} fuel I	87	-	-	3	-	17.0	-	0.07	14.71
4	do. II	87	88.1	-	4	-	9.0	43.7	0.08	14.85
5	do. III	87	90.6	-	3.5	-	8.5	44.2	0.09	14.86
6	Special fuel	100	-	0	2	-	40.0	-	0.08	14.32
7	Pure isooctane	100	-	0	0	100	0	0	0	15.18
8	Ethyl alcohol	99.5 1)	-	99.9	0	0	0	0	0	9.04
9	Techn. pure benzole	108 2)	-	0	0	0	100.0	0	0	13.33 3
10	Standard fuel I.G.7	44.6	44.6	0	0.6	77	2.4	20.0	0	15.0
11	do. + 1 cu.cm $Pb(Et)_4$ per lt	74.5	73.1	0	0.6	77	2.4	20.0	0.1	15.0
12	do. + 1.53 cu.cm Eth per lt	74.5	73.2	0	0.6	77	2.4	20.0	0.1	15.0
13	Fuel No.2 + 1.3 cu.cm. Eth per lt.	87	87.8	0	5	-	4.1	-	0.085	14.94

1) By W. Jost: "Explosions - und Verbrennungsvorgänge im Gasen", Berlin, Spring 1939, p. 550.
2) Extrapolated from data supplied by I.G.
3) For technical benzene containing some toluene.

4. Test results

a. Test fuels.

Table 3 contains the fuels used in the tests and their main properties. The octane numbers were determined by the engine method. The nominal octane number is the commercial one, the measured ones were kindly determined for us on some fuels by I.G. on the I.G. test engine at Oppau. The composition includes only those constituents covered by the analysis. Zero means that the constituent in question was not present, a dash that its quantity was not ascertained.

Aviation fuels 3, 4 and 5 (nominal octane number 87) were considered as being the same. As noticeable differences appeared only in the evaluation of the pre-reaction tests, it was omitted to check the octane number of fuel No. 3, which however lies between 89 and 90. Not enough was known of No. 4 to carry out a complete test ~~plan~~; the tests were therefore not reproduced, particularly as they did not differ considerably from the results of No.3 and 5.

Fuels 10, 11 and 12 are all basically the same standard gasoline I.G. 7, No.10 has no additive, No. 11 1 cu.cm. lead tetraethyl/lt., No. 12 1.53 cu.cm. ethyl fluid/lt. As 1.53 cu.cm. ethyl fluid contain exactly 1 cu.cm. lead tetraethyl, the added quantity of lead tetraethyl is the same in both cases.

Fuel No.13 is the same as No. 2 with an addition of 1.3 cu.cm. ethyl fluid per litre.

b. Dependence of pre-reactions on mixture strength and compression ratio.

Fig. 6 shows the typical process of temperature increase in a mixture due to pre-ractions, for an aviation fuel of octane number 87 with 0.07% lead tetraethyl, No. 3 in Table 3. Actually, as mentioned in a), the octane number may have been rather higher. The graph shows the temperature increase Δ t of the mixture computed from the exhaust temperature plotted for various compression ratios against the fuel ratio β. The position and the very small difference of the various test points are shown clearly by spacing the curves. Actually they all start from the co-ordinate origin. The same curves without the single test points, are plotted in Fig. 7, superimposed in their correct position. In this fuel the pre-reactions become noticeable at a compression ratio $\varepsilon = 5$; at first they grow with the fuel ratio, showing a marked peak for a very lean mixture of $\beta = 0.37$. A further increase of the fuel ratio reduces the pre-reactions which practically disappear at $\beta = 1$, i.e. when the mixture is exactly stoichiometric. As the compression ratio rises, the curves also rise; the peak moves towards higher fuel ratios and the right side falls off more steeply. For a compression ratio of $\varepsilon = 7$ and beyond, the decline becomes a discontinuous jump, occurring always at the same point even when the tests were repeated. The peak values of temperature increase due to pre-reactions are at the left of the jump; at its right a slight increase of the fuel ratio reduces the pre-reactions nearly to zero, leaving only a small temperature increase, practically independent of the fuel ratio but increasing somewhat with the compression ratio. If the compression ratio is increased to $\varepsilon = 7.5$, the point of discontinuity shifts to richer mixtures and becomes higher. With $\varepsilon = 8$ it is no longer possible to reach the point of discontinuity from the left; at a fuel ratio of about 2.2 spontaneous ignitions occur first in the exhaust and then also in the cylinder, the latter being quite similar to violent knock impacts. For $\varepsilon = 8.5$ these violent spontaneous ignitions had already started below the stoichiometric fuel ratio. The tests had to be discontinued after these spontaneous ignitions set in, because the engine heated fast with spontaneous detonations on further running. Only by rapidly increasing its speed by about 200 rpm. was it possible to eliminate self-ignition, just as knocking can be eliminated by acceleration as long as this does not cause a temperature rise.

The final temperatures of adiabatic compression for some points of the pre-reaction curves were determined by means of Fig. 5 and plotted in Fig. 6. These are the results: —

Going from rich mixtures to smaller fuel ratios, at all compression ratios pre-reactions appear discontinuously or gradually at the same final temperature of adiabatic compression, i.e. about 380°C. Peak pre-reactions set in at adiabatic compression temperatures of 410°C. At the left of the peak value, the adiabatic compression temperature grows for each compression ratio as the fuel ratio falls off, as it appears from the temperatures marked on the curve $\varepsilon = 6$. From this behaviour it follows that the intensity of the pre-reactions is largely determined by the final temperature of adiabatic compression and, as we shall see later when investigating the speed effect, by its induction period. Owing to the smaller adiabatic exponents of richer mixtures, this temperature sets in at higher compression ratios; the higher fuel content produces however a greater conversion and temperatur increase.

The sudden disappearance of pre-reactions at higher compression ratios remains surprising. It seems as though with sufficient concentration the fuel molecules combine with radicals thus breaking reaction chains.

The curve shape at the left of the peak is also remarkable. As shown in Fig. 7, the curves for higher compression ratios are below the middle and lower ones. For the same fuel ratio β, stronger compression with higher final temperature produces less complete pre-reactions than weaker compression with lower final temperature. Such negative temperature coefficients of reactions have been repeatedly found. We should also mention the two ignition limits observed by Townend and co-workers during the combustion of hydrocarbon-air mixtures.

Fig. 8 shows for the same fuel how the torque M_d required to drive the engine diminishes as a result of pre-reactions. Roughly speaking this reduction corresponds to the temperature increase, within the limits of accuracy of these measurements due to the varying friction conditions.

c. Influence of the octane number and fuel composition.

Fig. 9 shows the temperature increase due to pre-reactions for a commercial basic gasoline (No.1 in Table 3) of octane number 56.4. The character of the curves is similar to that of fuel No. 3 of octane number 87, but for the same compression ratio the curves have more than double the height, they begin more steeply and the higher compression ratio curves are initially not so far below those of lower compression. No points of discontinuity are reached here, because for compression ratio $\varepsilon = 6.5$ self-ignition occurs with temperature increases of 70°C.

Fig. 10 shows the test results on a load-free aviation fuel of O.N. 72 (fuel No. 2 in Table 3). O.N. 87 aviation fuel is produced by adding T.E.L. to it. As was to be expected, the pre-reactions lie between the figures for O.N. 56.4 of Fig. 9 and O.N. 87 of Fig. 7. The point of discontinuity appears again for $\varepsilon = 6$. With $\varepsilon = 6.5$ the point of discontinuity can no longer be reached from the lean mixture side, as self-ignition occurs earlier. A test on a rich mixture of $\beta = 2.08$, in which the pre-reactions have disappeared, shows however that the point of discontinuity is far below $\beta = 2$.

Dash-dot curves in Fig. 10 apply to Fuel No.13, produced by adding 1.3 cu.cm. ethyl fluid per litre (corresponding to 0.85 cu.cm. pure T.E.L.) to Fuel No.2, whereby the O.N. rises to 87.8. The comparison of these curves with Fig. 7 shows that the lead addition has actually made the fuel similar to No. 3 of O.N. 87. The curves are lower and their initial gradient has become much flatter.

Fig. 11 shows the measurements on a lead containing fuel of O.N. 90.6 (Fuel No. 5 in Table 3); the curves are quite similar to aviation fuel of O.N. 87 (No. 3 in Table 3), but for the pre-reactions being less pronounced, as expected. The dash-dot curve refers to oxygen-rich air, which we shall consider again later.

This distinct influence of the lead addition is not always noticeable, as shown by the tests on I.G. standard fuel (No.10 in Table 3). Without lead addition this fuel has O.N. 44.6 and presents strong pre-reactions at $\varepsilon = 5$, which at this low compression ratio and $\beta = 0.9$ produce temperature increases of 65°C. Curve a in Fig. 12 rises almost linearly and its discontinuity occurs below the stoichiometric fuel ratio. At this compression ratio, with stoichiometric mixture the engine runs above the region of pre-reactions. The addition of 1.53 cu.cm. ethyl fluid per litre (No.12 in Table 3), which pushes the O.N. to 73.2, varied but little the curve shape, as shown by curve b in Fig. 12; it merely rounded off the sharp peak before the point of discontinuity, which remained unaltered. To check on this surprising result, 1 cu.cm T.E.L. was added to the same fuel (No.11 in Table 3), which is equivalent ot 1.53 cu.cm. ethyl fluid as used in fuel No.12. This mixture produced however almost the same curve (c in Fig.12) as ethyl fluid. No tests could be made at other compression ratios, as the engine did not allow lower ones and higher ones caused early self-ignition.

Fig. 13 shows the temperature increase curves for pure iso-octane of O.N. 100. Again the curves are of the same type, but their height for the same compression ratio is considerably lower than O.N. 87. With $\varepsilon = 10$ the curve still runs without the discontinuity. If the compression is boosted to 11, strong detonating self-ignition occurs at fuel ratio of1, thus preventing the formation of a discontinuous curve. It is remarkable that the whole series of curves is strongly displaced towards richer mixtures. Pre-reactions are very weak in the vicinity of stoichiometric mixtures, i.e. in the practical operation region.

The graph contains further a flat curve for $\varepsilon = 9$, referring to a special fuel of O.N. 100, but with 40% aromatic compounds, presumably in the form of benzole. In contrast to a fuel of equal O.N. free of aromatic compounds, the pre-reactions are very slight. Pre-reactions were not found with pure benzole or alcohol; with benzole, a compression increase produced sudden self-ignition, without any noticeable previous temperature increase; this occurred for $\varepsilon = 11$ at 140°C mixture admission temperature and 1.800 rpm. Alcohol which required an increased heating of the admitted mixture, owing to the high evaporation heat, gave similar results.

The above proves that a relatively unequivocal relationship between O.N. and the intensity of pre-reactions is possibly only in chemically similar fuels. The study of the pre-reactions brings to light many more individual properties of the fuel than can be expressed by a single figure, such as Octane number.

All the recorded pre-reaction curves would present however a common property if the peak temperatures of adiabatic compression were determined for the various points by means of the graph in Fig. 5. These temperatures are marked on various points of the curves. For the same compression ratio this peak temperature drops as the fuel ratio grows, because the adiabatic exponent also diminishes. Surprisingly enough the curve peaks for the same speed are approximately at the maximum temperature of adiabatic compression, 390° to 400°C, for all the fuels used and at all compression ratios. Also the temperatures, at which pre-reactions set in starting from rich mixtures, vary but little between 360° and 390°. The result is that the temperature and, as we shall see later, the induction time are the main influences on the pre-reactions.

d. Influence of test conditions on pre-reactions.

For a better comparability all tests were made under the same test conditions tabulated in page 45. The effect of varying these conditions should now be investigated. With fuel No. 5 (O.N. 90.6) the speed was altered at compression ratio $\varepsilon = 6.5$, mixture and coolant temperature remaining at 140°C. Fig. 14 shows the result; the pre-reactions fall off steeply as the speed is increased and the calculated final temperatures of adiabatic compression show, in Fig. 14, that the reactions set in at higher temperatures; the actual final temperatures of compression at higher speeds are rather higher owing to the smaller heat transfer to the cylinder walls. This points to the importance of the induction time and temperature on the extent of pre-reactions. Also the tendency to knocking of engines falls off as the speed rises; this however is often aggravated in practice by the influence of the higher temperature of valves and combustion chamber walls consequent to higher speed and output.

Fig. 15 shows the influence of the variation of mixture inlet temperature on fuel No. 5 for $\varepsilon = 6.5$, speed 1,800 rpm. and coolant mean temperature 140°C. An increase of the mixture inlet temperature has a similar effect as a compression rise. In the tests of Fig. 16 the coolant mean temperature t_k was varied with constant mixture inlet temperature; in Fig. 17 various values of speed, mixture inlet temperature and coolant mean temperature are investigated for fuel No. 5 at constant compression ratio $\varepsilon = 6.5$. An increase of the coolant mean temperature intensifies the pre-reactions; this effect is however considerably smaller than the variation of the mixture inlet temperature, as it acts on the mixture only through heat transfer from the cylinder walls.

Tests on pressure variation in the inlet pipe are reproduced in Fig. 18. The reported strong pressure effect, especially with negative pressure, is probably an indirect one due to secondary causes.

Fuel No. 5 was also subjected to a test with oxygen-rich air. The dash-dot curve in Fig. 11 was obtained with a 34% oxygen volumetric content in the admitted air before the carburettor at $\varepsilon = 6.5$; the fuel ratio is referred to the augmented oxygen quantity. The pre-reactions grow in the same proportion as the oxygen content. The peak of the curve does not shift noticeably. Powerful ignitions occurred when the oxygen content was further increased to 42% by volume.

e. Indicator diagrams, chemical tests and various observations.

The pressure variation in the cylinder was recorded with a quartz indicator. Fig. 19 shows these graphs with several cycles recorded on the same film, mounted on a drum not quite synchronized with the test engine. Fig. 19a was taken with lead-free aviation fuel (No. 2 in the Table) of O.N. 72 at 1.800 rpm., $\varepsilon = 6.5$, mixture admission temperature 140°C and a rich mixture of $\beta = 1.58$, corresponding to a 75°C temperature increase (cf. Fig.10). The unsymmetrical humps near the TDC of the curves show the pre-reactions. It is remarkable that they do not occur at each cycle but almost exactly at every second cycle. The curves without the hump are not quite symmetric however but are rather fuller on the expansion side, i.e. the pre-reactions are well on the way but not quite developed. If a complete pre-reaction appears only at every second cycle and the average temperature increase Δ t is 75°C, the temperature increase during the effective stroke must be still considerably higher, even if it does not reach the double value. Unfortunately the accuracy of the diagrams and particularly of the position of the dead centre mark was insufficient to determine more accurately the proportion of working cycles to the pre-reactions.

The following conclusions can be drawn from the regular alternation of strongly marked and nearly negligible pre-reactions in Fig. 19a:

The end products of a market pre-reaction, part of which gets mixed with the residual gases of the new charge, do not favour the appearance of pre-reactions. It is however different in the case of a pre-reaction just started and prematurely interrupted. Here the end products of the first phase of the pre-reaction, added to the residual gases of the new charge, apparently have a strong positive action on the pre-reactions of the next cycle. These considerations help to explain the more or less regular alternation of strong and weak reactions, found in other fuels too. It would be particularly interesting to undertake chemical analyses of pre-reaction products in various development stages.

Fig. 19b shows the pressure curve under the same conditions as in Fig. 19a with the same fuel but after the addition of 1.3 cu.cm. ethyl fluid per litre (No.13 in Table 3). As shown by the dash-dot curves in Fig. 10, the temperature increase Δ t is considerably reduced by the lead addition. Still stronger is the effect on the pressure curve: the hump behind the TDC has disappeared and the curve looks almost symmetrical, even if it shows in the average higher pressures during expansion than during compression. The Pb addition does not eliminate pre-reactions but it only abates them and lessens the steepness of their rise. The measured temperature increase up to 75°C shows that up to 4% of the combustion heat can be liberated during the pre-reactions. A considerable proportion of the fuel molecules, estimated at 15 - 20%, participates in the pre-reactions. In agreement with previous observations, a sharp and pungent smell of exhaust gases was observed during all tests. The exhaust pipe was covered by a brown oily smear.

At our request G. Damköhler and W. Eggersglüss made a chemical analysis of the reaction products on I.G. standard fuel (No.10 in Table 3), more thoroughly dealt with elsewhere (1). The engine ran at compression ratio 5, fuel ratio 0.9, coolant mean temperature 140°C, mixture admission temperature 140°C, speed 1,800 rpm.; the temperature increaseddue to pre-reactions (cf. Fig. 12, curve a). The exhaust gases were condensed in freezing traps in series, cooled by ice, in dry ice methanol and liquid air. If the molecular weight of the fuel is assumed to be that of heptane, i.e. 100, the analysis gave the following reaction products in molecules per molecule of fuel: aldehydes 0.141 (of which 0.084 was formaldehyde and

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(1) Zs. f. phys. Chem. Abt. B Vol 51 (1942) p. 157.

0.047 acetaldehyde), alcohols < 0.05, acids 0.024, carbonic acid 0.0045, water 1.07. As determined from another source, the aldehydes constitute the main component.

A bluish flash in the cylinder was noticed only once with a special fuel, used as an ignition accelerator for diesel fuels and having an O.N. < 0. At $\varepsilon = 5$ and a mixture inlet temperature of 110°C this fuel gave very strong pre-reactions and was characterized by a particularly sharp exhaust smell. It is not impossible that weak flashes appeared with other fuels too, but the oil on the windows prevented their observation. In some tests the pre-reaction energy sufficed to keep the engine running without ignition or drive, which implied no combustion noise.

f. Directives for further work.

The purpose of the described tests was to refine the qualitative methods of investigating the pre-reactions by the mixture temperature increase in an engine without ignition, in order to achieve unequivocally reproducible and quantitatively evaluable results. Once we reached that far, we wanted to survey the behaviour of various fuels and the effect produced by a variation of the working conditions of the engine. Not only the compression ratio but also the mixture strength were widely varied. The results considerably extend our empirical data and show new relationships between knock behaviour and pre-reactions. The tests must be extended to other fuels in connection with a more accurate chemical analysis of the reaction products. The necessary improvement of the methods of chemical analysis has already been started. In the present 1 litre engine the complete test on a fuel requires about 150 litres, and moreover the size of the engine necessitates quite long test periods; in future, tests will therefore be carried out on a specially built smaller engine which is so designed that it permits sudden compression and expansion, the result being that the mixture can be kept for a certain time at a highly constant and well defined compression temperature.

C. Summary.

By measuring the temperature increase of the mixture during its passage through the engine, the pre-reactions of several fuels were investigated on an external drive four-stroke engine without ignition, aspirating fuel-air mixture in the conventional way. The temperature increase curves plotted as a function of the fuel ratio for various compression ratios show distinctive features of the various fuels. With fuels of the same family the temperature increase due to pre-reactions mounts as the O.N. diminishes. An addition of TEL generally reduces the temperature increase due to pre-reactions roughly in proportion to the O.N. rise. The tests were completed by pressure measurements with a quartz-indicator and by chemical analyses of the reaction products.

Fig. 1 - Multiple indicator diagram with pre-reaction for three fuels of different octane number. Pelétier.

Fig. 2 - Cylinder head section of test engine.

Fig. 3 - Test lay-out.

Fig. 4 - Ribbed thermometer to measure the mixture temperature before and after the cylinder.

Fig. 5 - Final temperature t_v of the adiabatic compression in test engine as a function of fuel ratio β and compression ratio ε for an initial mixture temperature of 140°C.

Fig. 6 - Temperature increase Δ t of the fuel-air mixture due to pre-reactions, for Fuel No.3 (O.Nr. 87) as a function of fuel ratio β and compression ratio ε, at 1.800 rpm., mixture inlet temperature $t_g = 140$°C coolant temperature $t_k = 140$°C.

Fig. 7 - has the same title as Fig. 6.

Fig. 8 - Reduction ΔM_d of the necessary driving torque M_d of the engine due to pre-reactions in Fuel No.3 as a function of fuel ratio β and compression ratio ε. The ordinate is the weight in kg. on the lever arm 0.716 m. For curve $\varepsilon = 6.5$ a torque $M_d = 2.75$ kg. corresponds to the top part of the graph ($\Delta M_d \equiv 0$), whereas M_d is - 1.85 kg in the bottom section. Rather different initial values apply to the computation of torque M_d for the other compression ratios, owing to the variations of the friction conditions in the engine.

Fig. 9 to 13 - Temperature increase Δ t due to pre-reactions as a function of fuel ratio β at 1.800 rpm., mixture admission temperature $t_g = 140$°C and coolant mean temperature $t_k = 140$°C for fuel of different octane number. The temperatures marked on the curves are the calculated temperature peaks of adiabatic compression for the points indicated.

Fig. 9 - Fuel No. 1 (O.N. 56.4).

Fig. 10 - Continuous curves, Fuel No. 2 (O.N. 72). Dash-dot curves Fuel No. 13 (O.N. 87.8) obtained by adding 1.3 cu.cm. ethyl fluid per litre to No. 2.

Fig. 11 - Fuel No. 5 (O.N. 90.6). The dash-dot curve refers to operation with oxygen-rich air.

Fig. 12 - Fuel No.10 (O.N. 44.6) Curve a
Fuel No.11 (O.N. 73.1) Curve b
Fuel No.12 (O.N. 73.2) Curve c
The compression ratio is 5 for all curves.

Fig. 13 - Fuel No.7 (O.N. 100) pure isooctane. The flat curve for $\varepsilon = 9$ refer to Fuel No. 6 (O.N. 100) with 40% aromatic compounds content.

Fig. 14 - Effect of speed variations on the temperature increase Δ t due to pre-reactions of fuel No. 5 (O.N. 90.6) at compression ratio $\varepsilon = 6.5$, mixture inlet and coolant mean temperature = 140°C.

Fig. 15 - Influence of mixture inlet temperature t_g on temperature increase Δ t due to pre-reactions for fuel No.5 (O.N. 90.6), at $\varepsilon = 6.5$, $t_g = 140$°C, $t_k = 140$°C.

Fig. 16 - Influence of coolant mean temperature t_k on temperature increase Δ t due to pre-reactions for fuel No.5 (N.O. 90.6), at $\varepsilon = 6.5$, n = 1.800 rpm., $t_g = 140$°C.

Fig. 17 - Influence of the variation of various test conditions on temperature increase Δ t due to pre-reactions for fuel No.5 (O.N. 90.6), $\varepsilon = 6.5$.

Fig. 18 - Influence of pressure variation in the admission duct, indicated in m. water column of positive pressure (+) or negative pressure (-) compared with the atmosphere, on the temperature increase due to pre-reactions for fuel No. 2 (O.N. 72) at 1,800 rpm., $\varepsilon = 6$, $t_g = 140°C$, $t_k = 140°C$.

Fig. 19 - Pressure diagrams of pre-reactions in the engine recorded with a quartz indicator at 1.800 rpm. and $\varepsilon = 6.5$.