List of Tables and Diagrams

TABLE I.

THERMAL STABILITY OF AVIATION OILS

Call-Mark		1	2	3	4	5	6	7	8	9	10	11
Entry No.		136/37	69/37	Lg.5	183/34	17/37	192/34	20a/37	56a/37	78/37	414c/36	414B/36
Original Weights												
Original	g	150.0	150.0	150.0	150.0	150.0	150.0	150.0	150.0	150.0	150.0	150.0
After heating	"	145.3	144.2	143.3	144.6	143.3	146.5	119.2	129.3	130.5	137.5	137.1
Loss	"	4.7	5.8	6.7	5.4	6.7	3.5	31.8	20.7	19.5	12.5	12.9
Vol. of gas from 150 gm.oil free of N_2 at 0°/760 mm Hg	Ltr.	0.105	0.087	0.087	0.115	0.106	0.067	0.236	0.210	0.139	0.117	0.061
Refraction	n_D 20											
Original		1.4878	1.4900	1.4969	1.4987	1.4885	1.5018	1.4782	1.4783	1.4808	1.4736	1.4727
After heating		1.4841	1.4874	1.4949	1.4962	1.4866	1.4992	1.4777	1.4763	1.4783	1.4710	1.4712
Sp. gr. at 20°C.	kg/L											
Original		0.882	0.887	0.893	0.902	0.883	0.906	0.861	0.861	0.863	0.854	0.851
After heating	"	0.875	0.880	0.887	0.896	0.877	0.902	0.859	0.855	0.856	0.847	0.848
Decrease	"	0.007	0.007	0.006	0.006	0.006	0.004	0.002	0.006	0.007	0.007	0.003
Viscosity at 50°C.	°E											
Original		23.2	17.0	28.1	22.0	22.4	21.9	21.5	21.6	21.4	20.6	21.1
After heating	"	7.21	6.63	9.1	7.66	8.5	11.9	4.8	4.9	4.3	5.98	8.4
Decrease	%	68.9	61.0	67.9	65.0	62.0	45.5	77.5	77.7	80.0	71.0	60.2
Acid Number	mgKOH/g											
Original	"	0.0	0.0	0.0	0.0	0.04	0.03	0.0	0.05	0.0	0.23	0.0
After heating	"	0.0	0.0	0.0	0.0	1.30	0.0	0.03	0.03	0.0	0.0	0.0
Change	"	plus or minus 0	plus or minus 0	plus or minus 0	plus or minus 0	plus 1.26	minus 0.03	plus 0.03	minus 0.02	plus or minus 0	minus 0.23	plus or minus 0
Sap. No.	mgKOH/g											
Original	"	0.06	0.25	0.17	4.84	3.81	0.17	0.0	0.22	0.24	0.61	0.16
After heating	"	0.11	0.09	0.32	2.24	2.24	0.22	0.16	0.17	0.14	0.32	0.14
Change	"	plus 0.05	minus 0.16	plus 0.15	minus 2.60	minus 1.26	plus 0.05	plus 0.16	minus 0.05	minus 0.10	minus 0.29	minus 0.02
Conradson Coking	%											
Original	"	0.25	0.20	1.23	0.77	0.43	0.73	0.03	0.05	0.13	0.13	0.13
After heating	"	0.33	0.26	1.47	0.81	0.45	0.74	0.14	0.13	0.30	0.14	0.14
Change	"	plus 0.08	plus 0.06	plus 0.24	plus 0.05	plus 0.02	plus 0.01	plus 0.11	plus 0.08	plus 0.17	plus 0.01	plus 0.01
Ramsbottom Coking												
Original		0.26	0.29	1.03	0.76	0.49	0.63	0.07	0.16	0.22	0.18	0.17
After heating		0.33	0.39	1.23	0.81	0.52	0.76	0.20	0.15	0.79	0.19	0.19
Change		plus 0.07	plus 0.10	plus 0.20	plus 0.05	plus 0.03	plus 0.10	plus 0.13	minus 0.01	plus 0.57	plus 0.01	plus 0.02
Bromine No.(McIlhiney)	g/100 g											
Original	"	1.3	1.1	5.2	10.4	5.1	1.1	0.0	1.8	2.2	3.7	4.6
After heating	"	8.4	8.2	10.5	8.9	10.9	6.3	9.4	9.4	11.2	8.2	10.6
Change	"	plus 7.1	plus 7.1	plus 5.3	minus 1.5	plus 5.8	plus 5.2	plus 9.4	plus 7.6	plus 9.0	plus 4.5	plus 6.0
Molecular Wt. Determination												
Original		691	635	665	567	697	569	734	719	758	730	668
After heating		499	465	450	451	553	506	468	478	460	503	545
Change		minus 192	minus 170	minus 215	minus 116	minus 144	minus 63	minus 266	minus 241	minus 298	minus 227	minus 123

TABLE 2.

THERMAL STABILITY OF AVIATION OILS. ANALYSIS OF COLLECTED GASES

Oil No.	% Converted to air-free condition				
	CO_2	CmHn	CO	H_2	CH_4-C_2H_6
1	1.0	0	3.7	0.4	3.5
2	1.2	0	4.3	0.2	3.3
3	1.2	0	4.4	0.2	4.2
4	1.6	0	7.5	0.5	3.4
5	1.5	0	8.2	0.2	3.8
6	1.2	0	4.5	0.2	1.2
8	1.8	0	4.7	0	6.9
9	1.7	0	3.8	0	5.6
10	1.1	0	3.9	0	3.9
11	1.0	0	5.2	0.1	2.6

TABLE 3

THERMAL STABILITY OF AVIATION OILS.
COMPARISON OF TWO THERMALLY-TREATED OILS (6 hours, 400°C.)

		Oil No. 6 Napthenic	Oil No. 7 Synthetic
Losses due to heating	%	2.3	21.2
Volume of gas (N_2-free)	Ltr.	0.067	0.236
Decrease of viscosity at 50°C.	%	45.5	77.5
Decrease of Molecular weight		63	266
Increase of Bromine Number	g/100g	5.2	9.4
Running time in Siemens Test engine	h	5.5	12 (Eng. No. 1/36)
Temperature of plug ring	380°C.		
Ageing properties D.V.I. method 4 hrs. 275°C.			
Volatility	%	80.0	80.0
Asphalt	%	15.2	4.2

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Physico-chemical investigations into the combustion process in the engine.

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Summary.

After discussing the most important of the previous physico-chemical investigations into the combustion process of organic compounds with reference to engine behaviour, our own research in this field, as well as the conclusions drawn, are briefly outlined. On the basis of this material, we share the opinion that knock in the engine is caused mainly by spontaneous oxidation reactions in the unburnt part of the mixture in the cylinder. The question as to how far a true detonation can occur here is left open. By applying the conceptions evolved for chain reactions regarding the chemical reactions that take place in the unburnt part of the compressed charge, it is possible to arrive at a clear arrangement of the material on knock with different fuels, behaviour in mixtures and the effects of anti-knock agents. It is already possible to reach approximate quantitative ratios. The extent to which conclusions may be drawn regarding other possibilities of development is discussed.

Index.

I. Introduction and general summary.

1. Object of the investigations.

The attainable degree of efficiency of the Otto-engine is limited, among other things, by the knock of the fuel which occurs with rising compression. As shown by photographs of flames and indicator diagrams, the knock must consist of a highly accelerated combustion of the last part of the charge, combined with sudden rise in pressure and possibly by shock waves and gas oscillations. (cf. also p. 7). It is a well known fact that the tendency to knock is very closely connected with the chemical composition of the fuels, and that knocking may be influenced favourably by very slight admixtures of certain substances (lead tetraethyl, iron carbonyl etc.) or unfavourably (peroxides, ozone, nitrites etc.). The object of research must be to examine with accuracy the reactions taking place in the adiabatically compressed gas mixture and in the area of combustion in the engine cylinder, in order to provide some idea of the behaviour of a fuel in the engine and the possibilities of modifying it. Such a complete insight into the process taking place in an I.C. engine must undoubtedly be a long term affair, and even so, a reliable comprehension of the processes should not be expected, as is possible in an electric motor. Nevertheless, in order to make use of the possibilities available for increasing the efficiency of I.C. engines, a more accurate knowledge of the combustion process is a necessary presupposition.

Experiments with the general physico-chemical fundamentals of these processes should only be of significance in so far as they influence investigations on the engine itself, and enable one to eliminate unnecessary or unprofitable experiments. In what direction experiments on the oxidation machinery itself should be conducted, and what are the immediate objects, are matters that will be explained in the following review.

2. Regarding the nature of knock.

Photographs of the combustion process, both in a bomb and in the engine itself (with visual window in the cylinder head, recorded on a rotating drum, or by a series of instantaneous exposures), furnish qualitatively the following diagram (1), Fig. 1. The flame moves, sometimes with a certain ignition delay, from the point of ignition at a speed which is certainly not constant, but is steady and varies comparatively little, through the gas chamber. The pressure increase runs on corresponding lines; it is not indeed proportional with time, but steady, without sudden surges and rises (Fig. 1b). The flame speeds observed are a few m/s in bombs, in engine experiments up to about 30 m/s, the increase over the bombs being due to gas turbulence in the combustion chamber.

If a piston which closes a cylindrical gas chamber is accelerated, there will be set up in the gas a pressure wave (2), which moves at least with the velocity of sound: with the velocity of sound when the amplitude is very small, over the speed of sound when the amplitude is finite. By means of a flame accelerated in the primary stage (cf. Fig. 1), the unburnt gas is compressed in a similar way as by a moving piston: the possibility of shock waves must therefore be reckoned with. Such shock waves in the unburnt gas may be rendered visible by direct means with shadow and Schlieren photographs. In Fig. 2 we reproduce a photograph by Payman and Titman (3), which shows quite clearly a shock wave of this type in the unburnt gas. On the left may be seen an ordinary

flame photograph with irregular speed of flame; from a bend in the front of the flame, a multiply reflected retrogade shock-wave appears to run. As shown by the corresponding Schlieren photographs on the right, the bend in the front of the flame is produced by a shock-wave, which was produced in front of the flame front and was reflected at the end of the tube. The propagation of the shock-wave obeys rather complicated laws, as gases at different temperatures with superimposed currents are present. In the figure on the right the conditions are shown diagrammatically; it is worthy of note that the wave starting from the ignition spark is so weak that it does not appear on the Schlieren picture and does not make itself noticeable by any action on the flame front. In burnt gases the shock wave often travels up and down, a fact which may be verified quite simply by the repeated lighting of the gases. In Fig. 3 we give some of our own photographs, which do not indeed show the shock-wave in the unburnt portion, as Schlieren photographs are not available; the existence of the shock-waves is however revealed by their effect on the flame front, while they are at once visible in burnt gases. In all cases, the flame speeds, some hundred m/s, are considerably higher than under engine conditions, even though our experiments were carried out with hydrocarbons, not indeed in mixtures containing air, but with nitrogen and oxygen mixtures that are richer in oxygen. It should nevertheless be emphasised that the course of combustion in Fig. 2 and 3 is different from the case of knocking combustion. With a shock-wave as in Fig. 3 there is obtained an indicator diagram as Fig. 4, and the oscillations will be set up before the maximum pressure is attained, since of course the pressure waves travel ahead of the flame. Diagrams such as Fig. 4, which however have small oscillation amplitudes, can be obtained with non-knocking combustion. It appears that gas oscillations can be produced in other ways than by shock-waves, cf. the observations made by Lewis and v. Elbe (4). We cannot here go into the authors' proposed interpretation of their experiments, but we should point out that we do not consider the connection with the knocking process assumed by Lewis and v. Elbe to be probable.

A theoretical computation of the speed of flame propagation, a knowledge of which would admit of inferences as to the production of pressure waves, is so far not possible. It is indeed known that there is a value designated as "normal combustion speed", which gives the rate at which a combustion surface normally moves towards the quiescent unused gas. The flame speeds observed are always higher than in the first case owing to the additional action of currents. The observed figures for normal combustion speeds are between 10 to 20 cm/s and 10 m/s; flame speeds are known up to some hundred m/s. Regarding the mechanics of flame propagation, it is a known fact that the combustion is carried from the combustion surface into the unused gas by heat conduction and by the diffusion of the free atoms and radicals which are formed in most flames; the normal speed of combustion therefore depends on the heat conductivity, diffusion velocities and chemical reaction velocities.

There is a completely different set of machinery by which an explosion can be propagated. If the intensity of the above-mentioned shock waves is great enough for the chemical reaction to proceed sufficiently fast in the front of the wave, a coupling of shock-wave and reaction will take place. If this process becomes stationary, we speak of

detonation. The detonation velocities are quite independent of heat conductivity and the velocities of diffusion and chemical reaction (it being assumed that the reaction speed is sufficiently high, otherwise the reaction cannot keep pace with the shock-wave and no detonation will occur; this is the case with many mixtures which are actually explosive) and may be computed from the general basic equations for hydrodynamics and thermodynamics, whereby they agree with the experiment; the order of magnitude for speeds of detonation may be given as about 2 km/s. According to information so far available, most of the organic compounds used as fuels, when mixed with air are incapable of propagating a detonation wave; however, experimental conditions deviate considerably from conditions in the engine (lower pressure and lower initial temperature).

Since in engine knock, highly accelerated combustion and shock waves may be observed, it was tempting to regard knock as merely a detonation of the residual charge. It would, however, be preferable not to use the term detonation for the knocking process, as long as it remains unproved whether it is really a detonation in the usual physical sense of the term.

If in a cylindrical tube there is a combustion outlet, where combustion passes into detonation, indication of pressure at the end of the tube remote from ignition would show a curve in accordance with Fig. 5; pressure maximum and inception of oscillations co-incide, as the detonation wave is the most rapid process occurring in the mixture. When pressure is indicated at other points, this is no longer the case; before the maximum pressure has been reached, reflected waves may already have been recorded. The facts against the presence of true detonation in engine knock are as follows:

Determinations of the speed of knocking combustion produced figures which, although quite high, were considerably below the speed of detonation, about 300 to 500 m/s (5).

The observation that under normal conditions the mixtures used in the engine do not detonate.

Instantaneous photographs of engine combustion by Rassweiler and Withrow (6), which do not reveal a progressive detonation wave in knock, but self-ignition occurring at varying points in the combustion chamber.

The fact that stationary detonation waves are known only in cylindrical tubes, and in any case remain in narrowing vessels, while in expanding spaces they are extinguished owing to the attenuation of the divergent waves. In an engine, therefore, the preliminary geometrical conditions for detonation are not in all cases present. On the other hand, the well known dependence of knock on the shape of the combustion chamber makes it tempting to assume the possibility of the combined action of shock-waves in connection with knock.

Just like flame photographs in the engine, laboratory experiments, which produced in adiabatically compressed gas mixtures a combustion similar to knock, did not appear to indicate any detonation, although they did indicate shock-waves travelling up and down in the burnt gas (1). Our own experiments certainly produced no detonation, but rather augmented flame speeds compared with the normal speed of combustion.

Only experiments by Sokolik and Voinov (1) with flame photographs in the engine, speak in favour of detonation. Nevertheless, most of these photographs only show clearly the shock-wave travelling back through the burnt gases, whereas a primary detonation wave can only be seen in a few photographs and even there only over a very short distance. The photographs of Sokolik and Voinov, one of which is reproduced in Fig. 6, seem to us at the moment to contradict those of Rassweiler and Withrow, while in regard to other writers, it may be said that the accuracy of their measurements is inferior to that of Sokolik and Voinov. The question as to the nature of knocking combustion must therefore temporarily be left open; all the same, it is evident that the flame speed under such conditions is at least ten times greater than under normal conditions.

However important it may be to obtain an answer to the question as to the nature of knock, for the practice, and even for the theory, of the combustion process, an even more important question is: when and how is knocking combustion caused, and in what way it can be prevented. We shall therefore keep this question well in view in the course of our investigations. From this standpoint, the following may be stated: The fuel-air mixture drawn into the engine cylinder is brought by adiabatic compression to a temperature at which very often the oxidation reactions (without spark ignition) which occur automatically in the mixture can no longer be overlooked, and perhaps become so rapid that after a shorter or longer period of induction self-ignition takes place. Instead of this, it may also be said that the mixture is heated to the vicinity of or even beyond the "self-ignition temperature", it being well known that at the self-ignition temperature, ignition does not take place instantaneously, but only after a finite period of induction, and that the self-ignition temperature is not a characteristic constant for the type of fuel in question, depending as it does, not only on the composition of the mixture and the pressure, but on further factors such as the dimensions of the vessel, the material and temperature of the walls, the presence of certain impurities etc. The processes taking place in the compressed mixture in the engine may be shown in the following rather simplified manner: Fig. 7. For the sake of simplicity, it is assumed that the piston is halted at the end of the compression stroke; in the diagram, the abscissa is the time and the ordinate the reaction. With the advancing flame through spark ignition alone, the reaction would take place as shown in Fig. 7b (continuous line); even without spark ignition, with a sufficiently high compression the spontaneous reaction would finally lead to complete transformation, Fig.7. This spontaneous reaction in the unburnt mixture will take place in all cases, even next to the advancing flame, but of course it is not unaffected by the latter, and vice versa. Various limiting cases may arise, Fig. 7c; spontaneous reaction leads rather to the spontaneous ignition of the mixture, premature ignition; or else, Fig. 7d, combustion takes place normally, but owing to the advancing flame, the transformation is caught up by the reaction in the unburnt part which leads to spontaneous ignition. A reaction as in Fig. 7d presents the typical aspect of knock combustion. (From instantaneous photographs of engines made by Rassweiler and Withrow (6), it will be seen that this description corresponds to actual conditions). Before we discuss this at greater length, we should like to point out that the diagram in Fig. 7d points to two ways of eliminating knock:

a) Acceleration of the normal combustion, so that the flame

reaches the end before the speed of the reaction of the unburnt portion has exceeded a critical figure;

b) Keeping the reaction to the unburnt mixture, e.g. by suitable additives.

These are precisely the methods that have been adopted in practice: acceleration of the flame by turbulence in the gases, restriction of the reaction in the unburnt portion by anti-knock agents such as lead tetra-ethyl, iron carbonyl etc.

If the aspect of Fig. 7d (which is of course to be viewed as a very much idealised approximation) were essentially correct, parallels might be expected between knock behaviour, spontaneous ignition properties and the influencing of the reactions leading to spontaneous ignition. This is to a great extent the case.

"Spontaneous ignition temperatures" and maximum rates of the pressure rise (in bomb explosions), i.e. figures closely connected with the speed of the flame, have been brought by Brown and Watkins (7) into relationship with knock resistance, expressed by Ricardo's highest useful compression ratio. The latter is higher, the higher the spontaneous ignition temperature and the lower the maximum speed of the pressure rise. The connection with the spontaneous ignition temperature is that which might have been expected, but really quantitative relations with it cannot be anticipated owing to the lack of definition of the spontaneous ignition temperature. The effect of the pressure rise with Brown and Watkins is slight; in the group n-heptane, n-octane, benzol and toluol, the deviations from the mean value of this factor is only about ± 5%, and in the most extreme case, ethanol is eliminated. It is, however, doubtful whether the speed of the pressure rise, in the sense adduced by Brown and Watkins, actually plays a part; this, owing to the very slight influence of this factor, is not of decisive importance for Brown and Watkins' conclusions. It is not quite certain whether a rapid pressure rise is unfavourable for knock. If a true detonation were involved, this might be the case, but the observation made, that turbulence restrains knock, belies this. Furthermore, the bomb experiments, from which Brown and Watkins obtained the speed of the pressure rise, were carried out, not with fuel/air, but with hydrocarbon/oxygen/nitrogen mixtures which were richer in oxygen. It is therefore not certain whether the figures obtained are of any significance for the very much less rapid combustion in air.

Fig. 7 shows that the course followed by the reactions leading to spontaneous ignition, especially those relating to dependence on pressure, temperature and composition of the mixture, must be known, and that the ignition temperatures obtained under conditions deviating from engine conditions are not in themselves adequate. (This does not of course preclude the fact that in comparing various fuels, careful assessments etc. carried out with ignition testers of some kind, will provide results that are of some use.) Here we have the object of research into the physico-chemical basis of engine consumption. The oxidation machinery of the fuels in question must be studied from slow reactions to extreme conditions of knock combustion.

3. General data on the oxidation mechanics of hydrocarbons.

The combustion of hydrocarbons results in carbon

dioxide and water, with excess air, and in carbon monoxide, soot etc. with excess fuel. The assumption that when hydrocarbons are burnt, appreciable quantities of hydrogen are formed, or that when ready for combustion they break down, by the action of oxygen, into carbon monoxide and hydrogen, finds little support in experiments. (From the known speed of decomposition of hydrocarbons (cf. p.23), it will be found that with the times and temperatures occurring in engines, such a decomposition does not take place to any appreciable extent). It has been found that many hydrocarbons react very much more readily with oxygen than do carbon monoxide and hydrogen, so that it may be assumed that the combustion machinery does not, as a rule, produce these substances as intermediate products. This does not exclude the possibility that combustion is a chain reaction, which is brought about by an extremely slight decomposition of the fuel. The theories about so-called "chain reactions" have proved extremely fruitful here as elsewhere in the kinetics of reactions and have made it possible to establish certain general laws, whereby order may be brought to experimental fact and predictions may to some extent be made. (cf. p. 38 et seqq).

If hydrocarbons of the paraffin series, mixed with air, are heated for a certain length of time - in the region of 1 minute - to various temperatures, there will be observed (except in the case of the first members of the paraffin series) from about 200° onwards a noticeable reaction, which rises with temperature and may result in ignition in about the region of 500°. More accurate investigation (8) results in the observation that has long been known in individual cases, viz that:

Even at low temperatures the reaction is accompanied by a luminescence and that in the vicinity of 250-300° "cold flames" occur. These are flames that are associated with a pale glow and advance slowly (about 10-20 cm/s) through the reaction vessel and although causing a certain amount of heat do not result in the complete ignition of the mixture. The reaction products are carbon monoxide, aldehydes, possibly hydrogen, water and a slight quantity of carbon dioxide; furthermore, slight traces of peroxide may be detected. Nevertheless, a true explosion may develop from the "cold flame" (9).

The temperature at which the cold flame is brought about is reduced with increasing length of chain of the paraffin molecule, whereas if the chain is branched (as in isooctane), it is augmented. It is a well known fact that n-paraffins are more prone to knock the longer their carbon atom chain, whereas branched paraffins are free from knock (isooctane); there is thus a complete parallel between the occurrence of cold flames and knock phenomena. It is therefore scarcely to be doubted that the reaction resulting in the cold flame is the same as that which causes knock in the engine. In support of this, it may also be stated that a spectroscopic examination of the unburnt mixture in the engine just before knocking takes place pointed to the presence of formaldehyde (10), which almost certainly represents one of the main reaction products in cold flames and is responsible for the luminosity of cold flames (11). Furthermore, both cold flames and knock may be suppressed by the addition of lead tetraethyl and other anti-knock substances. Even at atmospheric pressure, the reaction in the range of cold flames may occasionally develop into an ordinary explosion

(Curiously enough, no longer at a temperature about 50° higher ! This peculiarity may be explained by the special nature of the chain machinery of the reaction, which cannot be discussed in detail here), but when the pressure is suitably increased, it is regularly the case (9). For medium paraffins (propane, butane and olefine), investigations are available by Townend and his collaborators (12) from the Dones Institute, which show that with rising pressure, the ignition which originally took place at higher temperatures, comes within the range of the cold flames, and that the addition of lead tetraethyl can displace it again to the higher temperature range.

Fig. 8 shows a typical reaction curve as a function of temperature for n-heptane, in accordance with Edgar and collaborators (13), it has been investigated in different quarters (including ourselves). In the diagram, the reaction, expressed as the oxygen consumption or carbon monoxide formed (at low temperatures there is produced, even with excess of air, very much more monoxide than dioxide) is plotted at the top, while the temperature forms the abscissa. A steep rise in speed occurs in the region of 250°C, marked in the diagram as A; this is the region in which cold flames are to be found. Above 300° the speed drops again in a certain temperature range. In the range of maximum speed in Fig. 8, increase in pressure would bring about a true explosion. Direct experiments of this type are not available for n-heptane, but we may refer to experiments by Neuman and Aivazov (14) with pentane-oxygen mixtures, which are reproduced in Fig. 9. As these are mixtures free from oxygen, all the pressures are naturally relatively low, and it will be noted that in the vicinity of 340° a relatively slight increase in pressure would raise the speed of the reaction very considerably. As regards mixtures with air, reference should be made to the investigations by Townend and his collaborators, which have already been mentioned.

We shall not discuss in detail here the many articles on the slow oxidation of hydrocarbons and the correlation of the data obtained with anti-knock data; we shall revert to our own experiments, but refer here principally to general demonstrations (15), (16) and furnish only a few results by Estradère (15), who has investigated the speed of oxidation in a number of hydrocarbons, mixed with oxygen. She calls "transition temperatures" those of the rapid rise in speed, corresponding approximately to A in Fig. 8. (in her experimental conditions there is no maximum speed in mixtures with oxygen), and those temperatures are tabulated in the following Table I; their sequence corresponds roughly to the rising resistance to knock, which we give, after Lovell, Campbell and Boyd (17) in terms of critical compression ratios. On the whole, to rising reaction temperature there corresponds rising resistance to knock, but in individual cases there are a number of divergences, and it is certainly not permissible to characterise hydrocarbons of the most varied groups merely by a factor such as the transition temperature. To take an example, only the n-paraffins were seen to give strict parallelism between the transition temperatures and the resistance to knock. It must also be remembered that a mixture with oxygen does not behave in exactly the same way as a mixture with air.

Table I. Temperatures of the transition to violent reaction for various hydrocarbons mixed with oxygen, after Estradère, as well as critical compression ratios for the same hydrocarbons after Lovell, Campbell and Boyd.

Hydrocarbon	Transition temp. °C	Crit. compression ratio
Heptane	300	2.8
1-Heptene	320	3.7
Hexane	330	3.3
Cyclohexane	345	4.5
Methylcyclohexane	340	4.6
1-Heptine	355	4.9
Cyclohexadiene	355	5.9
1-Hexene	370	4.6
Cyclohexene	410	4.8
Isooctane	500	7.7
Benzol	650	15

A collation of the results of slow oxidation, as in Table I, does indeed reveal parallels with knocking, but is naturally inadequate for quantitative purposes only. For this purpose, the reaction at higher pressures must be studied, and here, in the vicinity of the explosion limit, the method of Tizard and Pye is probably the most suitable. The mixture is compressed adiabatically, the compressing piston is maintained at the upper dead centre and the pressure-time curve is plotted. A reaction (which here is associated with the generation of heat) is announced by deviations from the normal cooling curve, and of course the most interesting case is the one where spontaneous ignition occurs after a period of induction. The method has not so far been used for investigating kinetics; we feel that it is very important and have prepared measurements for this purpose. It is anticipated that with a knowledge of the combustion process, important statements on knock behaviour will be possible over a wide temperature and pressure range.

Attempts have moreover been made to obtain on a laboratory scale combustion corresponding to knock, but here a whole host of difficulties arise. As it is a well known fact that knocking starts when the mixture before ignition was kept to a certain minimum temperature and compressed to a certain minimum pressure, attempts might be made to fill an experimental bomb, under the same conditions, with the mixture and then ignite it. In practice, however, this cannot be done, as under such conditions spontaneous ignition takes place while the bomb is being filled. This difficulty vanishes if, as in the engine, the mixture is brought by adiabatic compression to the experimental conditions and at once ignited. A suitable process for this purpose was first evolved by Duchêne (19) and produced serviceable results on knock behaviour. A few defects that were present were avoided in the device used by ourselves (cf. p. 34 et seqq).

As already mentioned on several occasions, it is probably essential for the inception of knock that a definite part of the residual charge should remain for a definite minimum period above a certain critical pressure and temperature limit. In addition to augmented cooling, this is why, in small cylinders, knock only begins at higher compression ratios than in large cylinders (because in small cylinders, combustion is over sooner). On the other hand, it is possible

to obtain on a laboratory scale a combustion analogous to knock, if a mixture of gas in a bomb is ignited under relatively mild pressure and temperature conditions. The bomb, however, must be such that exclusively as the result of adiabatic compression by the gases being burnt, a sufficiently large residue of gas is maintained during a sufficiently long period of induction above a critical temperature and pressure. By this means Wheeler (20) and his colleagues obtained knock combustion by using an extremely large combustion chamber, a cylinder 38 cm long and 15 cm in diameter. It might well be expected that with protracted period of burning and reduced cooling, knock is obtained under conditions that would not occur in the engine and in normal laboratory conditions. This tallies with the results obtained by Wheeler and his colleagues, who secured, even under quite mild conditions knock and towards the end increased flame speed, as well as increased pressure rise and movement of the gaseous mass (shock waves). It was also found (and this has also been mentioned by other observers) that with knock combustion, the luminosity of the flame is weak to start with, while intense luminosity (afterglow) occurs at the end, owing to sudden compression, compared with more uniform luminosity with normal consumption. The experiments of Thompson and Wheeler also showed that gas vibrations alone do not entail knock.

It is striking that, when conditions are otherwise identical, knock does not occur if the nitrogen in the mixture is replaced by helium or argon, when the flame speed and pressure rise are both doubled. The explanation of this phenomenon is probably simpler than the writers suppose. Knock is absent not although the speed of combustion is increased (as Thompson and Wheeler observe) but because it is increased, for the last part of the mixture does not remain sufficiently long above the critical pressure and temperature limits. The addition of inert gas (which raises the flame temperature and speed mainly owing to the low specific heat) thus has the same effect as eddy.

Of particular importance are, moreover, the experiments (chiefly of American research workers) into anti-knock properties as a function of the composition of the fuels, as well as the action of lead tetraethyl with various substances. For practical reasons we shall discuss these in connection with our own experiments later on.

As we had repeatedly to make use of theories about chain reactions, a few remarks will be inserted about these reactions here. The development of a reaction from quiet early stages to final conflagration was at one time, after van t'Hoff, merely thought to be what to-day is known as heat explosion (21). Owing to the exothermic, originally slow, reaction, the temperature of the mixture rises, and this involves a speed up of the reaction and therefore an increase in heat production. This again causes a rise in temperature, etc. until finally the speed of the reaction knows no limits. These theories still hold good to-day, but we now know that there is a second way by which the reaction speed, at first without increase in temperature, can increase out of all limits - the so-called explosion by chain branching (22):

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If a reaction, such as the combustion of hydrogen:

$$2\,H_2 + O_2 = 2H_2O \qquad (1)$$

does not proceed in accordance with the mechanics of the

emperical equation, but passes through a series of intermediate reactions (such as is often the case in practice), such as, (selected arbitrarily from the series of conceivable reaction diagrams):

$$H_2 = 2\,H \qquad (2)$$

$$H + O_2 = OH + O \qquad (3)$$

$$OH + H_2 = H_2O + H \qquad (4)$$

$$O + H_2 = OH + H \qquad (5)$$

$$H + H + M = H_2 + M \qquad (6)$$

$$H + OH + M = H_2O + M \qquad (7)$$

$$O + O + M = O_2 + M \qquad (8)$$

$$OH + OH = H_2O + H \qquad (9)$$

we speak of a chain reaction. (In the equations 6 to 8 the third reaction partner is in each case a further molecule M, because it is well known that such reactions cannot proceed as the collision of two bodies). The disintegration of the hydrogen molecule into atoms commences the reaction chain; the reactive H atoms continue reacting in accordance with (3). This is a reaction chain, because owing to the reactions (3) to (5) continuing the chain, no reactive particles are consumed; indeed fresh ones are formed. The newly formed particles can then in their turn react in accordance with one of the reactions (3) to (5), until they are finally consumed by one of the last reactions (6) to (9). The reactions (3) to (5) have a further peculiarity: they are each started by an active particle (H or O atom); on the right hand side, as products of the reaction, two active particles however appear (O or H atom plus OH radical) and these two continue the chain. Whether the reaction speed assumes a stationary, finite value, or increases beyond all proportion depends on whether the chain-breaking reactions (6) to (9) preponderate or otherwise over the reactions of the chain-branching (3) and (5). Should the chain-branching reactions predominate, the number of active particles will steadily increase, along with the reaction speed, and we thus have an explosion. This increase in the speed of the reaction may take place without the temperature necessarily rising. When the explosion has taken place, with exothermic reactions the temperature must eventually rise as well, but only as a result of the explosion. (If a reaction takes place as a chain reaction and explosion occurs, it must not be inferred from this circumstance alone that the explosion is brought about by chain branching). The formal ratios with chain explosions have been treated by Semenoff in particular, but it would be too formidable a task to discuss this in detail here.

It is characteristic of chain reactions that an introductory stage, e.g. reaction (2) above, is often associated with a large number of dependent reactions (3), (4), (5), as the active particles are not consumed in these reactions. Reactions are known which have a chain length of 10^6 members. If a substance is added in small quantities which suppresses such chain carriers, e.g. H atoms, it is obvious that through the elimination of a single H atom a large number of reaction stages may fail to take place which would otherwise have ensued. This means that the reaction can be considerably restricted; on the other hand, by the artificial production of chain

carriers, e.g. free atoms by photo-chemical means, the reaction is very much accelerated.

Reactions of this type are known in the oxidation .. reactions of the hydrocarbons. Lead tetraethyl (but only when decomposed in the presence of air-oxygen, i.e. when it is probably converted into oxide) restricts the reaction very considerably (Egerton (23)), while organic peroxide substances, which are capable of disintegrating into two radical fragments, accelerate the reaction to a very great extent (24). These are the same substances that suppress or provoke knock (lead tetraethyl has no effect when combustion has developed).

Chain reactions of the type described above are frequently complicated by the fact that chain starting and/or breaking reactions can take place wholly or partially on the wall. In the engine the wall - apart from the effect of overheated points, which may bring about ignition - scarcely plays so important a part; it merely has a cooling effect on the compressed and burning gases. This is due to the fact that the wall is cooler than the compressed gas mixture and that for purposes of diffusing activated particles from the wall to the interior of the gas times are required which far and away exceed the time available for combustion. If it is desired to follow more closely the processes taking place in the compressed gas, the reaction must be allowed to take place more slowly, so that it can be observed in all stages. (By taking samples at determined intervals by means of special valves, a number of important results will be obtained directly from the engine itself. Cf. Egerton (25) and his colleagues). Then the wall at once comes into play; this must always be remembered in evaluating such experiments, which cannot, however, be dispensed with.

II. Our own investigations.

1. Examination of the thermal decomposition of hydrocarbons.

In accordance with what has been said above, we extended our experiments both to the slow oxidation of hydrocarbons as well as to the rapid reaction resulting in spontaneous ignition and to combustion with and without knock. As it can be assumed with certainty that the combustion of hydrocarbons is a chain reaction, and since there is much in favour of the fact that the reaction may be initiated by a primary decomposition of the fuel, we examined this in greater detail. (In the case of slow oxidation on a laboratory scale at low temperatures, the reaction is probably started on the wall; an operation in which the wall plays an important part may, however, be rejected in the case of the engine for the reasons mentioned above). Boerlage and van Dyck (25 a) were the first to call attention to the relationship between thermal decomposition and cetene numbers or octane numbers of fuels, and give details of experiments with a number of substances, including n-heptane and i-octane. Whereas on the whole there was a smooth relationship between the tendency to decompose and the readiness to ignite in the Diesel engine (cetene number), or else the contrary relationship to anti-knock (octane number), iso-octane behaved irregularly. It decomposes about twice as readily as n-heptane, although it has greater anti-knock properties than the latter. As a matter of fact, this is not to be wondered at because, if the thermal decomposition determines the start of the reaction

chain, the primary stage is only one of the factors determining the speed. Thermal decomposition can therefore only be used as a measure of anti-knock when all the other factors remain the same, as particularly in the series of n-paraffins.

We thought it would be of some use to go over the above relationships and we give here some information concerning the results, which are of interest especially concerning the cracking process. In order to obtain some insight into the thermal decomposition of hydrocarbons, we used a flow apparatus, in which the hydrocarbon to be examined was passed through a spiral of Supremax glass tubing, heated in an electric oven. We passed the hydrocarbons with a carrier gas through the oven (hydrogen or nitrogen) and compared, by means of a calorimeter, the heat conductivity of the gases emerging from the oven with that of the gases entering it. It will be realised that under our conditions the main feature noted in the stream of nitrogen was the splitting off of the hydrogen from the hydrocarbon as shown by increase in heat conductivity, whereas in the hydrogen stream, decomposition into hydrocarbon fragments was manifested by a decrease in the heat conductivity. Furthermore, we obtained, generally by absorption in bromine, the quantity of olefins formed, which served as a check on the other measurements. For a more accurate investigation of the reaction process (which is not a simple monomolecular decomposition), we followed in a few substances the reaction in a static apparatus, by means of the pressure increase and analysis of the cracked gases. The salient results are contained in Table 2 below:

Table 2. Decomposition constants of hydrocarbons.

Compound	Partial Pressure mm Hg	$k.10^2$ at 570 °C	600	640	680	710	800
1-Octene	12.8	22	---	---	---	---	---
Diisobutylene	38.6	14.4	43	---	---	---	---
γ-Heptene	40	14.0	40	---	---	---	---
Cyclohexene	70	6.4	18.5	---	---	---	---
α-Hexene	20	6.3	18.2	---	---	---	---
β+γ -Hexene	20	5.5	15.5	---	---	---	---
Diisobutyl	23	4.5	13.6	---	---	---	---
n-Octane	10.6	3.9	11.7	---	---	---	---
Isooctane	38	3.9	11.7	---	---	---	---
n-Heptane	35.5	2.2	6.9	31.7	---	---	---
Dimethylcyclohexane	19.6	---	4.6	19.3	---	---	---
Methylcyclohexene	20	---	3.7	14.7	---	---	---
Cyclopentene	20	---	3.5	14	---	---	---
n-Hexane	120	1.0	3.1	13.4	---	---	---
Methylcyclohexane	31.8	---	---	2.4	17.4	---	---
Ethylbenzol	10	---	---	2.9	11.6	---	---
Cyclohexane	77	---	---	0.7	6.2	---	---
Ethanol	44	---	---	1.9	6.0	14.4	---
Methanol	54.7	---	---	---	1.2	3.2	---
Toluol	21	---	---	---	1.1	2.6	---
Benzol	45.4	---	---	---	0.2	0.44	4.0

Having regard to the tendency to knock, the following was ascertained as the result of our experiments: in a homologous series (n-paraffins, n-olefins), the tendency to decompose increases in a similar way to the tendency to knock. Branched hydrocarbons with the same number of carbon atoms

possess only a slightly different tendency to decompose with very different anti-knock value; the differing anti-knock value is not, therefore, brought about by a different thermal stability. Non-paraffinic (or olefinic) hydrocarbons of higher anti-knock value are distinguished by their relatively high thermal stability, but conditions were not so simple as to provide a quantitative parallel. It may nevertheless be stated that with substances of particularly high anti-knock value, vigorous thermal **oxidation** (cf. p.25 et seqq) is only set up at temperatures where the thermal decomposition is also noticeable (order of magnitude 1% per s). This statement and the decomposition constants in Table 2, which show how much of the hydrocarbon would disintegrate in one second if disintegration were to proceed at the initial **speed**, makes it possible to calculate that no appreciable separation of hydrogen takes place during the times available in the engine. It would be far below 1%).

Investigation of thermal stability initiated by ourselves, with a view to the possibility of influencing the course of combustion by additives, promise to be extremely interesting, since Pease (26) has recently found that by the addition of nitrogen, the decomposition of butane is considerably restricted. As do a number of other observations, including our own experiments, these investigations favour the assumption that the thermal decomposition can take place to a considerable extent over radical chains, and this can be made to harmonise with the findings of Patat, Sachsse, Steacie etc. (27). A discussion here would, however, occupy too much space.

2. Examination of the slow **oxidation** of hydrocarbons.

In order to obtain an insight into the **oxidation** behaviour of a large number of hydrocarbons, we made use of a flow apparatus such as was used by Edgar and his colleagues. The reaction vessel was cylindrical, about 3 cm in diameter and 20 cm long, with a volume of about 120 ccm; it was made of Jena instrument glass or Supremax glass and could be heated in an electric furnace to the temperature of the experiment. Investigations were carried out with hydrocarbons mixed with air and of different compositions, with various reaction times. We only give below experiments with stoichiometric composition (corresponding to the combustion of CO_2 plus H_2O), and at a flow speed of 10 litres/hour at room temperature (we selected this speed as a standard), corresponding to a duration in the reaction vessel of about 21 sec at 300°C (at other temperatures altered in inverse proportion to the absolute temperatures). The flow speed was measured with a differential gauge with calibrated capillaries; the gas mixture was first made by air being passed through a suitably temperature-controlled spiral washing flask filled with hydrocarbon, so that the gas analysis could be checked on the completion of combustion. Subsequently, the following arrangement was adopted, which was more convenient, whereby the process could be carried out with a few ccm of hydrocarbon (Fig.10): through the horizontal portion of a T-tube flowed fresh air; the vertical branch, which consisted in part of a capillary, was filled with fuel up to a certain level so that it dropped precisely in the desired quantity. The T itself was gently warmed (to about 50°). In order to smooth out any time fluctuations in the composition (in the dropping rhythm), we allowed the mixture to enter first of all a 3 litre mixing flask, then for checking purposes it was placed in a calorimeter device, the readings of which were calibrated for each hydrocarbon by means of gas analyses on the completion of combustion. The reaction was normally

recorded by gas analysis in the Orsat apparatus.

With paraffins, olefins and naphthenes there generally takes place a course of oxidation which is a function of the temperature, as shown qualitatively in Fig. 8. The sudden steep increase in velocity at A corresponds to the occurrence of cold flames which occur rhythmically (about every 20 sec) but which cease when the temperature is about 50° higher. Their occurrence could easily be detected by fluctuations in the rate of flow of the gases. The composition of the mixture affected the speed of the reaction to the extent that increased richness raised it considerably. Our investigations altogether cover some 40 hydrocarbons of the following groups: paraffins, olefins, saturated naphthenes, unsaturated naphthenes, aromatics, alcohols, ethers and ketones. Investigations were also carried out with mixtures of two substances, as well as with substances of the various groups with the addition of lead tetraethyl, iron carbonyl, and aniline. Of the paraffins examined, some have already been studied by Edgar and his collaborators (13), and data was already available regarding some of the other substances (Estradère's experiments are not quite comparable, as they were conducted with pure oxygen, and since the presence of nitrogen, even though it does not itself take part in the reaction, nevertheless affects it). Since, however, only experiments carried out under really identical conditions are comparable and fit to serve as a basis for far-reaching conclusions, and since contradictory results were frequently obtained a certain amount of repetition was unavoidable. On the whole, we were able to confirm Edgar's conclusions, that the oxidisability of paraffins decreases with increasing branching and the primarily oxidation corresponds to the extent of decomposition of the longest side chain of the molecule.

Besides isooctane (2.2.4-trimethyl pentane), the most stable paraffins are hexamethyl ethane and isoheptane (2.2.3-trimethyl butane). Within the paraffin group, the sequence of decreasing oxidisability approximately corresponds to that of rising octane numbers, and similarly in the olefin series. Olefins and naphthenes are much more stable during oxidation than the corresponding paraffins, but not in all cases; e.g. di-isobutylene, despite greater knock stability, is more easily oxidised than iso-octane. That a comparison between substances in different groups is only permissible up to a point as regards knock behaviour, may easily be appreciated on the basis of theories regarding chain reactions. In addition, relationships may be worked out regarding mixed octane numbers and the ability to be influenced by additives (cf. p. 41 et seqq).

A number of other results have been collated in Figures 11-15. These diagrams reveal a good many irregularities. As already stated, there is found in the paraffins, olefins and naphthenes (with the exception of the high anti-knock value substances such as isooctane) a curve such has already been met with in Fig. 8. The first steep rise in velocity (A in Fig. 8) would, at high pressures, entail spontaneous ignition and pave the way for knock; we therefore generally find that when anti-knock additives are used, this steep rise is toned down. If as the result of pressure increase, this steep rise in velocity passes into self-ignition, it will at once be apparent that the pressure increase required for this purpose need by no means be the same for all substances. Therefore the sequence of oxidisability may not be exactly that of anti-knock value; such secondary influences can least disturb the sequence in homologous series, such as the n-paraffins,

the paraffins generally, the olefins etc. Our experiments have accordingly confirmed the observation that has already been made, namely that within the various groups, the sequence of oxidisability is to a very large extent that of anti-knock value and that, broadly speaking, there are parallels outside these limits as well, while deviations occur in individual cases. A valuable contribution is afforded by the fact that for most of the hydrocarbons investigated by us, information on anti-knock value is available by American authors (28). By careful evaluation (comparison with only really analogous combinations) such experiments should enable us to predict the knock behaviour.

It is furthermore evident that the pronouncements as to anti-knock value, which have already been evaluated qualitatively from behaviour during slow oxidisation, could also be extended to quantitative statements if behaviour at higher pressures were examined for the various materials; this is therefore one of the most important aims of our measurements.

Some detailed references must also be made to the notable oxidation stability of ketones, especially those with branched carbon chains, and also mesityls. If these substances were available at reasonable prices, it would probably be possible to obtain combinations with a particularly high octane number and at the same time considerably increased combustion heat compared with alcohols.

With the object of securing a quantitative determination of the experiments, a large number of measurements were carried out on selected substances in a static apparatus, which made it possible to vary more considerably the conditions of the experiments and also the pressure, although here only up to maximum atmospheric pressure. Out of a very large number of individual measurements, only a small selection will be illustrated here, Figs. 16 to 18. Fig. 16 is explained by the caption. It is noteworthy that with increased enrichment (the alteration in composition attains a degree which no longer concerns engine combustion) the speed of reaction attains a sharp maximum in the region of 240-270°, sometimes accompanied by explosion, whereas at lower temperatures the reaction is completely quiescent. Having regard to knock, it must be stressed that merely from the variation in the reaction speed due to the composition, it is impossible to draw conclusions as to the corresponding variation in anti-knock value, for as a result of the change in the mixture, the flame speed is also altered (cf. p.30 et seqq).

The extent to which the reaction speed can depend on pressure is shown by Fig. 17, in which the reaction in stoichiometric iso-octane-air mixtures, with 1 minute's duration of the reaction at 532°, is shown as a function of the total pressure. When the pressure is doubled, there is transition from a field of scarcely noticeable reaction to explosion.

Fig. 18 shows some highly interesting results which we obtained with diethyl ketone; the reaction is plotted in terms both of pressure increase and of oxygen consumption and CO formation, for a stoichiometric ketone-air mixture and also for ketone plus nitrogen. In the latter case only a thermal decomposition is observed, and it must be emphasised that it is to be seen in approximately the same area as the oxidation. The oxidation of the ketone appears to proceed very much more simply than that of the hydrocarbons and its dependence

on temperature is shown as a simple exponential function. A knowledge of the oxidation behaviour of ketones is also important having regard to the combustion of knock-resisting, branched paraffins, for when side chains are decomposed by oxidisation, ketones should be produced as intermediate products. It was for this reason that we subjected ketones to closer research.

3. Spectroscopic investigations.

When, in chemical reactions, it is deduced from the general course of the reaction that a chain reaction is taking place, but the intermediate products formed are so unstable that it is out of the question to detect them by direct chemical means, spectroscopic investigations occasionally permit of further conclusions. In normal flames it is a well known fact from the emission spectrum (29) that CH, CC and OH radicals are present. Vaidya (30) has recently found in many flames the presence of a hithorto unknown band system, which is perhaps emitted by a radical HCO. We are able to show that the same band system is contained in the flames of atomised fluid fuels such as have been examined by Neumann and his colleagues (31) in regard to Diesel combustion.

Rassweiler and Withrow (32) in particular have conducted spectroscopic investigations with engines under normal and knocking combustion conditions; the investigations embraced both emission and absorption. In addition to differences in the emission spectrum, they detected (what for us is more important) formaldehyde in the knock area, by means of absorption photographs, just before knocking. In the case of slow oxidation, Egerton and his colleagues in particular, by means of absorption photographs, have been able to verify the occurrence of intermediate products.

*Since the slow oxidation of hydrocarbons as already mentioned, is associated in certain temperature ranges with cold flames, and above such temperatures with at least luminescent phenomena, it seemed to us that a spectroscopic examination of these luminous phenomena would be of importance. Spectral photographs of cold flames were already known at the commencement of our work (34), but the attribution of the emission bands observed to formaldehyde was only published by Ubbelohde-London (35) during our experiments. We took photographs mainly with a view to finding whether, with slow oxidation, it was possible to detect OH bands. In the case of heptane and octane we were able to confirm the luminescence spectra of Emeléus but beyond this, up to temperatures of only about 50° below the ignition limit, we were unable to find any further bands. This is of importance as it enables certain reaction operations under discussion to be ruled out, but details of all this cannot be given here.

4. Measurement of flame speeds of hydrocarbons, mixed with air at room temperature and atmospheric pressure.

Having regard to the behaviour under knocking combustion, it was important to possess first data for normal flame propagation in pure combinations. Strangely enough, only very little data for the combinations in question were available. In our experimental arrangement we followed closely the standard apparatus used by Bone, Wheeler etc. so that our results can be compared direct with those of the English school. The flame travelled in a horizontal tube of 2.5 cm internal diameter and about 60 cm length; the gas mixture

inside it was ignited at one end of the tube by removing a ground stopper, the flame being a small one. For filling purposes, the tube could be evacuated with a mercury vapour pump primed with the normal apparatus; the gas mixture was then admitted from a gasometer (the mercury acting as the sealing fluid). The flame was photographed on standard film with the rotating drum used for our other experiments, and a glow-lamp was used to record the time. Photographs made of the same mixture showed flame speeds which differed from each other at most by a few percent; among the sources of error for the final results, unreliability in measuring the flame photographs is therefore negligible, and uncertainties in the composition of the mixture are chiefly to blame, as minor fluctuations could not be excluded owing to the presence of greased cocks.

In the ensuing Fig.19 we reproduce a typical flame photograph; for evaluation purposes the first, rectilinear portion of the uniform flame propagation was always used. At the end of this portion, the uniform portion (except in mixtures with a very low flame speed) passed into an oscillating movement, which is not, however, identical with the oscillations observed with knock combustion.

Our results are collated in Figs. 20 and 21; they reveal a number of characteristic relationships but not a simple connection with the knock behaviour, as might have been expected. In almost all the substances examined, the maximum of the flame speed is displaced far towards the rich mixture side, sometimes up to and beyond twice the stoichiometric figure. This is a well-known experience.

In regard to the knock behaviour, according to Fig. 7 a high flame speed, i.e. a rich mixture is favourable, but since, on the other hand, the reaction in the unburnt portion, which initiates knock, is enhanced by increased enrichment, conclusions should not be drawn from the flame speed alone. On the whole, differences in the flame speeds under the mixture conditions occurring in practice are extremely slight.

Having regard to the engine, it must be remembered that the flame speeds found by ourselves are first of all considerably increased by turbulence and that they are also modified by the higher pressure prevailing in the engine and by the higher temperature. Increasing the pressure does not necessarily raise the flame speed; indeed, experience points to the fact that increasing pressure indeed increases the quantity involved in the reaction, but lowers the flame speed (the flame speed being approximately in inverse proportion to the root of the pressure).

5. Flame speeds at higher temperatures and pressures.

We went on to carry out a long series of experiments on flame propagation at high temperatures and pressures. These did not, indeed, aim at the measurement of flame speeds, but rather at finding conditions under which knocking combustion can be obtained. Since, as already mentioned, we finally found it more profitable to work with adiabatically compressed mixtures, the older experiments will only receive brief mention. After a series of preliminary experiments, where the main difficulty was to find a window material capable of resisting the stresses met with (temperatures up to and beyond 250°C, initial pressures up to about 10 atm.), and which we successfully solved by using mica windows of a few tenths of

a mm in thickness, we eventually worked with a copper tube, containing 4 windows about 10 cm long and sealed with plate glass and lead packing. When well placed, no difficulties were experienced in working with these windows. The tube could be heated in a suitable electric oven and was filled by a supply cylinder and a suitable system of valves; a mixture of the hydrocarbon with air or air plus oxygen in the desired proportions was prepared in this cylinder. The supply cylinder and all the pipelines and valves had to be heated in order to prevent the fuel from condensing, and special precautions were necessary against explosion. The photographs obtained in this arrangement with mixtures rich in oxygen showed the characteristic shock waves already mentioned, but it was not possible to secure knock; indeed, in the experiments conducted to this end with fuel-air mixtures at high temperatures and high initial pressures, spontaneous ignition occurred in filling the explosion tube.

We shall only quote a few examples here. Fig. 22 clearly shows for a relatively disruptive mixture (benzol stoichiometrically with (52 O_2 plus 48 N_2)) the shock wave which distorts the front of the flame and is propagated in the burnt gases at a speed of about 1.5 km per sec; for n-hexane and i-octane, almost the same photographs are obtained.

Fig. 23 shows n-hexane in stoichiometric mixture with (29.6 O_2 plus 70.4 N_2), 1.0 atm. initial pressure and 185° initial temperature; owing to the low speed of the flame, however, the flame front is very much jagged by the pressure wave, yet without abnormal rise in speed.

In contrast to this, Fig. 24 shows a photograph of n-heptane-air (stoichiometrically) at 225° initial temperature and 8.1 atm. abs. initial pressure. Here the flame front is not noticeably affected by distortion, but all the same towards the end there occurs a sudden rise in speed with retrograde wave, which may perhaps be interpreted as a transition to knock.

We are not clear whether the speed increase of flames observed by Nielsen (36) as the result of oscillations, is identical with the increase in speed with knocking.

6. Examination of combustion and knock in adiabatically compressed mixtures.

An arrangement for laboratory scale study of knocking combustion and the spontaneous processes taking place in the compressed gas was developed after lengthy preliminaries on the following lines: Fig. 25. The mixture of gas is admitted at atmospheric pressure into the vertical cylinder Z, dimensions 30 mm diameter and about 700 mm length, and the reaction vessel R is attached at right angles at the lower extremity. It is then compressed by the piston K with the 50 kg. drop weight G. The piston is kept in its lowest position by a special arrangement of pawls, and the burden of the drop-weight is borne by two powerful spiral springs. Furthermore, a simple mechanical device ensures that an ignition spark passes when the piston reaches its lowest position (or at an earlier moment if desired). The course of the flame can then be recorded, both photographically on a rotating drum by means of visual windows in the reaction vessel or by pressure indication with piezo quartz. In order to follow the reaction which takes place automatically in the compressed mixture, the ignition spark is omitted and only the pressure is recorded. The whole apparatus can be heated

by electricity to over 200°, and the compression ratio can be varied from about 1 : 5 to 1 : 10. For the various measurements several different reaction vessels are used, and for knocking combustion, a vessel 100 mm in length, 25 mm internal diameter and window throughout the whole length was found to be the most suitable. In order to investigate spontaneous reaction in the adiabatically compressed mixture, a vessel was used 40 mm in diameter and of the same length, which was more suitable in regard to heat conduction. The gas mixture was prepared on similar lines to that described above for the flow apparatus for slow oxidation. The composition was again checked by measuring the heat conductivity, after calibrating by Orsat analysis on complete combustion.

In proof of the phenomena observed, Fig. 26 shows a series of typical photographs, obtained with an old type reaction vessel, about 20 cm long, with 2 windows. It shows clearly the various types of combustion: ordinary flames (speed about 10 m/s), flames with self-ignition only in one portion of the unburnt mixture, but without knock, transition from normal combustion to knock combustion (speed greater than 100 m/s) and finally premature ignition before the passage of the spark and simultaneous knock.

Further experiments were conducted in a shorter reaction vessel with a somewhat wider bore (see above), because here knock combustion is obtained under milder temperature conditions. Fig. 27 shows a few photographs obtained in this way, while Fig. 28 contains the results of a series of experiments with n-heptane for determining the knock limit as a function of the initial temperature. The initial temperatures are plotted for various compression ratios (abs.) at which knock started, as well as calculated final compression pressures and temperatures, on the assumption of adiabatic compression. Owing to cooling losses, these figures are therefore too high and they only have relative importance for experimental purposes. It must, however, be mentioned that under the conditions of this series of experiments, spontaneous ignition was always associated with knock.

In accordance with the main object of these investigations, we devoted our attention more to the physical characteristics of knock than to the conditions for its inception, and in like manner our subsequent experiments will deal mainly with the knock behaviour of mixtures and the influence of additives.

7. Investigation into the action of anti-knock substances.

It is a well-known fact that the anti-knock substances only have a slight effect on the flame or detonation, once formed, but that they can appreciably restrict the spontaneous reaction in the unburned mixture. Experiments by Egerton have moreover shown that lead tetraethyl, for example, is not active as such, but only when it has disintegrated at a moderately high temperature (about 300°) in the presence of oxygen, probably in the form of a lead oxide. There are no available analogous experiments for iron carbonyl.

Egerton (37) has also drawn conclusions from these experiments and has investigated on the engine itself the influencing of knock by the addition of metallic vapour. Owing to its low vapour pressure, lead was regarded as unsuitable, but thallium and potassium both had a pronounced anti-effect, while sodium, cadmium and zinc were inactive.

In the case of thallium, it was found that pronounced action only took place when it was fed to the engine with air (not with nitrogen). It is therefore only active as an oxide. This is consistent with Egerton's experience with lead tetra-ethyl. (Contradictory results by Berl and his colleagues (38) might have been caused by a deviation in the experimental method). In any case, it is certain that the decomposition products of metallic anti-knock substances restrict the thermal oxidation of the hydrocarbons.

From the point of view of our reaction-kinetic experience, this can only mean that the anti-knock agents affect the chain reaction of combustion, by breaking the chain or preventing it from branching. Only in this way can the activity of extremely small amounts be accounted for. It is also known that the wall of the vessel restricts the reaction, and it was therefore tempting to assume, as Bodenstein (39) has done, that the anti-knock substances, since they are only effective when decomposed, likewise act as "walls" in the form of metallic or oxide dust. It appeared to be of some importance to explore these questions and to ascertain in what way finely divided metals and other solid substances affect the oxidation of hydrocarbons.

Passing over experimental details (the experiments with lead vapour, for instance, required considerable preparation in order to exclude all the possibilities of trouble), we will mention the results of the experiments carried out in this connection. Lead vapour restricts the slow oxidation both of n-heptane and of iso-octane, and to a less extent that of benzol. In these experiments, the lead was supplied by molten lead at 800-900° and mixed with a current of nitrogen. Since before entering the reaction vessel the stream of gas was cooled down some hundreds of degrees, it follows that the action is to be attributed, not to molecularly dispersed lead, but to metal or oxide in the form of very fine solid particles. The interesting experiment of feeding the lead in a current of oxygen, so that oxide would be present from the outset, could not, unfortunately, be carried out without ambiguity. In all cases special control experiments had to be carried out to eliminate the action of the lead deposited on the surface of the vessel.

With a different apparatus, a series of experiments was then carried out on the action of finely divided solids carried along in the gas. The solids selected were: soot, magnesium, aluminium oxide, kieselguhr, lead oxide; these substances also restrict the oxidation of hydrocarbons. It is therefore to be assumed that the addition of substances which disintegrate in the engine forming solid particles, may have a favourable effect on knock. This is particularly interesting in the case of soot.

III. General conclusions and survey.

We now propose to collate the conclusions which have been drawn from previous experiments and from our own, regarding the knocking process. In the unburnt, adiabatically compressed mixture, spontaneous reactions take place which are oxidation reactions based on a chain system, and may result in knock. The nature of the chain reactions themselves has not yet been explained, although various theories have been built up concerning them, e.g. combinations of the peroxide type or radicals are supposed to play a considerable part. However, we shall not dwell here on the more or less hypothetical considerations (40) concerning the reaction system, and will only give such conclusions which are based on the fact of the presence of a chain reaction and on the possibility of its being influenced by additives, but not on the

nature of the various members of the chain.

If in a chain reaction the primary process is followed by a series of reaction stages, the average length of chain $\bar{l}$, if b is the probability that the chain will break at a given stage is given by:

$$\bar{l} = 1/b \qquad (10)$$

since the speed of the reaction is proportional to the number of transformed molecules and therefore to the length of the chain, this speed, v, is proportional to $\bar{l}$, thus:

$$v = \text{constant}/b \qquad (11)$$

If the probability of the chain breaking is proportional to the concentration of a chain-breaking substance, d (the ratios for chain reactions are shown here in very plausible, but not strictly well-founded form. Reference should be made to a general explanation of this subject (e.g. by Semenoff)), then we have:

$$b \text{ is proportional to } d \qquad (12)$$

therefore

$$v = k/d \qquad (13)$$

As the reactive gas mixture, in our case hydrocarbon plus air, either itself has a chain breaking action, or else substances of this nature arise in the course of the reaction, we have without additives:

$$v = k/d_o \qquad (14)$$

and with the addition of a chain-breaking substance:

$$v = k/(d_o \text{ plus } d) \qquad (15)$$

where d_o and d are not both merely concentrations, but one of them contains a factor allowing for different probabilities of chain-breaking. It will be seen from (15) that if d signifies about 3 ccm lead tetraethyl per gallon of fuel (as is customary in English and American work, which we quote here), the relative decrease in speed by the addition of 1 ccm lead tetraethyl becomes less the more lead is added. This is familiar experience with the activity of anti-knock agents, which does not happen to be the case with lead alone, but is a general fact. It thus seems purposeless to seek an anti-knock agent which, with the same efficiency as lead, has the same specific efficiency in large quantities as in small. (x)

(x) A theoretical grasp of knock-behaviour with increasing supercharging and its influencing by anti-knock agents does not at present seem possible. On the one hand we have no reliable knowledge as to the change in the speed of the reaction as the result of pressure (the variation in the flame speed with pressure would have some influence on knock behaviour); furthermore, it must be assumed that the main effect of supercharging on knock behaviour is derived from the altered initial temperature of the mixture and from the changed conditions for the relative heat conduction in the combustion chamber. All this makes it rather improbable from the start that the ratios obtained for changes in compression can be applied without modification to the case of supercharging.

Attempts may be made to deduct approximate quantitative ratios between the lead additive and knock behaviour of a fuel, perhaps expressed by the maximum useful compression ratio after Ricardo. (x) The reaction speed (15) generally depends on temperature, i.e.

$$k = k' \exp\,(-Q/RT) \quad (xx) \qquad (16)$$

where T is the absolute temperature, R the gas constant and Q the so-called heat of activation; k' is then a further function of composition and pressure, but as a first approximation we shall regard it here as a constant. Approximately, therefore, the whole speed of the reaction may be written thus:

$$v = k' \exp\,(-Q/RT)/(d_o + d) \qquad (17)$$

If T_o is the initial temperature of the gas drawn into the cylinder, the final temperature of compression (ignoring the cooling losses) is T, where,

$$T = T_o \varepsilon^{x-1} \qquad (18)$$

where ε is the compression ratio and x the ratio of specific heats $x = c_p/c_v$. From (18) we have (17) becoming:

$$v = k'/(d_o+d) \cdot \exp(-Q\,\varepsilon^{1-x}/RT_o) \qquad (19)$$

We assume that under certain conditions knock occurs if the speed of the reaction exceeds a critical figure, which, particularly in the case of the compression ratio ε and without anti-knock additives is given by

$$v_{kr} = k'/d_o \cdot \exp(-Q \cdot \varepsilon^{1-x}/RT_o) \qquad (20)$$

Now if anti-knock additives were to be added in the concentration d, the speed of the reaction would drop in accordance with the above formula, and knock would accordingly cease. We now imagine that the compression ratio has been increased to such an extent, by $\Delta\varepsilon$, that the speed regains its critical figure and knocking is resumed. Thus we have:

$$v_{kr} = k'/(d_o+d) \cdot \exp(-Q(\varepsilon + \Delta\varepsilon)^{1-x}/RT_o). \qquad (21)$$

From (20) and (21) there results the desired relationship between the anti-knock substance, d, and the increase of the critical compression

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(x) Even if the maximum useful compression ratio is not a particularly suitable standard for a practical knock value determination, as it depends on the engine and working conditions, it is nevertheless recommended for correlation with all physico-chemical ratios because - once the working conditions are known - it furnishes a direct relationship with other determining physical factors, such as temperature and pressure. To compare the maximum useful compression ratios with octane numbers, we publish a diagram after Campbell (41) and his colleagues, which gives the maximum useful compression ratio for n-heptane/isooctane mixtures (CFR Research Method), Fig. 29. Under normal engine conditions compression ratios were about one unit higher.

(xx) $\exp x = \varepsilon^x$

ratio . The next equation is:

$$(d_o+d)/d_o = \exp(-Q(\varepsilon+\Delta\varepsilon)^{1-x} - \varepsilon^{1-x})/RT_o) \qquad (22)$$

For the sake of simplicity we assume (which is true only to a limited extent) that $\Delta\varepsilon$ is small compared with ε, so we have finally:

$$\log([d_o+d]/d_o) = +Q/RT_o.(x-1).\Delta\varepsilon/\varepsilon^k \qquad (23)$$

or

$$\Delta\varepsilon \cong \text{const.}\log((d_o+d)/d_o). \qquad (24)$$

The fact that this equation, whose applicability should not be overestimated, agrees well with the experiment, is shown by Fig.30, in which four series of experiments by Hebl and Rendel (42) are plotted; the curves are, in accordance with (24) calculated with constant values as given in the figure. Proceeding backwards in (23) one can calculate Q from these figures and this will be found to be ~ 20,000 cal. which, so far as the order of magnitude is concerned, agrees well with observed heat of activation.

From the point of view of the theory of chain reactions, this not only enables us to understand the influence of various quantities of anti-knock substances, but more lucid connections between knock resistance and lead sensitivity will be found, as well as the behaviour in mixtures of the individual groups of fuels (mixed octane numbers), so that some idea is obtained as to what can be achieved in practice and may therefore be aimed at.

For the observed anti-knock value of a hydrocarbon combination under given conditions, it is in our opinion of decisive importance that the spontaneous reactions (oxidation reactions) taking place in the adiabatically compressed mixture should not exceed a certain critical speed. We saw above, Equations (11) and (13), the reaction speed written in the form $v = k/b$, where k contained the probability of the chain forming and b that of it being broken. Semenoff in particular has stressed the importance of chain-branching reactions. These are reactions set up by an active particle continuing the chain, and in the course of which two or more such particles are formed, that is to say, reactions by which the number of the chain carriers and therefore the speed of the reaction, are increased (cf. p.19). If "a" represents the probability of the branching of the chain, we have for the speed of the reaction:

$$v = k/(b - a) \qquad (25)$$

an expression which increases out of all proportion for $a \rightarrow b$, even without a temperature rise occurring in consequence of the heat of the reaction. Although such processes are of importance for the oxidation of the hydrocarbons, we must content ourselves here with a more summary treatment. (25) states qualitatively: The speed of the reaction is lower, the smaller the number of the chain-forming processes (proportional to k) and of the chain branchings (a), and the larger the number of the chain breakings (b). If we no longer mention the chain branching expressly, we may accordingly say that a fuel is the more knock-resisting the fewer the chains formed and the more they are broken. A given, good knock behaviour can therefore come about in several ways, e.g. either by very few chains being formed, while the probability of breaking is normal to great; or else, by a normal amount of chains being formed, while the probability of breaking is great. If, out of a series of conceivable cases, we

number these two groups I and II, all observations favour the fact that if we place a certain paraffin or naphthalene in Group I, an analogous unsaturated combination of the same knock-resisting properties must be assigned to Group II. To take an example, more chain-forming processes take place in olefins than in paraffins, and however a larger number of chain-breaking processes so that, on the whole, the structure being otherwise the same, an olefin is even more knock-resisting than the corresponding paraffin. This can only be explained by the fact that the chemically more reactive olefins are less rapidly oxidised than the corresponding paraffins. From this simple statement there emerge a number of important deductions as to lead sensitivity and behaviour in mixtures with other fuels.

In the same way as we concluded above, that the action of a given lead additive is less, the more lead was previously added to the fuel, we can now arrive at the conclusion that the action of the lead is based on its chain-breaking (or anti-branching) character and that a lead additive will be less active the greater the chain-breaking activity already possessed by the mixture of fuel. Therefore, the knock resistance being the same, a substance from Group I will exhibit a higher sensitivity to lead than another substance of Group II. This has to a very large extent been confirmed by experience (cf. Fig.31).

The question may also be asked, how is the knock-resistance of a given fuel altered by the addition of a second fuel? (e.g. expressed as mixed octane number). If, for instance, we prepare an n-heptane-isooctane mixture, containing 10% isooctane, according to the definition the octane number will be 10. If, instead of iso-octane we added to the n-heptane another fuel in the same quantity and with the same octane number as iso-octane (i.e. 100), the octane number of the mixture can be greater or less than 10, i.e. the mixed octane number of the fuel in question can be greater or less than 100. From the point of view of the chain theory, it is to be expected that the addition of a knock-resisting fuel not only acts as a diluent of the less knock-resisting fuel, but also a reciprocal influencing of the course of reaction takes place, which may result in a higher or lower degree of anti-knock, according to the law of mixtures. In particular a fuel of the afore-mentioned Group II (i.e. one with a powerful chain-breaking effect) when added to a fuel from Group I, will considerably restrict the speed of the reaction by breaking the chain, i.e. it may exhibit a particularly high mixed octane number; this has been observed (cf. Fig.32). As substances of Group II have a low lead-sensitivity, compared with equally knock-resisting substances in Group I, it follows that extremely high (i.e. higher than can be expected from the law of mixtures) mixed octane number and high lead sensitivity are to a large extent mutually exclusive. (x) There is also documentary proof of this, cf. Fig. 32. Attempts may be made to obtain in the same way an approximate quantitative ratio for increasing the knock resistance of various hydrocarbons by the same lead additive, as was done above for the action of different types of lead additive in the same fuel. (The approximate character of the considerations is emphasised; out of a number of factors, we took one which probably exerts the strongest influence). There will then be found for groups of analogous fuels a ratio between knock resistance ε of the fuel (again expressed by the maximum useful compression ratio) and its improvement by a given lead additive $\Delta\varepsilon$, a simple relationship which we mention here without inferences (43). By "analogous fuels" we mean - quite arbitrarily - those in which the critical speed of oxidisation at the knock limit is reduced by the same lead additive in the same way. Such substances may be regarded as analogous, but

(x) When evaluating the present material, it should be borne in mind that the scale of the octane number is a very uneven standard for the anti-knock value, measured approximately in the natural scale of the critical compression ratio. Cf. Fig. 29.

whether such a classification is a practical one, is a matter for experience to teach. (In order to avoid misunderstandings, it is pointed out that in the range of high octane numbers (about 60), the raising of the octane number and increase in the critical compression ratio are by no means proportional. The increase in the critical compression ratio becomes more strongly marked with rising octane number; e.g. if the octane number rises from 90 to 91 (after Campbell, Lovell and Boyd, SAE Journal Vol. 26, 1930, p. 163) the result will be three times the amount of rise in the critical compression ratio compared with an increase in the octane number from 70 to 71. It must also be remembered that our ratio can only apply to pure combinations within determined groups of materials of similar chemical behaviour (e.g. paraffins, naphthenes, olefins, acetylenes etc.) and not necessarily to technical fuel mixtures with varying content of aromatics and possibly alcohols).

The ratio deduced is:

$$\Delta\varepsilon = \text{const.}\,\varepsilon^{x} \qquad (26)$$

where ε is the critical compression ratio, $x = c_p/c_v$ and where the constant can be expressed by values that are in principle capable of observation. We will merely add, that the constant is greater the more the speed of the reaction is reduced by a given lead additive at the knock limit and that it may occasionally assume negative values (e.g. when the reaction is accelerated by lead). In Fig. 31 are plotted Campbell's results for the effect of lead on a large number of hydrocarbons (44) and the dashed curve corresponds to the equation 27

$$\Delta\varepsilon = 0.113\ \varepsilon^{x} \qquad (27)$$

the factor 0.113 has not been calculated theoretically, and may be obtained with reasonable values of the factors making up the constant. A striking point, and one which would never have been anticipated, is that the limiting law (27) reproduces faithfully the behaviour of both paraffins and naphthenes, and this points to certain assumptions regarding the mechanism which will not be discussed in detail here. In all the other hydrocarbons, with the same knock resistance, the lead effect is less than in the case of these two; indeed, in a number of combinations, the addition of lead even impairs the knock resistance, corresponding to negative values of the constant in Equation (26). This behaviour agrees with the theories which we have evolved above regarding the influence of chain-forming and breaking processes on knock behaviour; i.e. the chain-breaking effect in these fuels is actually greater, so that the addition of lead has less effect on the speed of the reaction or else the chain-forming action of tetraethyl lead (which is able to split off radicals thermally) predominates.

From this it might be expected that the hydrocarbons farthest to the right in Fig. 31 have relatively the lowest mixed octane number and vice versa (x). This too is obtained direct from the experiments by the Americans, which we have collated in Fig. 32, where lead sensitivity ($\Delta\varepsilon$) is plotted against aniline equivalent (as a standard for the mixed octane number).

The individual hydrocarbon groups follow in this figure in precisely the same sequence as in the previous one. This is the

(x) That is to say, not that they must necessarily have low mixed octane numbers, but merely that, measured by the octane number of the pure substance, the mixed octane numbers to the right are on an average smaller than those to the left.

relationship already given above, viz. that extremely high mixed octane numbers and high lead sensitivity do not occur together. It is regrettable that so far there is no analogous material regarding the engine behaviour of oxygen-containing organic combinations (mainly alcohols, others, ketones) and the effect of lead on them. Our past investigations into slow combustion give rise to the following assumptions regarding the behaviour of ketones. With dilute paraffins (and similarly, in practice, with alcohols and aldehydes as well) the chain reaction produces aldehydes and a gradual break-up of the molecule:

$$R.CH_2.CH_3 \rightarrow R.CH_2.CHO \rightarrow R.CHO \quad \text{etc.}$$

In molecules with branched chains, e.g. isooctane (in order to avoid misunderstanding, it is emphasised that the word chain is used both for chains of atoms in the molecule and for chains of partial reactions in a complicated reaction system), an analogous reaction is not possible, but instead of the branching in the molecule, in the case of the C-atoms marked thus @, only a ketone instead of an aldehyde can form

$$H_3C.\ \overset{H}{@C}H/3\ .CH_2.\ @C.\ (CH_3)_3$$

and the course of the reaction in the above sense would come to a standstill (in accordance with the observation first voiced by Edgar, that the primary slow reaction goes as far as corresponds with the break-up of the longest side chain in the molecule):

$$\begin{matrix} R_1 \\ R_2 \end{matrix}\!\!>\!CH.CH_3 \longrightarrow \begin{matrix} R_1 \\ R_2 \end{matrix}\!\!>\!CH.CHO \longrightarrow \begin{matrix} R_1 \\ R_2 \end{matrix}\!\!>\!CO \text{ (Ketone)}$$

We were therefore of the opinion (43) that the **oxidation** stability observed, like the knock-resistance of branched paraffins, is dependent on the stability of ketones which are formed intermediately. This assumption was confirmed by investigating the **oxidation** behaviour of various ketones, which caused particularly high knock-resistance to be anticipated for these substances. We should therefore like to assume that ketones resemble isoparaffins as regards all their attributes and that they perhaps only possess slight sensitivity to lead; this would be in agreement with the occasional hints that can be found (45).

Overall, our past investigations lead us to make the following deductions. Since the processes resulting in knock are chain reactions and the action of the anti-knock agents consists in breaking the chains, we have the relationships discussed above between anti-knock action, constitution of the fuel and its behaviour in mixtures. It would appear that the varying degrees of lead sensitivity are dependent on the different lengths of the reaction chains which occur in the various hydrocarbons before the addition of the lead, and the result of this would be that normally, in cases where satisfactory lead-effect is not obtained (except when this is brought about by the quantity of lead involved, etc) there will be no other anti-knock agent active in very small concentration. Whether as a general rule there is no agent superior to lead, cannot of course be stated, but it does seem tolerably certain that in the presence of lead appreciable increases in the activity are out of the question. As regards the choice of knock-resisting fuels that can be improved by the addition of lead, Figs. 31 and 32 refer to the branched paraffins and naphthenes, which are well known in this connection. For a still further increase in the knock-resistance of fuels, say over and above 100 octane number, new anti-knock substances of high efficiency will probably be less suitable than substances with a particularly high mixed octane number

to be added in greater concentration. As regards the remaining possibilities, our experiments in connection with slow oxidation as well as the general experience shown in Figures 31 and 32, will provide some information. Unfortunately, the choice is very much restricted by the demands other than knock-resistance that are made on fuels: e.g. freedom from prejudicial gum formation, suitable boiling point and highest possible heating value, and in the case of additives used in high concentration, a reasonable price -- all these limit the field considerably. Our further investigations will aim at extending existing experience, especially in regard to quantitative relationship with knocking. At the moment we should like to conjecture that ketones of branched hydrocarbons, such as di-isopropyl-ketone, methyl tert. butyl-ketone (pinacolin) and possibly isopropyl tert. butyl ketone will exhibit suitable behaviour; at least, our observations with slow oxidation favour such substances, but as regards practical application, the question of cost of manufacture would be the deciding factor. Furthermore, we feel that it is of the highest importance to study the peculiarities of the oxidation mechanism in general and the nature of the reaction chains of oxygenated organic combinations (with the exception of aldehydes, regarding which more is known, and which are closely allied to the corresponding paraffins, although more easy to oxidise than the latter).

IV. Summary.

Our investigations have shown that a knowledge of the behaviour of hydrocarbons during slow oxidation on the basis of theories regarding chain reactions, permits a systematic arrangement and an understanding of the material concerning knock behaviour, lead sensitivity and mixed octane numbers of the same fuels. The guiding principle here is always that when the oxidation reactions, which take place spontaneously in the unburnt portion of the adiabatically compressed mixture in the engine, exceed a certain critical speed limit, knock ensues. Attempts to establish approximate quantitative ratios in special cases (action of lead additives in different amounts, lead sensitivity of the paraffins and naphthenes) are successful in so far as inferences may be drawn to the correctness of our fundamental theories, and that it appears promising to continue the investigations with the object of ascertaining more general quantitative ratios for knock. In this connection, the investigations which have already been initiated for following the reaction in the adiabatically compressed mixture, as well as for studying knock by means of photographs of flames and pressure recording, should be of importance. For practical purposes, the experiments which we have so far conducted indicate in what direction it is desirable to orientate our work for improving knock behaviour.

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DEUTSCHE LUFTFAHRTFORSCHUNG

Research Report No. 1074

The Properties of Safety Fuels

Mayer-Bugström/Seeber

Synopsis: The purpose of the work was to establish a basis for the specification of a safety fuel. The influence of chemical composition and of chemico-physical properties, boiling range and vapour pressure in particular, on the liability to catch fire was investigated. The fire risk was measured not only by the ease of ignition (flash point, self-ignition point, ignition limits) of the liquid and atomized fuels, but particularly also by the velocity of flame propagation. The suitability of safety fuels for use in the engine was examined.

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1. Reason for the Investigation

When aeroplanes crash the impact produces fuel fires. This gave rise to investigations which aimed at replacing the light fuels responsible for these fires by fuels less liable to catch fire i.e.so-called safety fuels. Such an investigation must proceed by ascertaining for a large number of fuels those properties which are found to be responsible for the inflammability; the properties have to be compared among themselves and finally related to the chemico-physical properties and the constitution of the fuel. It should then be possible to determine the probable fire-safety of a fuel in the engine on the basis of laboratory experiments. The fire-safety should then be founded on a physico-chemical explanation and it should be possible to indicate new ways of producing suitable fuels.

2. General

After the crash and the disintegration of the fuel tank it can be taken that the fuel will exist in three forms, apart from the gaseous phase, i.e. free liquid, absorbed liquid (e.g. in sand) and in the form of floating droplets (mist). For all three cases the fire safety depends on the ease of ignition and the velocity of propagation of the flame. Ignition is favoured by a low temperature of ignition and by a large range of ignitability of the vapour/air mixture. Ignition also depends on the source of ignition (glowing point, spark or flame). For fuel mist the question of importance is how large a volume is within the limits of ignition for a given amount of fuel atomized.

Combining the factors mentioned, i.e. property responsible for catching fire (ignition temperature, ignition limits, velocity of propagation), source of ignition (glowing point, spark, flame) and distribution of fuel (open liquid, absorbed liquid, mist), would give rise to a large number of test series. These are not all of equal practical importance. Thus, when the running time of the flame is determined the source of ignition will be irrelavent. This running time determination will be superfluous for fuel mist since the velocity of flame propagation in finely distributed fuels is of such magnitude that differences are of no practical importance. The following tests remain:

1) For the ignition
   a) Ignition Temperature in relation to source of ignition
   b) Limits of Ignition also in relation to source of ignition

2) For the spreading of the flame
   a) Velocity on the surface of the open liquid
   b) Velocity in the absorbed liquid

For 1)a), Ignition Temperature for ignition at glowing points may be determined by an ignition value test instrument (e.g. Jentzsch); for flame ignition it may be determined by a flash point apparatus.

For 1)b) The fuel must be vaporised for the determination of the ignition limits. Comparisons between fuels in regard to the formation of an ignitable mixture at the surface may be made from the position of the ignition limits. In this connection it is necessary also to determine the volume within which fuel mists are ignitable. The source of ignition is here of particular significance.

For 2)a) The simplest method for determining the velocity of spreading of the flame on the surface of the open liquid, is to measure the time taken by the flame to cover a fuel path of small but uniform width. Thus the experimental vessel must be in the form of a groove. Since the temperature plays a large part in the determination, it must be controlled.

For 2)b) Absorption of the fuel may be carried out, e.g. in a wick.

3. Test Material

Typical examples of the various materials which qualify for use as fuels were investigated, i.e. paraffinic hydrocarbons (gasolines), aromatics, hydrogenated aromatics, alcohols, ethers and ketones. Besides chemically pure substances, blends were investigated, such as are used as fuels, or have been proposed as safety fuels. In the selection of substances we made a point of taking substances of widely varying combustibility from each class. The properties of the materials are summarized in tables 1 - 7. Unless otherwise indicated these values are from the DVL. The reception numbers refer to the samples examined by the DVL. In figures 3 - 5, the ignition limits and flash points taken from the literature, and the DVL values for the self-ignition points according to Jentzsch, have been plotted in terms of the numbers of carbon atoms in the molecule for several of the tabulated substances and some additional materials.

4. Method of Investigation

i) Laboratory Experiments

a) Running time of flame along surface of liquid:

Figure I shows the iron trough serving as the test apparatus. The inner part, 3 m. long, contains the fuel, while water at the desired temperature is contained in the outer section. 350 ccs. of fuel are poured in, and when the fuel has assumed the temperature of the water, it is ignited at one end. Ignition is effected by a glowing wire in the case of easily inflammable fuels, and in the case of fuels inflammable with difficulty, by a match or wick which is left in the fuel till ignition occurs. If the fuel did not catch fire after 10 mins. it was classified as non-inflammable. The time taken by the flame to cover the three metres was measured in seconds and called the "running time of the flame". The reproducibility of this value was good. (Thus the following values were found; for benzene: 1.7, 1.5, 1.7; for di-isopropylketone: 13.8, 13.0, 14.0; for iso-butyl alcohol: 71.0, 72.2; for xylene: 101, 108). Only for very long running times (several minutes) did differences arise through change in the amount, composition and temperature of the unburnt fuel. To avoid errors of this kind the total running time was calculated from the distance covered after three minutes.

The experimental temperature was normally 20°C. The high boiling fuels were also ignited at 30°C and 40°C . The experiments were carried out in a closed draught-free room. Draughts affect the results considerably.

b) Running time of flame in absorbed fuels:

Only fuels which are ignitable with difficulty were used for these experiments. A wick 6 mm. thick was soaked with fuel, and, without squeezing, freely suspended between two stands. The time taken by the flame to cover 1½ m. was measured, and twice this time was entered in the tables, since tests with a wick 3 m. long proved difficult because the wick breaks. It was ascertained, however, that the progress of the flame along the wick was uniform so that the above calculation is legitimate.

c) Ignition of Fuel Mist:

The arrangement for determining the ignition range of fuel mist (see fig.II) consisted of an injection pump with a nozzle, all firmly mounted on a table. On the same table an ignition device was moveable along the axis of the fuel jet, and could be fitted with a hot wire or an ignition plug. The injection pump was manipulated by hand and thus showed discontinuous injection pulses. The fuel was atomized at a pressure of 120 atm. using both quick and slow succession of injection pulses. In the first case the pulses followed each other so closely that a flame once started would be maintained during further injections. In the second case the flame died down in the interval between injections. The source of ignition, in action all the time, was slowly moved away from the nozzle until ignition of the fuel mist no longer occurred. The distance in cm. between nozzle and injection pump was called the ignition range. In determining this range it is of importance whether one judges ignition by observation of the visible flame or by means of the accoustic phenomenon (explosion). Even the lighting up of a small region of single fuel drops was taken as visible inflammation. The explosion only accompanied larger flames, thus leading to a smaller ignition range than the visible inflammation. The direction of propagation of the flame always conformed to the direction of the jet; striking back of the flame from the source of ignition to the nozzle was not observed.

The following fuels were examined: Shell Flugbenzin OZ.87, Benzene, Dekalin, Tetralin, Ethyl Alcohol, and the Safety Fuels St.1 and St.1a. The last was also examined in blends with 10% gasoline of different boiling range and with 10, 20 and 30% of aviation gasoline.

d) Ignitability of Hot Surfaces:

The ignition value test instrument of Jentzsch was used for testing the ignitability of hot surfaces (without flame). The ignition temperatures are measured in oxygen and cannot therefore be applied directly to practical conditions, but useful comparative values are obtained.

ii) Engine Tests

The Safety fuels St 1 (336/38) and St 1a (22/39) were tested for knock behaviour in BMW 132.N engine by the DVL supercharge method at boost air temperatures of 80° and 130°C

The test conditions of the experiment were:

R.P.M.	1600
Compression Ratio	6.5 : 1
Cooling Air Pressure	200 mm. water column
Start of Injection	13° B.T.C.
Injection Pressure	60 atm.
Ignition:	Optimum ignition at λ = 0.7; 0.9 and 1.1 for knock-free operation
Intensity of Knock:	6 to 10 impulses per minute

Furthermore the octane number was determined in the CFR engine according to the Motor and Research Methods.

5. Experimental Results.

It is clearly seen from Fig. III that paraffins and olefins have low self-ignition points and aromatics, alcohols, and ketones have high ones. Hydrogenated aromatic compounds have intermediate values. Lowering of the self-ignition point was observed with increasing size of the molecule in a homologous series (see paraffins, ketones.)

In a homologous series the flash points naturally rise with the number of carbon atoms in the molecule (see Fig.IV). Alcohols have particularly high flash points.

For the majority of the substances in question the ignition limits extend over a range of 5 to 10% vol. With increasing molecular size both ignition limits fall and the ignition region is reduced. Alcohols, ethers and olefins furnish some exceptions, the region sometimes being considerably larger.

In Fig. VI the ignition ranges of fuel mist are compared with the running times of the flame. Fig. VI shows that high boiling point fuels are more liable to catch fire when atomized than low boiling fuels; that is, they retain their ignitability at a greater distance from the fuel source when ignition occurs at a glowing point. (see curves 3 and 4)

This is explained by the property of high boiling fuels of forming an ignitable mixture for a longer time and of often having a lower self-ignition point than low boiling fuels. A different sequence is obtained for ignition with a sparking plug. The ignition range increases as the volatility of the fuels increases. A similar result is obtained with glow ignition if the occurrence of ignition is determined, not optically, but accoustically, that is by noting the explosion. That a rapid succession of injection pulses increases the ignition range for all fuel mists is understandable.

The velocity of flame spreading in the groove (running time of the flame) varies between very wide limits for the fuels examined (2 to 1540 secs at 20°C). Fig. VII represents the relation between velocity of propagation and the initial boiling point. The running time of the flame increases with the initial boiling point. No appreciable increase of the running time of the flame is shown by gasolines and paraffinic hydrocarbons up to an initial boiling temperature of about 120°C, the running time lying between 2.0 and 2.6 secs. For a higher initial boiling point the running time of the flame increases rapidly (iso-dodecane with initial boiling point 158°C and running time of the flame 443 sec.) Most other classes behave similarly. In these also, the running time of the flame up to an initial boiling temperature of 120° amounts to less than 2.5 secs and increases steeply with higher initial boiling temperature. The alcohols are a special case; the running time of the flame being considerably above that of the usual fuel groups. The high specific heat and latent heats of the alcohols are the reason for this.

The discontinuous change in the running time of the flame for various fuels which is observed when a certain limit of the initial boiling temperature is passed, can also be observed when the test temperature is changed with the same fuel. Thus xylene (ignition boiling temperature 136°C) gives a running time of the flame of 1.05 secs. at 30°C, but only 3.9 secs at 40°C (see Fig. VIII). The interval between the temperature of the fuel and its initial boiling temp. is clearly important. When this interval was less than 100°C, a running time of a few seconds was found for all the hydrocarbons examined; otherwise the flame spread very slowly. A similar, if not quite as steep, increase is given by alcohols when the temperature difference amounts to about 65°C. (Example: Isobutyl alcohol with initial boiling point 105°C and running times of 30 and 3 secs. at 30 and 40°C respectively). Ethers and ketones behave similarly to the hydrocarbons. If instead of the temperature difference, the deviation of the product of specific heat and temperature difference, the deviation of the alcohols from the other fuel types becomes less in regard to the steep part of the curve. It would therefore be interesting to establish a relation between heat capacity and running time of the flame. At present, however, there are not enough data on mean specific heats of the compounds in question over the temperature intervals examined.

The effect of temperature on the flame running time is considerable; this may be seen from Fig. VIII for some fuels of high boiling point. The following comparisons apply to a temperature of 20°C.

The safety fuel St 1a is one of the fuels which did not catch fire at all. Fig. IX shows the effect of various gasoline additions on the inflammability (Table IX). 10% of a highly volatile gasoline suffices to impart to the mixture the same running time as that of pure gasoline. In order to attain the same effect for AZ-fuel 20% is needed. The additions mentioned have much less effect on the ignition range of atomized St 1a (Table VIII). Thus in determining the amount of light fuel to be added to the safety fuel for the purpose of starting, the main point is to consider is the influence on the running time of the flame and on the flash point. It should be mentioned here that it would be possible to start on gas from cylinders or even light fuels, the containers of which could be jettisoned after starting.

Fig. X shows the influence of the vapour pressure (20°C) on the running time of the flame. Aromatic hydrocarbons having vapour pressures above 20 mm. give running times of about 2 seconds.

The running time increases steeply with lower vapour pressures. The other fuels (except alcohols) have very low running times of the flame (2 secs.), the vapour pressures being 35 mm and over. Alcohols of vapour pressure above 20 mm. have considerably longer running times than the other fuels. This difference disappears at lower vapour pressures.

The temperature limit for flash point below which the velocity of propagation is very great is at about plus 10°C (Fig. XI). This applies fairly uniformly to all types of fuels. The alcohols here show better agreement with the gasolines than when initial boiling temperature and flame running time are used for the comparison.

The relation between self-ignition point and flame running time is shown for a number of fuels in Fig. XII. Within single fuel groups the spontaneous ignition point seems to fall with increasing flame running time, as far as may be judged from the limited data available. (see ketones, aromatics, alcohols and ethers). This would also be expected from the above relation between self-ignition point and flame running time (but it is not to be assumed that there is a direct connection between self-ignition point and the running time of the flame). The number of the ignition values available is also too small to establish a relation (Fig. XIII) The ignition value could not be determined for many of the substances.

Fig. XIV shows the running time of the flame for the fuels absorbed in a wick as a function of the flash point. The running time in the open groove for the same fuels has been included for the purpose of comparison. The running times in the wick are much shorter than in the groove and closer together. The two aromatic fuels (both in wick and groove) have a longer running time in relation to flash point than the other fuels.

The results of the engine tests of the two safety fuels and of Shell-Borneo-reference gasoline are given in Figs. XV and XVI. The extent to which St 1a may be supercharged at boost air temperatures 80° and 130° in the rich region is almost equal to that of St 1. At weak mixtures St 1a is better at 80 and 130°, and at 80°C the curve lies appreciably above that of the Borneo reference gasoline while at 130°C it is approximately equal to the reference fuel.

Disregarding the increased consumption St 1a is equivalent in performance to the Borneo gasoline in the lean region and highly superior in the rich region.

The octane numbers according to the CFR - Motor and Research - method are given in Table X.

6. Summary

On the basis of the experiments the following indicate the most favorable characteristics of a safety fuel.
1) The conception of safety is relative. Flash point, self-ignition temperature and ignition limits are essential for fire safety; the state of distribution of the fuel must however also be taken into account.
2) High boiling fuels in atomised form may be ignited at greater range than low boiling ones, i.e. larger volumes are ignitable. All the same the former must be regarded as safer, since with these either absorbed or with a free surface, the flame spreads much more slowly than with normal gasoline fuels. The best measure of the fire safety appears to be the velocity of flame spreading.
3) The following order is obtained if fuels of equal initial boiling point are arranged according to their velocities of flame spreading at 20°C. Alcohols burn most slowly, followed by aromatics, ketones and ethers with the paraffins and hydrogenated aromatics burning fastest. Differences, which are small, anyway, occur only with alcohols boiling below 110°C.
4) When the difference between starting temperature and initial boiling temperature exceeds a certain value there is a discontinuous change in the running time of the flame. For hydrocarbons this temperature interval is about 100°C, i.e. a very steep increase in flame running time occurs for an external temperature of about 20°C when the initial boiling temperature reaches about 120°C. To include a safety factor , an initial boiling temperature of about 140°C would be required for this class of fuels.
5) The limit of rapid flame spreading is given by a flash point of about 10°C With a sufficiently large safety factor the minimum for safety would be 40°C.
6) The addition of 20% aviation gasoline or 10% of a lighter gasoline to the safety fuel has the effect of making the running time of the fleme equal to that for the gasoline without having much effect on the ignition range of fuel mist.
7) Absorbed fuels show considerably less differences in their flame running times than the corresponding open liquid surfaces.
8) Naturally high self-ignition temperature and low settling point are also desirable.
9) Experiments on the knock behaviour of safety fuel St la in the single-cylinder BMW 132N under the DVL conditions, gave the result that this fuel is in this respect, equivalent to Shell Borneo gasoline in the lean region and much superior to it at rich mixtures.

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THE CHEMISTRY OF DEPOSIT FORMATION IN HYDROCARBON OILS.

Author: J. Morghen, 12.7.39.

1. SHORT REPORT

A study of the oxidation products which are formed by the action of air on hydrocarbon oils at high temperatures.

Summary Oxygen combines with hydrocarbon oils when heated in air. Until recently, this absorption was controlled, up to a point, by means of the saponification number. In this report, additional methods of identifying and determining quantitatively further oxygen groups in aged oils are given. The oxygen compounds which were identified (converted to mg. KOH/gm) amount to about three times the quantity of those previously determined. The methods described are suitable for determining the character of the oils in the laboratory.

Contents:

INTRODUCTION

It is a well known fact that hydrocarbon oils have a tendency to form deposits, especially on machine parts at high temperatures. Sooner or later this causes the lubricating efficiency of the oil to be impaired, thus leading, in unfavourable cases, to local accumulation of deposits and to seizure of the moving parts. The purpose of this work is to review the possibilities of protecting refined mineral oils and synthetic hydrocarbon oils against such degeneration.

For chemical deposits to form, at least at temperatures up to 400°C, the presence of oxygen (or other substances such as sulphur, products of combustion etc.) is essential. In this short report the influence of air on a hydrocarbon oil at various temperatures is discussed, under conditions in which deposits in the oil are still unformed. The oxygen, which is absorbed by or has combined with the oil, is estimated qualitatively and quantitatively, without particularly taking

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into account the nature of the substances or the mechanism and the kinetics of the reaction. The oxygen compounds or types of oxygen compound thus determined are examined for thermal stability in the oil. This will not be discussed until later.

The volatile substances which are formed by the oxidation of hydrocarbon oils are not discussed in this paper.

II. SHORT SUMMARY OF THE PREVIOUS KNOWLEDGE OF THE REACTIONS AND METHODS DISCUSSED

Not much is known about the nature of the oxygen compounds in a hydrocarbon oil which has been oxidised (aged) in air. In the voluminous literature on the oxidation of a number of hydrocarbon oils with air or oxygen under various conditions, it is stated that the following substances are to be found in the residual oxidised oil: acids, carboxylic acids, asphaltogenic acids, pseudo-acids, esters or lactones and estolides and acid anhydrides (these substances are included in the saponification number). In addition to these resins, asphalts, (these substances are obtained by adsorption or fractional precipitation) and finally cokes are also found. Generally speaking, nothing definite is known about the acids or saponifiable substances, apart from the acid number, the saponification number, and acetyl number (1), the approximate average molecular weight and other physical constants of substances or mixtures of substances which have not always been completely isolated.

According to Sachanen (2), these "resins" are neutral compounds, which may be already present in the fresh oil and which may contain 2 to 3 oxygen atoms per molecule (3). These resins have an approximately constant average molecular weight roughly equal to that of the hydrocarbon oil. They are primarily formed in large quantities in heavy lubricating oils, and, according to Sachanen, they do not occur in gasolines. Marcusson (4) describes the resins as "saturated polycyclic heterocyclic compounds." Owing to "intra-molecular atomic displacement" or further oxidation accompanied by dehydration, they are converted into asphaltenes (substances insoluble in gasoline) and finally into oil-cokes.

Apart from its origin, the resistance of a hydrocarbon oil to oxidation depends on its degree of refinement. In general, as the degree of refinement increases, the resistance to oxidation rises at first, and then falls, this being accompanied by an increase in the formation of acid products (5). With regard to the mechanism of oxidation, Engler (6) assumed that the intermediate products were peroxides; this hypothesis is now being followed up, especially in experiments using pure compounds (7). Evers and Schmidt (8) give the quantity of combined oxygen, in hydrocarbon oils oxidised by their method (and calculated from the saponification number) as a constant 34% of the oxygen absorbed. Obenaus (9) finds the values are much lower and more variable. Iwanow (10) considers that the oxidation conditions indicated by him can be generalized, and shows that carboxylic acids are the main products of oxidation.

Subsequent to the completion of the analytical section of this paper, data appeared showing evidence of further oxidation products, the nature and quantity of which have only been approximately estimated. Thus, by means of the Grignard

reaction, Assaf and Gladding and other workers (11) found, in aged insulating oils, some substances which combine with the Grignard reagent (CH_3MgI) and others which evolve methane on reacting with the Grignard Reagent. They consider these reactions to be caused by, on the one hand, ketones, aldehydes, esters and peroxides, and, on the other hand, acids, alcohols, and active hydrocarbons.*)

III. SHORT SUMMARY OF THE REACTIONS AND METHODS EMPLOYED IN THIS REPORT.

Assuming that the hydroxyl groups present in an oxidised hydrocarbon oil are not included in the saponification number (and these need not necessarily occur only in combination with an acid group, e.g. in hydroxyacids), a slightly modified form of the Verley-Bölsing (12) method for essential oils - consisting of acylating in presence of pyridine, and back-titrating the unconsumed acylating agent - may be employed. The results obtained by this method, which will be considered in more detail later, have not always been found satisfactory. These results were therefore compared with those obtained by the Tschugaeff (13)-Zerewitinoff (14) method. The number of free hydroxyl groups found by this method are 4 or 5 times the number of free carbonyl groups.

An attempt was then made to obtain the remaining oxygen, which was temporarily present as oxygen bridges (acetals, ethers, stable lactones, stable peroxides etc.) or as free carbonyl groups, in a form which is easily analysed. For this purpose the oxidised oil was treated, in a bomb, with sodium alcoholate in an alcohol-benzene solution at various temperatures, in order that hydroxy-compounds may be formed (15). Here, too, expectations were fully confirmed, additional hydroxyl groups being formed in a considerably greater quantity than previously detected. It was not easy to deduce the structure of the original oxygen compound, which was apparently in the form of a "resin". From the ease with which the conversion to hydroxyl groups occurs, it appeared probable that it was rather a case of the reduction of the carbonyl groups. The ability of this oxygen compound to combine with a Grignard reagent was therefore examined. A positive result was obtained, so that one may fairly safely assume the presence of ketones, since ethers seldom react with Grignard reagents at low temperatures (16). In the meantime it appears that it is desirable to have more exact information about this oxygen compound, and therefore attempts are being made to gain more concrete knowledge of the compound by its concentration or isolation.

IV. GENERAL

The essentials of the method employed and the possibilities which it shows are discussed briefly, as far as appears necessary here. In the discussion of the analytical results which follows, it is assumed that this section has been read.

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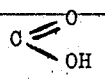
* (Assaf and Gladding believe, from experiments using pure compounds, that the "Esters" add quantitatively to the Grignard reagent, and assume that the small amount of residue remaining consists of the above-mentioned substances. How little this view is justified, will appear from the work carried out here.)

1. Determination of the acid number

The acid number covers the following classes of substances:-

(a) true carboxylic acids:

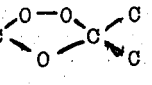


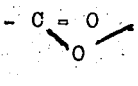
(b) pseudo-acids and substances of an acidic character. These are groups of substances such as ketones, phenols, hydroxymethylene compounds ("Oxymethylene"), hydroxylactones ("Oxylactone"), etc. It is improbable that they are present in large quantities.

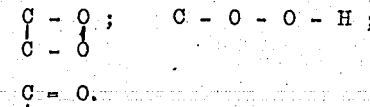
The acid number (and saponification number) are determined in principle by the conventional method, described in "Holde" (1936), using Alkali Blue 6B as indicator. A discussion of this determination in this report is unnecessary.

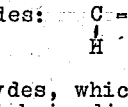
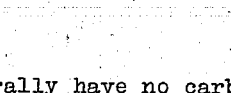
2. Determination of the saponification number

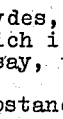
The saponification number, after allowing for the substances included in the acid number, covers the following classes of compounds:-

(a) acid anhydrides:  ; peroxides e.g. 

(b) normal esters:  lactones: 

Estolides: 

Peroxides:  ;  ;

Aldehydes: 

(i.e. Aldehydes, which generally have no carbon atom, bearing hydrogen which is directly linked with the carbonyl group; that is to say, those which give the Cannizzaro reaction.)

The substances given under (a) do not produce esterifiable hydroxyl groups on saponification, while those given under (b) produce hydroxyl groups which are, in some cases, formed in equivalent quantity. Thus, in principle, it is possible to determine the percentage of the substances given under (a) and (b). (acetylation by the Verley-Bölsing method, or determination of the increase in active hydrogen by the Tschugaeff-Zerewitinoff method in which the increase in the acid number is determined.) It is possible that the hydroxyl groups formed which do not come from esters (reduction of carbonyl groups) would have a disturbing influence on the reaction. The saponification and subsequent treatment should therefore be carried out under the mildest possible conditions.

Results naturally vary according to the time taken for saponification and the strength and the water content of the alcoholic caustic alkali solution employed. The effective value could be approached by first carrying out a preliminary saponification with a strong caustic alkali solution, quantitatively recovering the saponified oil, isolating the esters (possibly lactones) so formed and determining them with $N/_2$ or 2N-KOH.

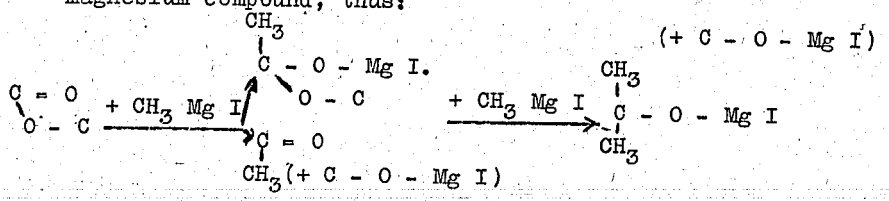
The behaviour of the substances, identified by means of the saponification number, with Grignard reagents is also of interest. A suitable procedure for this is as follows:

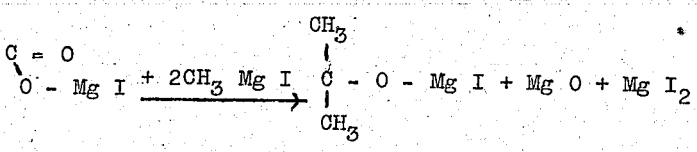
Aged oil is heated to 155°C with sodium alcoholate in alcohol-benzene solution (see page 12). This results in the almost quantitative conversion of the combined oxygen, which (according to previous experience) would combine additively with the Grignard reagent (if present), into hydroxyl groups, while the "esters" are not reduced, even at 200°C. (No reduction in the saponification number occurs in forming alcohols or hydrocarbons.) A fixed quantity of methyl magnesium iodide is added to the oil which has been pre-treated with sodium alcoholate; heat is then applied, resulting in the evolution of methane, the quantity formed corresponding to the amount of active hydrogen present:-

$$R - H + CH_3\,Mg\,I \longrightarrow CH_4 + R\,Mg\,I.,$$

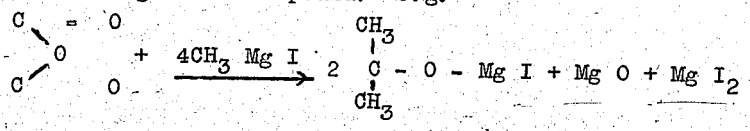
- while addition simultaneously takes place. If the excess methyl magnesium iodide is decomposed by an excess of a substance containing active hydrogen, e.g., aniline, methane will also be formed. Comparison with a blank experiment would then give the saponification number if:-

1) The "esters" and acids (17) take up two molecules of the magnesium compound, thus:





All the substances under IV 2, (a) and (b) (p. 6), including carboxylic acids, normally* act in this way (in presence of an excess of Grignard reagent), with the exception of acid anhydrides, which can combine with (one), two or 4 moles (18) of the magnesium compound: e.g.



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* If they react at the temperature of the experiment.

Other exceptions are the aldehydes, which add one molecule, and a few peroxides, whose behaviour towards the Grignard reagent is unknown.

2) The esters are practically speaking not enolised, since otherwise the Grignard reagent would react with the hydroxyl groups which form and thus displace the equilibrium in favour of enol formation. This is illustrated by the speed with which the equilibrium of the desmotropic mixture is adjusted and the speed with which the two Grignard reactions occur. However, serious error in this direction is not to be expected under the conditions of the test.

The value obtained with the Grignard reagent is actually much less than that obtained when carrying out preliminary saponification. However it is interesting to note that the two values become almost identical if we assume that the acids present after treatment with alcoholate (the acid number increases approximately 3 or 4-fold) do not react quantitatively with the organo-magnesium compound, while the remaining "esters" do. It is, however, impossible* to draw conclusions concerning the reactivity of the acids, normal esters, lactones, acid anhydrides etc., present in the used oil, towards Grignard reagents. In any case, a knowledge of the relative rates of reaction of the individual groups with the Grignard reagent greatly facilitates the evaluation of the Grignard analysis. Naturally the structure of the compound in other respects, i.e., its solubility, the solubility of the intermediate products of reaction with Grignard reagent, etc. must be taken into account (Thus, according to Houben (18), the reaction of citraconic anhydride with methyl magnesium iodide is almost "explosive" while succinic anhydride requires weeks or even months for reaction to occur.) According to C.E. Entemann (19), the reactivity of the groups is in the following descending order:-

$-CHO$ $-COCH_3$ $-NCO$ $-COF$ $-COC_6H_5$ $-COCl$ $-COBr$ $COOC_2H_5$.

The only interesting point here, which concerns us in this paper, is the greater reactivity of the carbonyl group compared with the ester group.

3. Detection and Determination of Free Hydroxyl Groups (Hydroxyl value, in mg KOH/g of oil):-

(a) Acetylation in presence of pyridine

The following compounds are discussed: primary, secondary, and, as an exception, tertiary alcohols, (enols), and phenols.

(b) Determination of active hydrogen with Grignard reagents.

The following compounds are discussed:

substances under (a) with quantitative determination of the tertiary alcohols, substances given under IV 1 (acid number), enols and other compounds containing active hydrogen, such as hydrocarbons (e.g. cyclo-pentadiene (20), indene, and fluorene (21) or their derivatives), ≡ CH groups and normal hydrocarbon compounds containing activated groups such as $C_6H_5CH_2COOMgI$ (22), etc.

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* It is doubtful whether we have to deal with those substances which can be determined by the saponification number.

Procedure (a):

Acetylation was carried out by the Verley-Bölsing method, i.e. with acetic anhydride in the presence of pyridine:-

$$R - OH + (CH_3CO)_2\ O.\ C_5H_5\ N \longrightarrow$$

$$ROCOCH_3 + CH_3\ COOH.\ C_5H_5\ N$$

The excess acetic anhydride which has been saponified with aqueous alkali or water, and the acetic acid, which was freed by acetylation, is then back-titrated using phenolphthalein as indicator. In order to observe the colour change, the determination was carried out in a carbon tetrachloride solution, care being taken to ensure that the concentration of sodium acetate in the remaining aqueous solution is always approximately constant, and has an approximately constant temperature.

The advantage of this method is that it is relatively speaking economical, and permits the degree of esterification to be measured directly, without isolating the acetyl product, or removing the unreacted anhydride. The disadvantage is that, in spite of the mild conditions, the acetic anhydride has a great tendency to dehydrate other substances, so that, in the presence of free acid, these other substances can actually be partially converted into anhydrides with or without formation of an acetylated compound. In the case of quantitative dehydration, with the formation of an acetylated compound, too high a hydroxyl value (Hydroxydzahl) is obtained in relation to the acid number and, in the case of a reaction involving quantitative "non-dehydration", the maximum hydroxyl value is too low. These two extreme cases cannot be assumed a priori, so that the error must be considerably less. With pure palmitic acid, there was a positive error of about 30% of the acid number (in this determination using pure compounds acetyl-acyl-ether types of compound predominate) (23). There is no danger of exchange of ester radicals (with a consequent dehydration of the freed acid) under the given conditions. The possible increase in degree of saponification of the acid anhydrides produced by pyridine is not shown by an increased consumption of aqueous KOH. Acylation by the type of anhydride present, or closing of the lactone ring by acetic anhydride was not observed.

The following facts and results are sufficient to show that the corrections to be applied for the acids present, cannot be great: sharp increase in the acid number is obtained on saponification and on comparing the hydroxyl values (Hydroxylzahlwerte) obtained with those obtained by the Tschugaeff method. The "neutral oxygen" present is converted into hydroxyl groups by means of sodium alcoholate (resulting in a sharp increase in the acid number) and the hydroxyl value is correctly determined with Grignard reagent. Thermal decarboxylation and treatment as under IV, 4a (page 13). The last-named tests will be reported in the next report. When the acid number is increased, it must be borne in mind that the OH groups, which form during saponification, might be of a tertiary nature and can thus be determined with a Grignard reagent, but not by acetylation. However, even in this extreme case, the error is only half the acid number (see the Experimental Section: Oil $S_{275^\circ 23}$ hrs.)

Procedure (b): Determination of active hydrogen by the Tshugaeff-Zerewitinoff method.

By the use of methyl magnesium iodide active hydrogen is obtained in the form of the methane produced. In this case, as

already mentioned, carbonyl groups, alcoholic and phenolic groups and hydroxyl groups formed by enolisation are also involved. Hydrocarbons can be ignored for the present. By comparing the values obtained by (a) and (b), we may deduce the presence of tertiary groups, or hydroxyl groups (including enols) which cannot be esterified or only esterify with difficulty. The possibility that the Grignard reagent has a reducing effect (towards carboxyl groups, esters etc.) must be borne in mind, since the formation of hydrocarbons may occur. When methyl magnesium iodide, which may form ethane, is used this contingency can be ignored (24).

With regard to analyses made with Grignard reagents, it can be stated that, in general, the results vary according to the experimental temperature and concentration, which may be due to either the slowness of reaction between individual compounds, or the displacement of the tautomeric equilibrium. The present method is to allow the reagent to react for 20 minutes both at room temperature and at 90°C. Higher temperatures cannot very well be used, since the ether used here for the smooth reaction (with which, according to Meisenheimer, the organo-magnesium compound combines) would otherwise react with the methyl magnesium iodide. Since the Grignard reagent also reacts (25) with molecular oxygen, the oil which is being tested must be freed from air in accurate determinations. The quantity of dissolved oxygen is, however, generally very small. After the Grignard reagent has been standardised, it must be kept free from air, and, if stored in a dark place, its quantitative efficiency will be preserved for some months.

The results can be satisfactorily reproduced.

4. Detection and Determination of "Neutral" Oxygen (in mg. KOH./g. of oil).

(a) Treatment with sodium alcoholate in alcohol-benzene solution at temperatures above 150°C and determination of the resulting hydroxyl groups as in Section IV, 3.

This covers the following:- ether-like substances, ketones (aldehydes) and peroxides.

(b) Treatment with Grignard reagent at temperatures below 100°C, and determination of the organo-magnesium compounds used up without the formation of hydrocarbons.

This includes the following substances: ketones (aldehydes), peroxides, substances determined under Section IV, 2, carboxylic acids, and compounds having a "weakened" ether link.

Procedure (a):

Sodium alcoholate was allowed to react with the oil at 155°C for 5 hours in a sealed bomb, the oil then being recovered quantitatively. Since the resulting alkali number (Hydroxyl-zahl) remains practically constant at temperatures between 130°C and 200°C, the reaction is assumed to take place quantitatively at 155°C. The saponification number also remains practically unchanged up to 200°C, so that the "esters" are not reduced to alcohols. One cannot assume the addition of the hydroxyl groups to double bonds etc., since hydroxyl values remain constant in oils having different thermal treatment. Although the possibility of the formation of even less common compounds should be mentioned, its discussion here is unnecessary. The secondary formation, at high temperature, of such oxygen compounds from hydroxyl groups present, (i.e. formation of

ketones by dehydrogenation, formation of ethers by dehydration) was not observed.

As already stated, treatment with sodium alcoholate may result in either a reduction of carbonyl compounds (ketones) or the fission of the ether link. The latter reaction would occur in the following way:-

$$R - O - R' + 2\ Na - O - R_1 \longrightarrow$$

$$R - O - Na + R' - O - Na + R_1 - O - R_1 ,$$

so that two hydroxyl groups per molecule would be formed.

It is scarcely necessary to consider peroxides and aldehydes here, owing to the great thermal stability of the compound in the aged oil (e.g. at 400°C) and the resistance to alcoholic caustic alkali and acids.

Since alcohol having a low water content (absolute alcohol from Kahlbaum) was used for preparing the alcoholate, the possibility of the additional formation of ethyl esters, when esterification is being carried out, must be considered, whereby additional hydroxyl groups would be identified in the oil. However, it would take too long to discuss here all the possible effects of the sodium alcoholate.

Procedure (b):

The organo-magnesium compound was allowed to react with the oxidised oil at 90°C (100°C) in different proportions. The values obtained, as already mentioned, cover practically all carboxylic acids and saponifiable substances with the exception of carbonyl compounds (and peroxides and ethers, which cannot be saponified to acids). When the saponification number was discussed (IV, 2), it was shown that, after treating a used oil with sodium alcoholate there remains a certain "capacity for addition" to the Grignard reagent, which, however, only corresponds to that part of the substances which can be estimated by means of the saponification number. It is impossible to say at present how far this "capacity for addition" can be attributed to substances which were already present in the oil, (e.g. esters, lactones, acid anhydrides, acids, etc.) or to secondary products of the aocoholate treatment, such as, for example, acids formed by saponification of the esters (the acid number increases 3 or 4-fold). One cannot, naturally, exclude the possibility that some of the substances dealt with here are not those included in the saponification number, but are any compounds which do not react with sodium alcoholate (i.e. ethers, ketones which are difficult to reduce, etc.). It is therefore by no means certain what, or how much, must be subtracted from the value obtained by direct reaction of the Grignard reagent with a used oil, in order that a comparison may be made with the values obtained for substances covered by IV, 4a.

These facts can be explained, however, by comparing the "capacity for addition" of the "esters" for Grignard reagent with that of the acids resulting from treatment with alcoholate, without considering the absolute quantity involved. For this purpose a preliminary saponification is carried out where necessary, under the same conditions as for the alcoholate treatment, except that lower temperatures must be used here. (See Experimental Section). The influence of possible esterification which might occur on treatment with the alcoholate and which could also alter the "capacity for addition" towards Grignard reagent, is best determined by comparing the results of the

alcoholate treatments using aqueous and absolute alcohol. The preliminary saponification is sufficient to show, without indulging too freely in speculation, that it should be possible to indicate and discuss here a few simplifications which would give a clear-cut picture of the situation and of possible available means of differentiation.

At the conclusion of the Experimental Section the facts are presented as they most probably occur, with examples, and it is shown that, in spite of the somewhat obscure state of affairs, it is possible for satisfactory conclusions to be reached. (A simplified summary showing the possible forms of oxygen compounds appears on p. 36)

V. EXPERIMENTAL METHODS

1. Oxidation (Ageing) of Hydrocarbon Oils.

To establish more general facts about the oxidation of refined hydrocarbon oils (aviation oils), an examination was made of two paraffin-base oils (Pg and Ps), a naphthene-base oil (N) and a synthetic oil (S).

Table 1.

Some Physical Characteristics of the Oils.

Type of Oil	Density (D_{20})	Refraction (n_{20}^{D})	Molecular weight	Viscosity E_{50}
P_g	0.882	1.4878	691	23.2
P_s	0.890	1.4927	715	24.2
N	0.911	1.5019	612	19.8
S	0.854	1.4736	730	20.6

The oxidation is carried out in a half-open steel vessel (30 cms diameter, 9 cms high), using charges of 2 to 3 kg. The temperature of the oil, which was heated in a tin bath, is kept constant to within ± 1°C. The oil was stirred during ageing, which was only carried out during the day-time (an iron stirrer is used; area of vanes = 10 x 3 sq. cms). The whole apparatus was placed in a well ventilated, half-closed fume cupboard.

The conditions of "ageing" in each case are indicated in the following manner. The oils are identified in such a way that the first letter indicates the character of the basic oil, while the numbers indicate the temperature and time of heating. The letters following the numbers indicate the nature of the subsequent treatment:

Pg 250° 23 hrs: Weight of oil, 2,500 to 3,000 gms aged at 250°C for 23 hours. Ash content of the oxidised oil, 0.21 mg/g.

Pg 275° 23 hrs: Weight of oil, 2,720 gms, aged at 275°C for 23 hours. Loss by evaporation, 24.5%.

Pg 275°: Weight of oil, 2,930 gms. Samples of 100 to 160 gms. were taken after 7.5, 15, 23, 31, 38.5, 46 and 53.5 hours. After 60 hours, oxidation was discontinued; 710 gms of a pitch-like material remained. The loss by evaporation was approximately 40.5%.

Pg 300°: Weight of oil, 2,860 gms. Samples of 50 gms were taken after 8, and 16 hours. Total duration of ageing, 23 hours; loss by evaporation, 42.6%.

Pg 300° H_2O: Weight of oil, 2,780 gms. Damp air was also passed through the oil (50 litres per hour; 2.9 gms H_2O per hour). Samples of 50 gms were taken after 8 and 16 hours. Duration of test, 23 hours. Loss by evaporation, 49.8%.

Ps 250° 23 hrs: Weight of oil 3,500 gms. (aged at 250°C for 23 hours).

N 250°: Weight of oil, 2,650 gms. 60 g. and 90 g. samples were taken after 8 hours and 16 hours. Total duration: 23 hours. Loss by evaporation: 24.3%.

S 275°: Weight of oil, 1,750 gms. Samples taken after 9 hours and 17 hours (85 and 80 gms.) Total duration: 23 hours. Loss by evaporation, 41.6%.

(The loss by evaporation is related in each case to the total duration of the test).

The asphalt determinations, which were carried out on the principle laid down by Holde in "Hydrocarbon Oils and Greases" (1933), (in determining the hard asphalt, petroleum ether from Kahlbaum having a boiling range of 30 to 50°C was used instead of normal gasoline.) gave the following results:

P_g 250° 23 hrs: Neither hard nor soft asphalt formed.

P_g 275°: No asphalt up to an ageing time of 38.5 hours.

P_g 275° 46 hrs: 5.4% soft asphalt, no hard asphalt.

P_g 275° 53.5 hrs: 15% soft asphalt, no hard asphalt.

P_g 275° 60 hrs: 22.1% soft asphalt, and traces of hard asphalt.

P_g 300° 23 hrs: Traces of soft asphalt, no hard asphalt.

P_g 300° H_2O 23 hrs: Traces of soft asphalt, no hard asphalt.

S 275° 23 hrs: No soft asphalt, no hard asphalt.

2. Acid and Saponification number:-

The acid and saponification number were determined, as laid down in Holde: "Hydrocarbon Oils and Greases" (1933), with 10 times the quantity of benzene-96% alcohol mixture (2:1) and using alkali blue 6B as indicator (1% solution in 96% alcohol). Unless otherwise indicated, saponification was continued for one hour with N/2 alcoholic caustic potash. Tables 2 and 3 show the influence of the strength of the alkali, the duration of saponification, etc.

Table 2.

Variation of the Acid and Saponification Number with Ageing Period.

P_g 275°

Ageing Period	7.5	15	23	31	38.5	46	53.5	60
Acid No. (N/10 KOH)	0.38	0.59	0.96	1.42	1.74	1.76*	2.06	2.21
Saponification No. (N/10 KOH)	1.15		3.54	4.62	5.78	8.04	10.68	11.23
(N/2 KOH)			4.43	6.88	8.21	10.13	14.95	17.24

*In this acid number determination the change of colour was particularly difficult to observe.

Table 3.

Variation of Saponification Number with Conditions of Saponification.

P_g 275° 23 hrs

Saponification Period (in hours).		0.5	1	3	7
Saponification Number:	N/10 KOH	3.32	3.54	4.18	5.27
	N/2 KOH	4.07	4.43	4.92	

S 275° 23 hrs

Saponification Period (in hours)		0.5	1	3
Saponification Number:	N/10 KOH		6.41	6.8
	N/2 KOH	8.35	8.90	9.25
	2N. KOH	9.0		10.6

An attempt to determine the acid anhydride by titrating the oil, after pre-treatment with pyridine, by means of an alcoholic solution of caustic alkali, was unsuccessful. (This pyridine treatment was carried out to increase the degree of saponification of anhydrides with water or aqueous alcohol.)

3. Hydroxyl Value.

The acetylation is carried out in a 100 cc Erlenmeyer flask with a ground-glass stopper or a ground-glass delivery tube, the upper end of which is drawn out to form a capillary. A fixed amount (7.00 gms) of the aged oil is weighed into the flask and 15 ccs of a solution containing 10 parts of acetic anhydride, 50 parts of pyridine and 115 parts of carbon tetrachloride is added from a burette. The flask is closed and allowed to stand overnight; a delivery tube is then fitted to the flask which is heated for three hours on a water bath at 65-75°C. After cooling, a solution of 3 parts by weight of sodium acetate ($CH_3COO\ Na.3H_2O$) in 10 parts by volume of water (10 ccm) is added to the reaction mixture and this is then shaken cautiously for one minute with simultaneous cooling. About 75% of the volume of N/2 Na OH given by a blank determination is then added from a burette, and this is shaken for half a minute. After adding 2 to 3 drops of phenolphthalein, the mixture is titrated until a permanent pink coloration is observed. The difference between the consumption of N/2 NaOH found in this way, and that found in a blank test with unused oil gives the increase in free hydroxyl groups.

To determine the effect of the free acids or anhydrides present, (apart from the acetic anhydride) the oil was treated with pyridine-carbon tetrachloride solution (without anhydride) as above and, after adding the same volume of sodium acetate solution as is formed at the end of a normal test, the titration was carried out. One may thus ascertain the maximum error which can occur if the acids are not de-hydrated or the anhydrides are saponified. The values obtained are, on the average, 50 to 75% of the acid number.

In order to find out the most favourable reaction temperature for the analysis, the following tests were made with an aged oil:

Table 4.

Heating Period (hrs)	1	1	3	5.75	5.75	17
Approximate Temperature (°C)	70	100	70	70	100	20
Hydroxyl value (mg. KOH/g)	5.2	5.05	5.6	5.55	3.30	4.1

It will be observed that at 100°C (boiling water-bath) there is a reduction in the Hydroxyl values. The addition of 0.15% water before heating does not alter the values. The results remain constant if the oil is first treated with pyridine-carbon tetrachloride for 3 hours at about 70°C, and then re-heated for a further three hours after the addition of acetic anhydride.

The increase of the hydroxyl value with ageing is illustrated in the case of P_g 275° 23 hrs:

Table 5.

Ageing Period (hrs)	7.5	15	23	31	38.5	53.5	60
Hydroxyl Value (mg KOH/gm)	2.97	4.27	5.60	7.78	7.30	8.00	8.10

The hydroxyl values in this report are given as they were recorded, without any corrections whatsoever and in the Discussion of the Experiments, reference is made to their probable effective values.

The reproducibility is good, as can be seen from the following hydroxyl values for P_g 250° 23 hrs and P_g 275° 23 hrs which were obtained throughout the course of a year;

P_g 250° 23 hrs: Difference, in N/2 Na OH, compared with the blank experiment: 1.00, 0.98, 1.02, 1.08, 1.10, (1.24), 1.10.

P_g 275° 23 hrs: Difference, in N/2 Na OH, compared with blank experiment: 1.98, 2.00, 1.95, 2.17, 2.11, 2.07, 1.98, 2.04.

The burette used was a normal calibrated one with divisions of 0.1 cc, so that the variations could have been due to errors in reading.

4. Treatment with Sodium Ethoxide

20 gms of the oil under test is weighed into a 50 cc Erlenmeyer flask and poured into a Durobax bomb with 50 ccs of benzene. 40 ccs of a sodium ethoxide solution are cautiously added to the benzene solution. (4 gms of sodium are added to 100 ccs of absolute alcohol*) in an Erlenmeyer flask with a delivery tube and a bunsen valve.) The bomb is then sealed, the reaction mixture is dissolved by warming, if necessary, and heated in a bomb furnace for, e.g. 5 hours at 155°C. After cooling, the bomb is opened, the contents are poured into a 100 cc distillation flask (rinsing once with benzene and once with absolute alcohol) and the liquid evaporated down, in a stream of nitrogen, on an oil-bath at a temperature of 65-70°C, the pressure being 20 mm Hg. The residue is left to cool in the stream of nitrogen, and is then transferred to a separating funnel with 100 ccs of ether and shaken with 30 ccs of water for a short time while cooling. During cooling, 20 ccs of 20% sulphuric acid containing 10% of sodium sulphate, are added in three portions, and shaken for 10 minutes. After allowing the mixture to stand, the lower aqueous layer is separated off, quantitatively if possible (adding if necessary some solid sodium sulphate). The ether layer is then shaken with a saturated aqueous sodium sulphate solution, the wash liquid is drained off and the ether solution is dried with ignited sodium sulphate. After filtering into a 100 cc distillation flask the ether is distilled off and the residue is finally "dried" for an hour in a stream of nitrogen at 10 mm Hg and at an oil bath temperature of 90 to 95°C (60°C is sufficient for light oils).

To establish the order in which the reaction occurs, an initial experiment was carried out in the bomb furnace used here, keeping the temperature constant to within $\pm \frac{1}{2}$°C by electrical control. The results obtained do not merit a profitable investigation of the kinetics of reaction to be made for the present. P_g 275° 23 hrs was heated on an "air bath" at 105°C for 215, 400, and 775 minutes. The resulting effective hydroxyl values are 3.7, 3.4 and 5.4 mg. KOH/gm.

*The "absolute alcohol" used was from Schering-Kahlbaum.

When 96% alcohol is used to prepare the sodium alcoholate solution, the characteristic numbers (including acid and saponification number) are practically the same as with "absolute" alcohol.

Table 6 shows the results of sodium alcoholate treatment on the various aged oils. The figures as previously found for the acid number and saponification number are given for comparison.

Table 6

Results of Treating Various Aged Hydrocarbon Oils with Sodium Alcoholate.

Aged Oils		Before treatment with Sodium Alcoholate				After treatment with Sodium Alcoholate				
No	Description	Acid No.	Sap. No N/10	Sap. No N/2	Hydroxyl Value	Acid No.	Sap. No. N/10	Sap. No. N/2	Hydroxyl Value	Effective Hydroxyl Value
1	P_g	0.0	0.04		0.0	0.0	0.0		0.1	0.1
2	$P_g 250^0$ 23 hrs	0.71	2.50		3.1	2.43	3.55		8.4	5.3
3	$P_g 275^0$ 23 hrs	0.98	3.47	4.43	5.6	3.50	5.30	6.12	15.2	9.6
4	$P_g 275^0$ 38.5 hrs	1.77	5.78	8.20	6.95	6.50	8.75		20.4	13.45
5	$P_g 300^0$ 23 hrs	1.45	4.70	6.42	7.2	4.6	8.10		19.8	12.6
6	$P_g 300^0$ 23 hrs H_2O	1.65	6.75		7.3	6.1	11.3		20.6	13.3
7	$P_s 250^0$ 23 hrs	0.67	2.6		3.9	2.2	4.14		10	6.1
8	N 250^0 23 hrs	1.15	3.90		5.0	5.15	7.36		11.6	6.6
9	S 275^0 23 hrs	1.92	6.40	8.90	8.1	7.25	10.5	11.5	25	16.9

Further tests will be made to ascertain whether it is better to use sodium amylate instead of the sodium alcoholate, and to avoid the use of bomb tubes.

5. Analyses with Grignard Reagent

The organo-magnesium compound is prepared by allowing 250 ccs of iso-amyl ether distilled over sodium, 19 gms of magnesium, and 70 gms of methyl iodide to react in an atmosphere of nitrogen. The excess of methyl iodide was expelled in a vacuum with nitrogen using an oil bath temperature of 50°C and the reaction mixture containing the excess magnesium filtered off in an atmosphere of nitrogen.

The analysis was carried out with the apparatus shown in Fig.1. This consists of a supply vessel (A) of 300 ccs capacity and a burette (B), which will hold 10 or 5 ccs. The latter is divided into 0.1 cc divisions, but can still be

accurately read off to 0.01 cc. The intermediate section (C), the reaction vessel (D), the delivery tube (F), the attachment (E), and the burette are supplied with normal ground-glass joints.

The supply vessel is filled (after the air in (A) and (B) has been entirely displaced by dry nitrogen) without allowing the reagent to come into contact with air, since otherwise a precipitate would form which would block the outlet tube of the burette. The burette is filled by creating an excess pressure in the vessel (A) with nitrogen*. On connecting up the gas chambers (A) and (B) the burette is emptied. The end of the burette, which is drawn out into a capillary, is closed with a glass rod inserted in a piece of rubber tubing**.

For carrying out the analysis, 2.5 gms of oil are transferred into the wide part of the vessel (D)***, which is first warmed and then uniformly dried, together with 8.0 or 4.0 ccs of anisole (distilled over sodium). The intermediate section (C) is smeared with "apiezan" grease (only the upper half of the stopper to be greased) and inserted into the reaction vessel. The air is expelled from the vessel (D) with nitrogen, by means of the induction tube (F). (blow out the two arms alternately, 4 times every 5 minutes). The tube (F), now closed, is carefully lifted out in the stream of nitrogen by connecting it to the nitrogen supply by means of the cock 4 (displace the air from the connection). This is carried out by laying a strip of dry cloth round the tube and stopper. After removing the rubber, the tube (F) is inserted through the burette connection, into (C) (D). A strip of filter paper is forced between the ground glass joints to enable the stream of nitrogen to escape. After connecting (C) to (B) (with the aid of spiral springs) a certain volume of Grignard reagent is allowed to flow into the narrow arm of (D).

After carefully removing the burette and fitting (E) (which serves to admit a certain volume (2 ccs) of a 1:1 mixture of aniline and anisole, first cock 5 and then cock 4 are closed. The reaction vessel, which has been filled in this way, is then connected to the three-way cock of the gas-collecting burette, the air between cock 4 and the burette is displaced by nitrogen and, after equalising the pressure of the reaction vessel at room temperature it is connected with the burette. The rest of the analysis is self-evident. It is advantageous to work always at the same reduced pressure (2 to 5 cm of mercury) when shaking the reaction mixture.

The duration of the reaction at 90°C was 20 minutes, while at low temperatures (20°C) it was allowed to continue (with repeated shaking) until the volume did not change within five minutes. Throughout the test the temperature of the reaction

*The Osram-Glühlampen Company, Berlin supplies nitrogen containing only 1/10,000% of oxygen.

**The rubber is changed each time before using the reagent, after draining off a small volume and also each time after use; it was not observed that the rubber had a bad effect on the reagent.

***The vessel is best dried at 110°C, especially if the reaction vessels have been used for analysis for a long time.

vessel is kept constant and equal to the external temperature. The reaction mixture is then heated (to 90°C) in a water bath next to the reaction vessel.

The collecting burette has a capacity of 100 ccs. The values of blank determinations shall not be more than 80 ccs. Table 7 shows the results obtained from the Grignard reaction compared with those obtained by acetylation, or, to put it another way, the results obtained by the sodium alcoholate treatment compared with those obtained by the effect of the organo-magnesium compound on the aged oil. The Grignard solution used was about 0.9 molar in Experiments 1 to 7 and 11-15 (Table 7), and in Experiments 8, 9 and 10 it was about 1.3 molar. The reaction mixture in its unreacted state (with the exception of Experiment 10 (0.4 molar)) was 0.25 to 0.28 molars in relation to methyl magnesium iodide. In comparing the results, the conditions as regards temperature, concentration, and time must naturally be taken into account. Under the test conditions which are given here, only the temperature has a pronounced influence.

The reproducibility is as follows:-
In determining active hydrogen ± 0.25 cc methane, i.e. about ± 2% of the actual value;
In determining the blank values (effective values) ± 0.5%;
In determining the acid groups with which the Grignard reagent combines, ± 0.5 cc of methane*.

In accurate experiments the blank value with 300 ccs of Grignard reagent does not alter by more than 1 cc.

6. Preliminary Saponification

The preliminary saponification was carried out in the same way as the normal determination of the saponification number. The conditions are evident from Table 8 and, in part, from Table 7. The saponified oil was worked up exactly as in V, 4 after treatment with sodium alcoholate. The relation of the volume of sulphuric acid added to the alkali present is such that the aqueous solution which results after neutralisation contains about 2% sulphuric acid.

As mentioned in the General section, the object of the preliminary saponification was to show how the hydroxyl value after saponification (determined by acetylation) compares with the increase in the acid number or with the hydroxyl value as determined by the Zerewitinoff method. In this way conclusions may be drawn about acid anhydrides and the influence of the acids on the method of acetylation, and whether and to what extent the "capacity for addition" to the Grignard reagent is changed by the saponification and subsequent working up (see Table 7, Experiments 9, 10 and 15). Finally, the maximum attainable saponification number, which probably approaches the effective value, is determined in the above way. The results of Test 2 may have been obtained, in some cases, by the formation of OH groups from the acetals present.

*When several tests were made and an average taken, the margin of error naturally diminishes considerably; the same is true when series of analyses are carried out.

Table 8.

Variation of the Saponification, Acid and Hydroxyl Numbers after Preliminary Saponification.

Expt. No.	Description	Acid No.	Increase in acid No.	Saponification No. N/10	Saponification No. N/2	Hydroxyl Value Det. by acetylation.	Increase in Hydroxyl Value	Hydroxyl Value at 20° by Zerewitinoff	Hydroxyl Value at 90° by Zerewitinoff	Increase in Hydroxyl Value Method
1		2.84	1.86	3.69		6.45	0.85			
2	P_g 275° 23 hrs.	1.69	0.71	3.32		5.60	0.0			
3		2.47	1.49	4.21		5.65	0.05			
4		2.45	1.47	2.96		5.4	-0.2			
5		3.65	2.67		6.65	8.08	2.48			
6	P_g 300° 23 hrs.	4.0	2.55			8.1	0.9		14.10	1.3
7		7.07	5.15		13.86			10.8		1.92
8	S 275° 23 hrs.	6.72	4.80	10.0				10.53		1.65
9		6.68	4.76		11.36	10.2	2.1	10.72	14.07	3.49* 1.84**

*Increase at 90°C.
**Increase at 20°C.

Table 8. (Test conditions)

1) 16 g P_g 275° 23 hrs: 160 ccs of benzene-alcohol (2:1)
50 ccs N/10 alcoholic KOH; 1 hour.

2) 16 g P_g 275° 23 hrs: 100 ccs of benzene + 50 ccs alcoholic H_2SO_4 (95 g abs. alcohol + 5 ccs H_2O + 3 g H_2SO_4). 1 hour. After saponification, neutralise with alcoholic caustic alkali, then work up in the normal manner.

3) 16 g P_g 275° 23 hrs: 160 ccs of benzene-alcohol (2:1)
50 ccs of N/10 alcoholic KOH. 1 hour.
After saponification, neutralise with N.HCl, then work up in the normal manner.

4) 20 g P_g 275° 23 hrs: 200 ccs of benzene-alcohol (2:1)
100 ccs of N/2 alcoholic KOH; boil for 30 minutes; after adding 100 ccs of H_2O, boil again for 30 minutes; mix in a separating funnel with a sufficient amount of water such that the solution contains 50% alcohol; shake, drain off and extract 3 times with 50% alcohol containing 2 to 3% of alkali.

5) 18 g P_g 275° 23 hrs: 185 ccs of benzene-alcohol (2:1)
50 ccs of 2N alcoholic KOH; 1 hour.

6)	23 g P_g 300° 23 hrs:	230 ccs of benzene-alcohol (2:1) 57.5 ccs of N/2 alcoholic KOH; 1 hour.
7)	16 g S 275° 23 hrs:	160 ccs of benzene-alcohol (2:1) 50 ccs of N/2 alcoholic KOH; 2 hours.
8)	20 g S 275° 23 hrs:	200 ccs of benzene-alcohol (2:1) 50 ccs of N/2 alcoholic KOH; 2 hours.
9)	25 g S 275° 23 hrs:	250 ccs of benzene-alcohol (2:1) 62.5 ccs of N/2 alcoholic KOH; 1 hour.

7. Reduction with Sodium in Alcohol-Benzene Solution

The reduction was carried out by adding small pieces of sodium to a solution of the aged oil in alcoholic benzene in the cold and allowing the reaction to take place on a water bath. The result is similar to that of the preliminary saponification, except that the acid number, saponification number, and hydroxyl number increase by 15 to 25%. Since too few experiments were made and they were also, in part, non-reproducible, it was not possible to go into these results in more detail.

(The increase in acid number and saponification number, apart from the peroxides etc., could also be caused by the presence of ortho-hydroxy-acids).

8. Attempt to Isolate the Hydroxyl Compounds by Forming the Sodium Alcoholate.

An attempt was made to form acid esters by esterifying with phthallic anhydride and succinic anhydride in the presence of pyridine, so that the hydrocarbons could be more easily separated. The result of the acylation was so bad that no further experiments were carried out. An attempt to acylate the hydroxyl group in the form of the sodium alcoholate was also unsuccessful (26).

Isolation of the sodium alcoholates (carrying out, among others, an experiment with tertiary sodium butylate) which should be converted, by the secondary alcohols formed by the treatment of the alcoholate, into the sodium salts of these secondary alcohol groups (27), also produced unsatisfactory results. (The alcoholate mixture - obtained by heating in the bomb tube as in V, 4 - was evaporated at an external bath temperature of 90 to 150°C in a vacuum in presence of nitrogen until dry, again suspended in sodium-dried petroleum ether and decanted (with the aid of a centrifuge), so freeing it of the hydrocarbons. The sodium alcoholates appear to be somewhat "soluble" in the petroleum ether.)

An attempt to isolate the compound by adsorption, from a dry petroleum ether solution, on to powdered, freshly heated calcium chloride likewise gave a negative result.

DISCUSSION OF THE EXPERIMENTS

A few examples are available to construct only a rough picture of the oxygen compounds present without going into details, since the number of experiments made is not sufficient to take into account and evaluate all the possibilities indicated in the General section. The conclusions which can be drawn from the above experiments are sufficient for the purpose of this work, so that there is no need for further work at the present.

The following conclusions on the influence of acids present in aged oil on the hydroxyl value and of the conclusions drawn as to the presence of acid anhydrides, still require final confirmation, since they are only based on the results of the tests in Table 8 (preparatory saponification). The other figures are averages of two or more experiments, and may be relied on.

1) and 2) Nothing need be said about the acid and saponification number. The acid anhydrides will be discussed in connection with the hydroxyl value.

3) Hydroxyl Value.

Table 4 shows that the hydroxyl values vary according to the test conditions. The conditions of acetylation (3 hours at 70°C) should bring about a practically quantitative esterification, at least of the secondary alcohol groups obtained after the sodium alcoholate treatment. Comparison of tests 3 and 5, Table 7, shows that the hydroxyl value obtained by the Zerewitinoff method, increases by 8.56 (from 8.90 to 17.46) and the hydroxyl value obtained by acetylation by 9.6 (from 5.6 to 15.2). The fact that the hydroxyl values obtained by acetylation is greater than that by the Zerewitinoff method is explained by the existence of enols, which would be reduced as the result of the alcoholate treatment, and replaced by secondary alcohols. The total hydroxyl value after treatment with alcohol is found to be 2.26 greater when determined by Grignard reagent than when determined by acetylation. It is impossible to say whether this difference is due to the presence of tertiary alcohols, active hydrocarbons, etc.

The influence of acids on the determination of the hydroxyl value can be seen in Table 8, Experiments 1, 3, 5 and 6. (P_g 275° 23 hrs., and P_g 300° 23 hrs.). Tests 1, 3 and 5 show that, given the test conditions specified on page 27 the hydroxyl number rises sharply with the strength of the caustic alkali used in saponification, but bears no relation to the acid number. (In Experiment 3, the compound was neutralised immediately with N/10 KOH after the saponification, and only then was the distillation carried out, so that it is here that the most correct values are to be found). It might be concluded from this, that when saponifying with strong caustic alkali and then working up, hydroxyl groups formed by reduction of carbonyl groups will appear.

It follows from Experiments 1 and 3 that there has either been a rise in the hydroxyl value, which has been obscured by the acid number (see General section), or that no new hydroxyl groups are formed in saponification (saponified acid anhydride). Judging from the results it appears impossible that the free acids should simulate hydroxyl groups (Experiment 3). In Experiment 6 (P_g 300° 23 hrs.) the hydroxyl number obtained by acetylation is 6.4 lower than that found by the Zerewitinoff

method, so that it is to be assumed that the increase in the quantity of acids (increase in acid number 2.25) obscures a small part (0.4) of the hydroxyl number, which is in accordance with the test already mentioned. The objection that this is a question of tertiary hydroxyl groups, can hardly be supported* It must be borne in mind that there may be fewer enol groups (tertiary alcohols) after saponification than before. The formation of enolic compounds (also of ketones) could be established by the Grignard determination with the help of various solvents. Experiment 9 (S 275° 23 hrs) presents a similar case. Thus, values found by acetylation hardly need correction, or if they do, then the correction will be a fraction of the appropriate acid number. The esters which are hydrolysed in the preliminary saponification are, to a great extent, acid anhydrides (cf. the increases in the hydroxyl number in tests 1, 3, (5), 6, 7, 8 and 9 of Table 8).

But these findings require to be checked and clarified, as already mentioned. Above all, by systematically investigating the increase in the acid number relative to the hydroxyl value, the degree of reduction of the carboxyl groups must be determined.

4) "Neutral" oxygen:

Table 7, examples 11 to 15 (S 275° 23 hrs.) reveals the following facts:-

After treatment with sodium ethoxide, the hydroxyl number (Experiment 12) is found to be 26.60 by the Zerewitinoff method, and 25.0 by the Verley-Bölsing method (Table 6, Expt. 9). This corresponds to an increase of 16.02 and 16.90 while the proportion which adds Grignard reagent falls from 17.1 to 13.65 mg. KOH/gm (Tests 11 and 12). The acid number increases from 5.58 to 7.5.

These results can be brought into agreement with each other if it is assumed that, when treating with sodium alcoholate, the ketones are reduced.

Test 15 shows that, in the saponification of "esters" corresponding to an acid number of 4.76 (the acid number increases from 1.92 to 6.68), the capacity of the oxidised oils to add Grignard reagent decreases by 1.55 mg KOH/g. Assuming, for the sake of simplicity, that the 1.55 mg KOH/gm are derived from the partial reduction of Ketones** (see Test 22: treatment with sodium alcoholate using an air bath temperature of 105°C),

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*As already mentioned here, it could be a question of secondary hydroxyl groups resulting from reduction. The acid numbers calculated from the Zerewitinoff value would have to be more accurately determined than was the case in the method shown in page 18.

**If the 1.55 mg KOH/gm were derived, not from ketones, but from "esters", the relative reactivity of the "esters" to the acids is at least 85% of the value obtained with synthetic oil, ("Esters" and acids add 2 moles of Grignard reagent) so that the situation only alters slightly. Test 15 was only made once. In the examples which are given here there is practically no difference in the additive capacity of P_g oils before and after saponification. The values given for the P_g oils are average values of several tests and determinations which agreed very well.

this experiment shows that the "esters" which cause the increased acid number have reacted with practically the same amount of reagent as the acid. It is impossible for the Grignard reagent to add quantitatively to the acids and "esters" since in Test 12, after the treatment with sodium alcoholate there still remains a capacity to add Grignard reagent amounting to 13.65 mg KOH/gm, while the saponification number of 13.86 (according to Experiment 7, Table 8) in the simple case requires 27.72 mg KOH/gm.

This is to say that nearly half the substances covered by the saponification number react with Grignard reagent and that, if the acid number increased during the treatment with alcoholate, this increase causes practically no change in the capacity to add Grignard reagent. The reduction in the reactivity of aged oil is therefore entirely due to some third substance. The extent of the decrease in capacity to add Grignard reagent is equal to the increase in the hydroxyl value after the sodium alcoholate treatment. Experiments with P_g 275° 23 hrs and P_g 300° 23 hrs show a similar result even more clearly (cf. experiments 3 and 5; 7, 8 and 9, Table 7. See also Table 6.) Experiment 7 also proves that the capacity to add Grignard reagent at 20°C is not very different from that at 90°C. Only a slight variation of the situation can occur from the limits of error of the Grignard reaction as laid down in the discussion and from other possible errors.

For this reason, and in accordance with the facts given in Section III, page 5 and Section IV, 4, page 13 the change produced in the hydroxyl value and in the capacity to add Grignard reagent by the treatment of an aged oil with sodium alcoholate can with certainty be attributed to ketones.

VII. SUMMARY

It was shown that in the ageing of an oil, independently of the type (mineral, synthetic), the following conclusions can be drawn:

(1) Free hydroxyl groups are formed in the order of magnitude of the saponification number (determined in the usual way) of the aged oil in question.

(2) "Neutral" oxygen compounds are formed in the order of magnitude of twice the hydroxyl value, which can be described with certainty as ketones. Thus the total oxygen (in mg KOH/gm) which is present is about three times as great as that determined by the saponification number.

(3) Methods, which can be employed as standard tests in the laboratory are described for determining these oxygen compounds quantitatively, thus characterising the resistance to ageing and the uses to which the oils can be put.

(4) The possibilities of gaining a more complete and differentiated knowledge of the saponification number are discussed, together with initial experiments to be carried out for this purpose.

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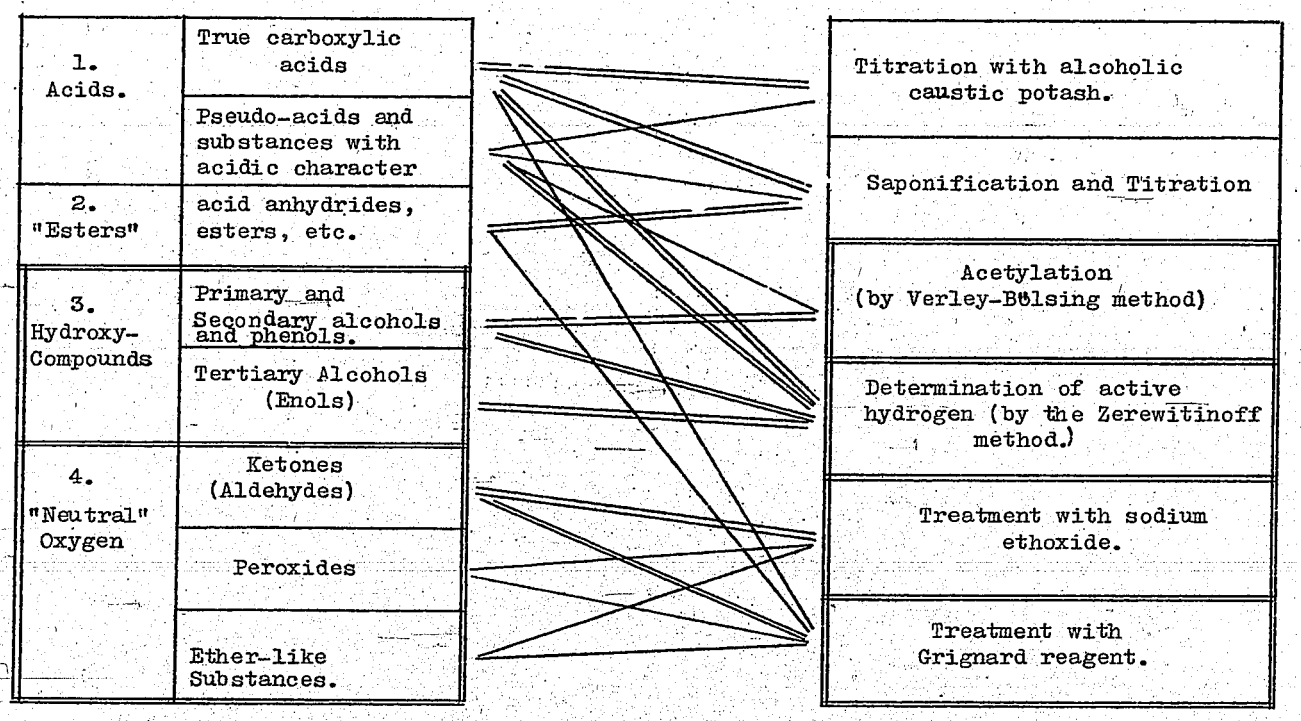
TABLE 7. Analyses with Grignard Reagent

Expt. No.	Description	Acid No.	Sap. No.	Groups estimated with Methyl Magnesium Iodide: With evolution of methane — wt. of oil taken. g.	ccs CH_4 @ 20°C	mg KOH/g	Hydroxyl value	ccs CH_4 @ 90°C	mg KOH/g	Hydroxyl value	Without Evolution of methane: ccs CH_4 @ 90°C	mg KOH/g	Hydroxyl value (estimated by acetylation.)
1	P_g	0,00	0,04	2,529	4,30			4,69			0,00		0,0
2	S	0,37	0,68	2,503	6,96			7,58	—		1,68		1,45
3	$P_g 275^o 23^h$	0,98	4,43	5,0	16,06	8,10	7,12	19,55	9,88	8,90	30,90	15,6	5,6
4	$P_g 275^o 23^h$	0,98	4,43	2,512				10,46	10,50	9,52	17,0	17,1	5,6
5	$P_g 275^o 23^h Na\ 155^o$	3,50	6,12	5,068				42,1	20,96	17,46	13,3	6,6	15,2
6	$P_g 275^o 31^h$	1,64	6,88	2,503	10,79	10,87	9,23	13,16	13,25	11,61	21,78	21,95	6,8
7	$P_g 300^o 23^h$	1,45	6,42	2,507							20,26	20,2	7,2
8	$P_g 300^o 23^h$	1,45	6,42	2,500	11,24	11,34	9,89	14,15	14,26	12,80	25,10	25,35	7,2
9	$P_g 300^o 23^h$ sap.	4,0		2,505	15,35	15,45	11,45	18,0	18,1	14,1	25,35	25,50	
10	$P_g 300^o 23^h$ sap.	4,0		2,150							21,85	25,63	
11	$S\ 275^o 23^h$	1,92	8,90	2,545	10,9	10,8	8,88	12,5	12,4	10,58	31,0	30,85	8,1
12	$S\ 275^o 23^h Na\ 155^o$	7,5	11,47	2,554				34,55	34,10	26,60	13,8	13,65	25,0
13	$S\ 275^o 23^h Na\ 200^o$	7,61	12,85	2,503	33,07	33,3	25,7	35,72	35,95	28,34	10,48	10,55	
14	$S\ 275^o 23^h Na\ 200^o$	7,61	12,85	1,241	17,12	34,8	27,2	18,56	37,71	30,10	5,11	10,37	
15	$S\ 275^o 23^h$ sap.	6,68	11,36	2,498	17,23	17,4	10,72	20,53	20,75	14,07	28,96	29,2	10,2

Note: The index Na. 155° signifies treatment with sodium alcoholate at 155°C.
" " sap. signifies that the oil has undergone preliminary saponification.
Experiments 1 and 2 have been taken as blank determinations.
In Expt.4 the Grignard reagent was allowed to react with the oil for 30 mins. at 100°C.
" " 7 " " " " " " " " " " 20 " " 20°C.
" " 10 4 cc. of anisole are used instead of the usual 8 cc.
" Expts. 13 and 14 the Sap.No. is estimated with 2N alcoholic KOH.

Simplified General Diagram of the Methods by which the Oxygen Compounds in a Used Oil are determined



The double lines give the individual methods by which substances can actually be determined.

The single lines give the other possible methods by which partial or total estimation of the substances can be carried out.

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FB 804

German Aviation Research
Report No. 804

Tests on a synthetic oil of the Ruhrchemie A.G. in the liquid cooled (Reissgekühlt) single-cylinder test engine

by K. Dehn

Synopsis:

An endurance test on the synthetic oil of the Ruhrchemie was carried out in the liquid-cooled single-cylinder test engine until the piston rings seized. The results are compared with those of other oils used with good results in aero-engine operations.

Contents:

I. Introduction:

On the basis of laboratory tests and of the test run in the Siemens oil test engine it must be assumed that the synthetic oil of the Ruhrchemie A.G., Holten, is an excellent oil for heavy duty aero engines. An endurance test was carried out in the single-cylinder test engine with the liquid cooled BMW VI cylinder in order to check this and particularly to obtain information on the behaviour of the oil in continuous operation.

II. Materials used:

The laboratory tests of fuels and lubricants used for this endurance test and for the test run with Stanavo 140 used as a basis of comparison are tabulated as follows :-

1. Fuels

	Endurance run 36_{II} with R.C. oil	Endurance run 9 with "Stanavo 140"
Fuel type	O.N. 87 aviation gasoline	Stanavo 87
Supplier	Olex (No. 258/36)	D.A.P.G.
Density @ 20°C (kg/l.)	0.731	0.728
Refractive Index	1.4096	1.4070
Gum test (glass dish) (mg.)	3.3	4.0
Sulphur content %	0.03	0.01
Iodine number	3.3	1.2
Octane number	87.3	87.6
T.E.L. (Vol. %)	0.083	

(continued on page 2)

Distillation on A.S.T.M. Method

	Endurance run 36II with R.C. oil	Endurance run 9 with Stanavo 140
I.B.P.°C	38	68
Distilled at 50°C (vol.%)	2.0	-
60 " "	5.5	-
70 " "	11.5	1.0
80 " "	21.0	11.4
90 " "	33.0	41.2
100 " "	49.5	69.0
110 " "	66.0	87.4
120 " "	80.0	94.4
130 " "	88.5	97.6
140 " "	94.0	-
150 " "	97.0	-
F.B.P.°C	152	134
Residue (vol. %)	1.4	1.5
Loss "	1.0	0.3

2. Oils

a) Test oil of Ruhrchemie A.G. Oberhausen/Holten
Type: SO 2001 (improved quality)
Rec. No. 41/36 (analysis) and 255/36 (endurence test)
The oils 41/36 and 255/36 supplied for the analysis and for the endurence test had to be delivered in the same quality. The figures for 255/36 are indicated in brackets in the following test results.

Colour: reddish-brown, slightly fluorescent
Smell: mild
Density @ 20°C (kg/l.): 0.863 (0.870)
Refractive Index : 1.4804 (1.4837)
Viscosity at 50°C (°E): 21.7 (22.5)
" " " (Cp): 139 (145)
Solid foreign matter : 0.0
Ash : 0.0
Asphalt : 0.0
Neutralisation No. : 0.0
Saponification No. : 0.0
Carbon Residue (Rams-bottom) : 0.30 (0.34)
DVL ageing:
Volatility (275°C) %: 79.0
Asphalt %: 8.8

Ageing Test (Air Ministry):

	Original oil	aged oil	increase
Specific gravity @ 20°C	0.863	0.893	0.030
Viscosity @ 37.8°C, °E (Cp)	44.5 (287)	150 (1002)	237 (249)
" " 50 " " "	21.7 (139)	64.7 (429)	198 (208)
Carbon residue (Ramsbottom)	0.30	0.82	0.52

(continued on page 3)

b) Reference oils

	Endurance run 0	Endurance runs 41, 44, 45
Type	Stanavo 140	Green Band
Supplier	D.A.P.G.	D.V.O.A.G.
Density @ 20°C (kg/l.)	0.892	0.883
Refractive Index	1.4964	1.4879
Viscosity @ 50°C (°E)	30.1	21.6
" " " (Cp)	199.4	141.4
Solid foreign matter (wt. %)	0.0	0.0
Ash	0.0	0.0
Asphalt	0.0	0.0
Neutralisation number	0.0	0.0
Saponification No.	0.0	0.0

III. Test procedure and results:

The test run was made on a DVL single-cylinder test engine, equipped with cylinder and piston of the BMW VI engine, series 7. The test was carried out as in the endurance runs described in the DVL report PB 172 Dehn/Glaser, "Use of motor-benzene in aero engines subject to high thermal load". One of these test runs carried out on O.N. 87 aviation gasoline and Stanavo 140 oil is used as a basis of reference for the following test run.

1. Reference run on "Stanavo 140" (endurance run 9)

Benzene-free "Stanavo 87" and "Stanavo 140" were used. The following operational conditions applied :

Power	4½ hours	45 H.P. at 1590 r.p.m.
	½ hour	50 H.P. at 1650 r.p.m.
Fuel consumption	gr/HP/h	245
	kcal/HP/h	2560
Coolant outlet temp.		140°C
Oil outlet temp.		88°C
Compression ratio		6.8
Ignition timing (° b. T.D.C.)		20
Temperature in the centre of the piston crown (determined by melting plugs)		between 290 and 305°C

The test curves appear in Fig.1. The endurance test was discontinued after 63-3/4 hours because repeated power drops gave rise to the assumption that one or more piston rings were stuck. It was found that the top ring was stuck between 70° and 170°, the second between 70° and 175° . Rings 3 and 4 were free. The oil holes of the oil scraper ring were partly choked. Otherwise the engine condition was normal. During the test, oil samples were taken from the return pipe after 10, 25, 35, 50 and 60 hours, as well as shortly before stopping the engine.

2. Endurance run on R.C. oil (test No. 36II)

The O.N. 87 aviation gasoline used with Stanavo 140 later became no longer available without benzene; an O.N. 87 Olex aviation gasoline having the same density as the previously used Stanavo 87 was therefore used. The results of laboratory tests for this fuel and for lubricant SO 2001 (improved quality) are shown on pages 1 and 2. The operating conditions for this endurance test are the same as those of the

the reference test (see page 3). On the test run a new cylinder and piston with "Goetze F.11" rings were also used. After a 13 hours running-in period, cylinder and piston were taken down, cleaned and measured. The engine casing and the oil lines were also carefully cleaned before starting the endurance run.

The test curves are given in fig. 2. After 20, 35, 50 and 60 hours the cylinder was lifted and a check was made. The valves were always slightly slack and consequently were re-ground. This, however, occurred also in the earlier endurance tests with "Stanavo 140" and is caused by a failure of the valve seats. When examined after 60 hours, the piston rings were completely free. The result at this stage is therefore more favourable than after 63-3/4 hours in the reference test with "Stanavo 140", when two rings were partly stuck. The cylinder was not taken down between 60 and 90 hours. No power drop or increased blow-by into the crankcase was ascertained before this stage. After dismantling the cylinder, the following results were found :-

Piston rings: The top ring sticks somewhat at one point, though it still moves in its groove. The second ring is seized on a narrow sector between 120° and 165°. The fact that no irregularities occurred in the engine operation up to the 90th hour, leads us to infer that the two top rings moved quite freely in their grooves during operation. The 3rd and 4th rings are completely loose. The oil holes in the piston and scraper rings are unobstructed. The appearance of the gudgeon pin is normal. The piston crown shows little oil-carbon (about 0.1 mm.); on the piston rim a thin ridge of oil carbon can be seen on inlet and exhaust side. The rubbing faces on both piston and cylinder have worn well and present no scoring. Both valves are not quite gas-tight. Connecting rod and bush are faultless. The sparking plug has a good appearance. Fig. 3 shows the piston after 90 hours operation.

If the two tests are compared, it appears that the running time until the piston rings stick was considerably longer for the R.C. oil (90 hours) than for Stanavo 140 (63-3/4 hours). In the former no power drop or increased blow-by into the crankcase had occurred; the result was even better than with the reference oil.

3. Alteration of the oil

The test results of the oil samples taken during the endurance run 36_{II} are shown on fig. 4. It shows the increase of foreign matter, ash and asphalt content, as well as of density, viscosity and saponification number with the running time. The drop in values after the 70th hour is due to topping up with fresh oil (see fig. 2). No fresh oil was added between 35 and 70 or between 70 and 90 hours, because the oil consumption can better be determined if the oil circulation is disturbed as little as possible. If the oil consumed by the engine is made up at very large intervals, the quantity of oil in circulation decreases considerably (see fig. 2). (The "lubricant weight in the tank" includes the weight of the tank, ca 26 kg.). This must be taken into account when analysing the test results, because the oil ageing increases as the quantity of oil in circulation drops. In the R.C. oil the considerable rise in saponification number and in density is particularly surprising. The other properties of the oil change to the normal extent.

Fig. 5 shows the alteration of the oil in endurance run No. 9.

4. Piston ring wear

The weight-loss of the piston rings at 1 hourly intervals in test No. 36_{II} is shown in fig. 6. The wear per hour of the piston rings in 3 runs which extended for 15 hours and in which "Gargoyle Aero Mobiloil

Green Band" was used, is also given for comparison. These short endurance tests were carried out within the frame-work of other tests, though on the same engine and under nearly equal test conditions as test 36_{II}. In particular the "Goetze F.11" piston rings used for all tests illustrated in fig. 6 came from the same delivery. In the tests carried out with "Green Band" however "special aviation gasoline" was used. The piston ring wear can be influenced by a whole series of factors. All the same, the results illustrated in fig. 6 lead to the conclusion that the R.C. oil has exceptionally good lubricating properties, because the piston ring wear in this oil is lower than in the well-known Green Band oil.

It can be assumed that the high saponification number and the low piston ring wear are interconnected. The high saponification numbers show that beside organic acids, large quantities of saponifiable products have been formed during the run. Among these are esters and lactones, which presumably have a positive effect on the lubricating ability similarly to the acids; metal soaps are also formed. From the ash content in the filtered oil it is possible to draw a certain conclusion regarding the amount of metal soaps, e.g. in the filtered used oil after 90 hours running time, 0.11% ash was found which means that at the most 40% of the saponifiable components are present as metal soaps, whereas the greater proportion are esters and lactones.

5. Oil consumption

Both for R.C. oil and Stanavo 140 the specific consumption varied between 4 and 6 g/HP/h., which corresponded to the normal consumption for the BMW-VI engine. On the basis of our tests it is impossible to decide whether the consumption was lower with one oil than with the other, because the variations lay within limits of errors in measurement. When "Green Band" was used the oil consumption lay within the indicated limits.

6. Behaviour of the oil in other endurance tests

After this test 36_{II} with the Ruhrchemie oil and Aviation Gasoline O.N. 87, three other runs were carried out with the same oil, but with other fuels. A detailed report on these tests with the 3 test fuels: R.C. alkyl benzene (No.38) and I.G. isopropylbenzene (No. 39_{II}) was already published (DVL report UM 428 Glaser/Dehn - "Testing of different alkyl benzenes in the liquid-cooled aero engine single-cylinder engine". The tests were carried out in the same conditions as No. 36_{II}. The running times were however shorter, which is due to the fuels employed. Test No.38 was discontinued after 57 hours. At that time no power drop or increased blow-by into the crankcase had occurred, just as in Test 36_{II}. Also the piston condition corresponds roughly to that of test 36_{II} because in both cases the time of onset of ring sticking was determined, but during the run the rings still moved freely in their grooves. Consequently a comparison of the piston ring wear in the two tests seems possible. The ring wear, especially the top ring, depends on whether a ring sticks. In this case the hot combustion gases can flow around the ring, thus considerably accelerating its wear. Beside test 36_{II} the weight-loss at hourly intervals, of the piston rings in test 38_{II} is also plotted in fig. 6. It appears that here too the piston ring wear is very low. For the first ring the wear is rather higher than in the previous test. This is due perhaps to the fact that in the operation with alkyl benzene mixture the mean temperatures in the combustion chamber are rather higher than when O.N. 87 aviation gasoline is used. This is most apparent in the case of the top ring which is most exposed to the combustion gases.

In tests 37 and 38 oil samples were also taken during operation. The test results are shown in figs. 7 and 8. Here too a comparatively

stoop rise of the saponification number appears although not to the same degree as in test 36II.

In both cases, however, a saponification number of over 3.0 is reached after 40 hours.

VI. Summary

In the comparison of the synthetic oil of Ruhrchemie "SO 2001, improved quality" in the liquid-cooled BMW VI single cylinder test engine with "Stanevo 140", a considerably longer running time before the piston rings stuck was found in the former than in the latter. Particularly surprising is also the low wear of the piston rings in the test on the synthetic oil. The investigation of the oil samples taken after 10, 25, 35, 50, 70, 80 and 90 hours showed generally the normal ageing tendencies. The saponification number, however, increases exceptionally rapidly. It is possible that the high saponification number and the good lubricating ability are interdependent. Later tests with the synthetic oil and different fuels mainly confirmed the previous results.

Fig.1 - Curves for endurance test No. 9.
" 2 - Curves for endurance test No. 36II.
" 3 - Piston after 90 hours run with Ruhrchemie oil.
" 4 - Alteration of the oil after endurance test 36II.
" 5 - Alteration of the oil after endurance test 9.
" 6 - Comparison of the wear of piston rings in the various endurance tests.
" 7 - Alteration of the oil after endurance test 37.
" 8 - Alteration of the oil after endurance test 38.

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THE LOW TEMPERATURE BEHAVIOUR OF LUBRICATING OILS

by K. Siebald

Summary

The physical processes which take place in multi-component mixtures up to the point of solidification are discussed and explained. The various methods used for determining the flow properties of mineral oils are described and the results thus obtained are compared, showing that, according to the methods used, faultless assessment is not possible. A method for determining the flow resistance was thus evolved in an experimental apparatus developed at the DVL.

CONTENTS

I. PURPOSE OF THE PROPOSED INVESTIGATIONS

The ability to use oils at low temperatures is one of the most important demands made by the aircraft industry. This stipulation is of far-reaching importance, since the serviceability of oils at low temperatures is one of the determining factors for the reliability of machines in service.

The resistance to cold of machine oils, including engine oils, whose low temperature behaviour is to be discussed in this article, is of particular significance. In contrast to the motor vehicle, aircraft are exposed, even in summer, to low temperatures and, in winter, temperatures of -50°C and below are not uncommon at high altitudes. If the normal limit of resistance to low temperatures is taken as about -30°C, it will be realised that, to eliminate possible risks, the operational safety of the engine calls for special properties of the lubricant.

In technical engine processes, e.g. starting up engines and maintaining lubrication, the lubricant, even under the influence of low temperatures, must be so fluid, that on the one hand the starting up of the engine is not made difficult (i.e. that the power consumed by freeing the engine-parts immersed in oil is not increased by additional resistance) and on the other hand that the engine does not seize up by the pipe lines becoming frozen. Inadequate lubrication would result in the destruction of the engine parts.

Even when these difficulties are to some extent countered by pre-heating or by placing the oil tank in the vicinity of the engine, an engine oil having lowest possible solidifying point as well as adequate flow properties is required for operational safety.

Laboratory investigations regarding the suitability of a certain lubricant have made it possible, in the past, to arrive at an approximate evaluation, but the highest degree of accuracy and reliability is always ensured by an engine test. However, the construction and operation of the cold chamber necessary for testing and accommodating an engine involves considerable expense, and the fact that it is unprofitable makes expensive engine tests out of the question. Recourse must therefore be had to an appropriate preliminary laboratory determination.

In this article, an attempt will be made to provide some information as to the physical processes occurring when an oil solidifies, and to develop a suitable procedure which sheds light on solidification processes and which simulates practical conditions.

II. GENERAL DATA ON THE LOW-TEMPERATURE BEHAVIOUR OF HYDROCARBONS

A. Theoretical Consideration of the Processes Involved in Solidification.

1. Terms used in this report (Colloids and Crystalloids).

The behaviour of mineral oils in the cold (e.g. changes in their flow properties which are particularly affected by low temperatures) calls for a special consideration of the physical laws which must be taken into account for evaluating the solidification process. At low temperatures, oils deviate from Newton's and Poiseuille's laws according to the amount of

solid matter formed; on the whole this tendency is more pronounced the richer the oils are in paraffin (?wax). For practical purposes, a marked deviation characterises a rather poor oil, since the oil circulation is greatly reduced by a great deal of precipitation.

On cooling, the viscosity is not solely affected by the gradual transition from the purely oily state to the solid amorphous form; the precipitation of solids in a colloid or crystalline form is also a deciding factor in viscosity changes. The speed and duration of cooling exert a considerable effect on the structural aggregates forming on solidification.

Since the colloid and crystalline solutions will be discussed below, the terms require some explanation as regards their actual significance and the distinction between the two must be defined. By "colloid" and "crystalloid" solutions are meant the apparently homogeneous mixtures of two or more substances. The difference between crystalloid and colloid (genuine and non-genuine) solutions lies in the order of magnitude of their smallest particles. Whereas crystalloids have a diameter of about 10^{-7} to 10^{-8} cm., colloids, which are generally an aggregate of molecules, have a diameter of 10^{-4} to 10^{-6} cm. On this fact are based the various experimental methods for crystalloid and colloid solutions. Owing to their smaller molecular diameters, crystalloids have a higher rate of diffusion and therefore a higher osmotic pressure, which results in a lowering of the freezing point under pressure and a rise in the boiling point. In the case of crystalloid solutions with a normally crystalline substance as a disperse phase, the solid is again deposited in its unchanged crystalline form when the solvent or dispersion medium has been evaporated. On the other hand, colloid solutions generally assume an amorphous, horny character on evaporation.

An important test for colloid solutions is that the dissolved substance will not pass through a parchment membrane. Owing to their large molecular diameter, colloids (also called "ultramicrons"), can be seen through an ultramicroscope. As a rule their inhomogeneous character can be ascertained by means of a good microscope. They can be detected by the naked eye from their Tyndall effect. At high temperatures colloid solutions are on the whole less stable than at the normal temperature. Their solubility must therefore decrease with rising temperature, in contrast to the crystalloids. Colloid solutions lie between crystalloid solutions and suspensions, but there is no sharp transition between crystalloids and colloids.

2. Changes in the flow properties as a function of:

   a. the composition of the lubricants.
   b. previous heat treatment.

It has already been mentioned that viscosity on cooling does not obey any particular law. Since mineral oils are multi-component mixtures, i.e. mixtures of different high-molecular hydrocarbons, their behaviour on solidification, for example, will not be correctly estimated by ascertaining the setting point which corresponds to the freezing point of the chemically homogeneous substances. Since the various components are precipitated partly in crystalline and partly in amorphous form under the influence of low temperatures, the solidifying process is highly complicated. Owing to this

fact Vogel (1) investigated more closely the processes of solidification and melting. He collates these very clearly and distinguishes between:

1. Chemically homogeneous substances which have a sharply determined melting point and freezing point that can be determined with rather less accuracy.

2. Mixtures of chemically homogeneous substances which form crystals on solidification, e.g. paraffin wax, which on freezing passes through all the melting points of its components and gives a mean melting point which may be determined with an accuracy of 1 to 2 degrees, providing the melting points of the various components do not diverge too much from this mean. The freezing point should not be far removed from the mean melting point if super cooling is avoided.

3. Substances forming an amorphous mass on solidification without having an actual freezing or melting point, but whose solidification point can be estimated from the viscosity curve.

4. Mixtures of substances solidifying in amorphous or crystalline form, such as is generally the case with mineral oils. For determining the solidification point in this case, the viscosity curve must also be taken into account. At the temperature where formation of solids occurs, the viscosity curve shows a definite break. According to Gurwitsch, this temperature is between 2 and 5 degrees above the true freezing point. It is possible that here colloid particles of paraffin wax separate out in the same way that gelatine gelatinises, but it can also be explained by the incipient crystallisation of the paraffin wax. Cloudiness would therefore point to crystallisation and glassy solidification to a colloidal state.

Many workers postulate the possible existence of a colloid solution of the paraffin wax in the mineral oil. More or less satisfactory explanations are given for the viscosity changes in the oils by comparing them with the viscosity anomalies of colloid solutions, but without (owing to experimental difficulties) adducing experimental proof. If it is a question of the existence of colloid particles in the solidifying oil, the viscosity rise at the setting point is understandable, since slight quantities of colloidal particles can make even thin substances viscous. A remarkable property of some colloid solutions, e.g. the albumens, is the transitional change in solidity caused by mechanical treatment. Dissolved colloids, which form gels on standing, pass reversibly into a sol when shaken or forced through a capillary, and decrease considerably in viscosity through this change of form. This condition is known as the "flow resistance". The change in viscosity, the determination of which was carried out at a fixed working temperature in multi-component mixtures such as would be found in motor oils, may equally well be caused by the liquid crystals. Until true crystallisation takes place, these liquids pass through phases, known as isotropic, nematic or smectic, in which no separation of crystals occurs. (Fig. 1a). Since various oils lose the principal properties of normal liquids in the low temperature range and occupy an intermediate state which may resemble that of the liquid crystals, there is some justification for speaking of "pseudo-plasticity", which denotes a state lying between normal liquids and actual plastic substances.

Very considerable influence on the low temperature behaviour of mineral oils is caused by previous heat treatment, inasmuch as both viscosity and solidification point, quite apart from the time factor, depend to a very great extent on

previous heating. This phenomenon is more pronounced in the case of oils rich in paraffins than in naphthenic or asphaltic oils. The viscosity and the solidification point may be raised or lowered by preliminary treatment. It frequently happens that viscosity and setting point rise on cooling when movement of the oil takes place, but fall when cooling occurs without disturbance of the oil. The paraffin wax which is precipitated at the usual temperatures and is dissolved by preheating, will not separate out on being left to cool without disturbance owing to supercooling, but when the precipitation of the dissolved paraffin wax takes place with movement, finer crystals are produced than originally and therefore the setting point will be higher.

If the cause of solidification is considered to be the formation of a paraffin lattice, (perhaps in such a way that the solvent, in this case the oil, is held by the paraffin wax crystals as by a sponge), it might be imagined that the quantity of liquid retained depends on the size of the crystals forming this lattice. The size of these crystals is determined by the previous treatment.

If the paraffin wax content of the oil is decreased, or if the paraffin wax is eliminated by suitable methods (pressing or filtering), the resistance to the influence of low temperatures becomes considerably greater. This does not mean to say, however, that the greater resistance to low temperature is also a standard for a qualitative high-grade lubricating oil comparable with ageing, lubricating properties, etc.

B. Experimental results in the literature.

1. Solidification.

For the low-temperature behaviour of oils as found in practice, two characteristics have so far been the determining factors: the setting point, and the flow properties under slight pressure. The setting point was used as a standard for the flow of the oil to the pump (flow under the influence of gravity), and the flow properties under pressure as a standard for the flow of the oil to the lubrication points.

The Pour Point or setting point (2), which is used for characterising the behaviour of hydrocarbons at low temperatures, does not, however, characterise the quality of an oil at low working temperatures sufficiently clearly, since conditions in operation may be quite different, e.g. the cross sections of the pipe-lines are, in practice, comparatively narrow. In all circumstances the oil will therefore tend to seize up in these pipes rather than in, say, the sump, the capacity of which is quite different. Since the oils have no components which solidify uniformly, the determination itself is inaccurate (See p. 3), quite independently of the subjective errors of the observer, and furnishes no information regarding the behaviour of the oils close to or below the setting point.

2. Flow properties.

The behaviour of the oil below the setting point is in the first place characterised by determining the flow properties, since these, of all the various properties of mineral oil, are most strongly affected by low temperatures. The apparatus evolved by Vogel (3), in which the commencement of flow (Fliesbeginn) can be estimated, makes exact measurements of viscosity possible. The reproducibility of the figures is accurate to within 1°; however the setting point and commencement of flow did not always agree in the case of the various

oils examined, since the commencement of flow in one case lay below and in other cases lay above the Pour Point determined by the ASTM method. When the method was applied, however, it was found that no reliable conclusions could be drawn as to its practical use, since various oils said to be resistant to low temperatures behaved less favourably than the poorer oils. W. Steinitz (4) refers briefly to the work of the Research Laboratory of the Texas Coal and Oil Company on highly dewaxed Ranger oils. Not only have these oils a very low setting point, but in contrast to other oils, which solidify completely below their setting points, they have well-marked flow properties over a wide range below the setting points. This shows that, by the method of determination used, the setting point does not correctly characterise the quality of an oil; indeed, the behaviour <u>below</u> the setting point is of more decisive importance. On examining the solidified oils in a pressure viscometer, the Ranger oils showed an equally as good behaviour as the high-grade Pennsylvania oils. Coastal oils and oils of Californian origin, which completely lost their flow properties below their pour points, behaved much less favourably.

Vogel's apparatus for determining the commencement of flow also enables the viscosity to be determined. Vogel points out the characteristic behaviour of oils, whose viscosities after previous heat treatment are much lower compared with the non-pretreated oils. Furthermore, the viscosities of paraffinous oils measured at decreasing temperatures, exhibit considerable viscosity hysteresis by comparison with the viscosities measured at increasing temperatures.

W. Ostwald and Föhre (5), and later M. Arveson (6), reported similar anomalies in the viscosity of various lubricating oils. In all cases the irregularities are attributed to the influence of the previous heat treatment of the oils.

The determination of the setting point, commencement of flow and viscosity in the low temperature range has formed the subject of an exhaustive investigation by S. Erk (7). On being supercooled, a number of oils of different origins and viscosities exhibited an increase in viscosity and, generally speaking, gave different characteristic viscosity curves; these curves, on passing from high to low temperatures, present a different shape compared with those produced by increasing the temperature of the supercooled test oil (Fig. 1). In addition to measuring the setting point, the commencement of flow and the low temperature viscosity of lubricating oils refined in different ways, Erk determined the paraffin content, the refractive index and the molecular weight of the oils. He concluded from these investigations that there is no definite relationship between setting point, commencement of flow and viscosity at 0°C. and the paraffin content and molecular weight of the oils.

The effect of previous cooling or heating on the solidification process was also examined by P. Woog (8). He agreed with previous workers that viscosity measured on cooling is less than that measured with increasing temperature after previous cooling, and he advances by way of explanation the well-known laws of crystal-formation. An oil cooled to -80°C, which is then brought to -20°C and afterwards heated, shows a higher melting temperature than when it is cooled to -80°C in the same way and brought at once to the melting temperature, i.e. eliminating the period at -20°C. The oil is found to be in a glassy, unstable condition, which disappears immediately at the moment of melting. The introduction of a stage at -20°C brings

about crystallisation, the number of crystals depending on the length of time at which the oil remains at the temperature of -20°C. The number of crystals again affects the melting point. These divergencies, observed in paraffinic oils during the determination of the melting point, were attributed to paraffin wax crystals contained in the oil. In order to obtain reproducible figures, Woog proposes that, before commencing an experiment, the oil is first warmed to 100°C, then cooling to + 20°C and further cooling to -80°C.

The aforementioned phenomenon of viscosity hysteresis could not be ascertained in the case of castor oil. On account of this S. Erk (9) carried out the microscopic investigations described below, which afforded some explanation as to whether the solidification phenomena could be caused solely by the formation of paraffin crystals without the assumption of existence of a mesomorphic state in the oil on solidification. The process of solidification was observed in polarised light. The liquids used consisted of high setting-point oils, distillates from a German crude oil rich in paraffin and oils obtained from the latter by dewaxing. On warming, the crystals, which were visible under the microscope, began to melt at 32°C, and at 50°C the last traces had disappeared. On slow cooling, first traces of crystal formation were observed at 30°C. The crystals grew rapidly, and at 20°C a fairly cohesive lattice had been formed. Within the limits of accuracy of ±2°, observations tended to show that the appearance of the first paraffin crystals coincides with the setting point determined by the standard process. Subsequent investigations confirmed the necessity of preheating test oil to 50°C. The liquefaction of the solidified oil by disturbance (in this case by gentle stirring) could likewise be observed under the microscope. Erk broke down the structure of the crystals by pressing the lens slightly on the cover glass. Gaps into which the oil flowed were produced between the clustered crystals, by the action of the pressure difference brought about by bending the cover glass. On further cooling, small crystals (about 8 microns long), were formed in the fluid part of the specimen, which impeded movement. A further breakage of the crystal lattice enabled the flow to be observed at very much lower temperatures. On heating, these crystals re-melted and the flow of the crystal-free parts again occurred, and only stopped after all the pressure differences in the specimen had been eliminated. (See Fig. 2 - 7.) The melting temperature coincides with the setting point obtained if the oil is constantly stirred. The fact that low pressure differences are sufficient to "liquefy" oils up to 50° below their real setting point, suggests that, below their setting point, the oils no longer possess any flow resistance when the crystal structure is destroyed.

This supposition was confirmed by Erk, using a capillary viscometer with varying pressures. He found that although the solidified oil no longer possesses any flow resistance, its viscosity is still dependent on the shear gradient. M. Bourdiol (10), who has also examined the solidification process under the microscope, has supplied a remarkable contribution to this work. He cooled castor oil for a brief period to -80°C and observed the formation of a glassy, translucent, salve-like structure. Only after treatment lasting several days at -20°C could the oil be solidified to form a hard, waxy mass. On heating to + 3° it became softer and at + 15° acquired the viscosity of normal fluid castor oil. Heating to over 50°C destroyed all the crystalline nuclei. The investigations, which were carried out in winter at a sufficiently low temperature, showed under the microscope the presence of spherolithic, double refracting crystals. Whereas at temperatures above

-20°C the crystal nuclei only formed with difficulty but grew very rapidly, at -21°C they form very rapidly but grow slowly. They attain the size of 20 microns, are readily deposited in small quantities, and, when examined in a capillary viscometer, caused considerable interference in the flow. The presence in the oil of many crystal nuclei, of diameter not greater than 4 to 5 microns, resulted in the formation of an apparently homogeneous, white paste. At higher temperatures, e.g. between 0°C and + 8°C, the crystal growth ceases and, at temperatures above + 8°C, they begin to melt; at 18-20°C they are completely invisible.

An oil, which is extremely resistant to low temperatures, may be obtained if a method of treatment is employed which makes use of these phenomena. The oil is cooled to -20°C over a period of 15 hours and allowed to remain at a temperature of 0°C for two weeks. The crystals will then be deposited and the oil may be decanted.

In addition to the formation of crystals, an investigation of 6 samples, obtained by the fractional solution of castor oil in petroleum ether, indicated the occurrence of mesomorphic phases which only become isotropic above + 11°C. The completely solidified castor oil must therefore be regarded as a heterogeneous mixture of a fibrous mesomorphic phase with spherolithic crystals.

3. Shear strength, plasticity and viscosity anomalies.

Further information on the processes occurring on the solidification of mineral oils and the viscosity anomalies thereby brought about in the range of plasticity is given in a very exhaustive article by M. Jordachescu (11). For his investigations he used a capillary viscometer, fitted with a constant vacuum device. The first experiments with paraffin oils of Pennsylvanian origin, carried out at a working temperature of 0°C at which the oils were plastic, gave considerable viscosity variations. When a constant working temperature had been attained, the first measurement was made followed by further determinations at longer intervals (about one determination daily), until after 14-22 days the viscosity figures remained constant. Fig. 8 shows the shape of the curve as a function of time, where Curve 1 illustrates the viscosity of the oil which has been cooled with a falling temperature to 0°C, while Curve 2 shows the reverse process after ½ hour's cooling to -80°C and immediate subsequent placing of the oil on ice. The measurements were carried out with the same capillary tube. On reaching the stable condition, viscosity measurements were made at various degrees of vacuum and the curve of discharged volume against pressure (See Fig. 9) was plotted with the discharged volume as ordinate and the subatmospheric pressures as abscissa. The pressure axis was cut by extrapolation thus giving a figure termed the "critical shear pressure", an expression corresponding to the Yield Value. If an oil has reached a state of equilibrium, the shear pressure is a constant. The progressive alteration of an oil at a definite working temperature is likewise shown by a change in the shear pressure which rises continuously. In all the oils investigated, the graph of discharged volume against pressure was found to be a straight line. Jordachescu comes to the conclusion that even at low pressures (10-20 mm) the oil flow could be determined, but that the curve meets the abscissa a few mms from the starting point owing to a definite rigidity in the oils.

In contrast to normal liquids, which have only one viscosity at a given working temperature and where the viscosity/pressure graph is a straight line running parallel to the axis of pressure, a rise in viscosity of 139 poises was observed in one test oil. To eliminate these viscosity variations, the oils were subjected to heat treatment and, for calculating the efflux figure, one of the commonest formulae proposed for determining the efflux constants of colloid solutions having similar irregularities in viscosity was employed.

Investigations, which were carried out with the above-mentioned samples of Pennsylvanian experimental oil a few days after their preparation, showed that differences developed in viscosity and shear pressure under the same experimental conditions; they show that, even under the same conditions, it is not always possible to secure the same values.

The oils which had been exposed for about one month to a temperature of 0°C and whose original colour was brown with a green fluorescence, exhibited considerable cloudiness and were slightly whitish in colour. This turbidity, which was found in all the "plastic" oils examined, could not be eliminated. It disappears at high temperatures, but reappears at 0°C, as soon as the oils have been exposed to this temperature for a sufficient length of time. If an oil is suddenly heated to +20°C, after it has been kept for a month at 0°C, plasticity will no longer be detected at this temperature.

The investigations were also extended to cover the maximum possible reduction in viscosity by measuring a flow-resisting sample which had already attained its stable condition. It was found that until a constant figure had been reached, the viscosity continually diminished but after attaining this figure fell no further.

All the investigations carried out with oils of different origins and viscosities showed the appearance of turbidity and viscosity anomalies, even though the periods in which their final viscosity value was reached varied; in their plasticity range these oils were flow-resisting. In the case of a Russian naphthenic oil, the viscosity in the plastic range decreased instead of increasing and at the same time cloudiness phenomena were more pronounced than with ordinary oils. The reduction in viscosity is expoained by the precipitation of a definite substance which could not be isolated, but the author concludes that this precipitate cannot be the cause of the plastic state of the oil.

Plasticity is a property common to all mineral oils, whatever their origin, and is always accompanied by a variation in viscosity at some constant working temperature and by the occurrence of flow resistance. On remaining for a prolonged period at some temperature within the plasticity range, cloudiness will occur, such a temperature being characteristic for each oil and lying somewhat above the temperature at which the oil no longer flows.

III. DESIGN OF THE EXPERIMENT

A. Materials Used

The materials used for the experiments were two oils with a paraffin base, one naphthenic oil and the one a naphthene base compounded oil. The experimental oils were distinguished by the letters A, B, C and D. Oils A, B and D were also subjected to additional refinement and these refined products

were included in the experiments. To eliminate resinous components, a Bavarian Fuller's earth "Bleichton G", of Messrs. Bleichton, Munich, was used. This is an acid activated material, having the following mean composition:

72.5% SiO_2; 13% Al_2O_3; 5% Fe_2O_3; 1.5% MgO; 0.8% CaO; 7.2% loss by ignition.

The properties of the experimental oils are collated in Table 1a.

B. Apparatus

The process adopted for determining the setting point was in accordance with the commonest and most usual methods, as given in "Richtlinien für den Einkauf und Prüfung von Schmiermitteln", DIN DVM 3662, (1936).

Commencement of flow and viscosity were obtained in Vogel's apparatus. The apparatus consists of a device for producing a constant excess pressure by a 600 mm column of water, a Dewar vessel of about 40 mm internal diameter and about 180 mm high, which was used for holding the cold bath and the test apparatus proper, a U-tube with a tube attachment for applying the pressure. In the lower limb of the U-tube a thermometer was inserted by means of rubber bungs, and a second thermometer was placed in the bath liquid. In order to obtain measurements as accurate as possible and free from the subjective errors of the observer, the narrow limb of the U-tube carrying the graduations was subdivided between each graduation. (See Fig.10.)

For the viscosity measurements, a precision model of the Höppler viscometer (12), fitted with an ultra-thermostat, was also used. (See Fig.11.) It was impossible to read off the measurements at temperatures below 0°C with this viscometer owing to the fact that the cooling jacket of the apparatus proper became completely iced up (dew point of air). However, the high degree of accuracy in determinations of viscosity above 0°C made it desirable to use this viscometer for low temperatures as well and, after suitable reconstruction, the defect of icing was eliminated.

In the method for viscosity measurement depending on the eccentric drop of a sphere, the full eccentricity of the falling sphere is ensured by the fact that the drop-tube is placed at a constant angle of 80°. The ball is thus easily guided. The factors used in this method are accurately defined mathematically; thus, the internal diameter of the hollow cylinder made of normal glass is measured with an accuracy of within ±0.002 mm, and the diameter of the corrosion-free metal balls measured with an accuracy of ±0.001 mm. The balls must have an exactly central centre of gravity. For filling the drop-tube some 30 to 40 ccs of liquid are required. The ball "E", which is intended for highly viscous liquids, was used in carrying out the experiments. This ball, which is made of tungsten, covers a measuring range of 20,000 to 400,000 centipoises. Owing to its low coefficient of expansion, the variation in the specific gravity of the ball is slight and can be omitted since it lies within the margin of error of the measurements. After the ball has been put into the drop tube and the stop-pin has been turned, the instrument is placed in the normal position in its holder. After rotating the instrument through 180°, the ball falls into its initial position; the instrument is rotated once more and measurement of the time of dropping is then commenced.

The calculation of the absolute dynamic viscosity in centipoises is made by the following formula

$$\eta = F. (S_k - S_f) . K,$$

where η = the absolute viscosity in centipoises, F = the time of falling of the ball, S_k = the specific gravity of the ball, S_f = the specific gravity of the liquid being examined at the experimental temperature and K = ball constant.

In order to eliminate icing, which generally occurs where cooling baths are used, smaller cold chambers were adopted. A cold box made by I.G. Farben was reconstructed in such a way that a constant accurate temperature could be obtained. The cooling apparatus which is used in place of the Höppler viscometer ultra-thermostat, consists of a double-walled cold box, the space between the walls are filled with kieselguhr and the inner chamber is divided into two compartments by an intermediate wall provided with slits (Fig.12). A metal case for holding carbon dioxide snow is inserted in the smaller of the two compartments; the front part of this case is made of wire netting. The advantage of this device is that, in the event of too great a consumption of refrigerant, it can be independently removed from the experimental chamber and filled again within a few minutes. Since the slit apertures may be closed by a lever which can be operated from outside, the lowest possible heat absorption occurs at the moment of charging. The larger compartment, which is intended to hold the Höppler viscometer, is fitted with a thermostatic heating resistance and a fan. A mirror placed behind the apparatus makes it possible to read off the scale by shining light through it. The three-walled window and the experimental chamber are perforated to facilitate the insertion of metal cocks; this makes it possible to evacuate with ease both the intermediate window spaces and the experimental chamber. The dew-point which occurs as a result of the temperature drop and the icing which accompanies it are thereby eliminated to a very large extent. The fall-tube, which is fitted with distance tubes instead of the glass jacket, is connected to two externally operated guides in the experimental chamber and is aligned by means of adjustment screws and an incorporated water-level.

The determination of the pour viscosity (Stockzähigkeit) was carried out in an apparatus proposed and developed by A. Baader (13). The apparatus consists of a Dewar vessel into which are inserted three test tubes (25 mm internal diameter) held by corks. The cork also contains an opening for filling the vessel with carbon dioxide snow. A copper tube, carrying a tin-plated metal disc close to its upper edge, is inserted centrally into the test tubes which are filled with 50 ccs of the test oil. A hook, which engages with the unhinged eye of the upper end of the tube, is fitted with a counter-weight attached to cord and roller. By carefully removing the support beneath the weight, the copper tube can be withdrawn slowly from the solidified oil. The formation of reduced pressure at the lower end of the tube is avoided by fitting in the tube a copper rod having a certain amount of play. The rod, which at its upper end has a knob bearing on the copper tube, is removed from the solidified oil before the tube is withdrawn. All slipping between the tube and the oil must be avoided. In order to secure the most uniform temperature drop possible, the refrigerant is added in small portions to the Dewar vessel filled with alcohol. After a temperature of -35°C is reached, this working temperature is kept constant for 30 minutes. As soon as the counter-weight of the copper

tube is withdrawn from the solidified oil until it leaves the surface. The same process is repeated with the second and third test tubes. The error of measurement amounts to ± 3% of the mean value.

A pressure viscometer was developed at the DVL in which operations can be carried out up to pressures of 10 atm. The apparatus, as shown in Figs. 20 and 21, consists of the following parts:

1. A pressure device, fitted with pressure-tight cocks and valves;

2. The actual experimental apparatus, consisting of a U-shaped capillary of 3 mm internal diameter carrying resevoirs at both ends. The object of the pear shape of the measuring vessel is to permit removal of the whole of the test oil at the end of the experiment. The capillary (and reservoir) is suspended in a Dewar vessel filled with alcohol. A small pump provides uniform stirring of the alcohol bath.

The measurement of the starting resistance was carried out in an experimental apparatus constructed by the I.G. Farben A-G., "Technischer Prüfstand" (14) - cf. Figs. 29 and 30. The cold box consists of two compartments, the container in the rear chamber being charged with compressed CO_2. The experimental arrangement in the test chamber consists of a test shaft and a test bearing ring (Lagerring). The test shaft is carried by two bearings and is driven by an intermediate shaft. The drive is by an electric motor whose speed of 2800 r.p.m. is reduced to 56 r.p.m. by worm gearing. The test shaft is put into gear by means of a clutch. The torque exerted on the bearing is transferred to a light impact rod on an indicator fitted to the top of the apparatus. Other devices in the test chamber, such as a slotted intermediate wall, a heater and a ventilator, enable the working temperature to be kept constant.

It must be mentioned here that in carrying out the experiments difficulties arose in manipulating the apparatus, which made it necessary to alter the experimental design proposed by the I.G. Farben A-G. It will be necessary - and provision has already been made for this - to subject the apparatus to a thorough reconstruction, which will then make it possible to eliminate these troubles.

C. Method of Investigation.

The investigations regarding the setting point and the determination of the commencement of flow as given by Vogel (Erdöl und Teer, part 33, III Jahrgang), were carried out in conformity with well-known methods. Since the rate of cooling has a considerable effect on the size of the crystals formed, the test oils were cooled in such a way (when determining the commencement of flow and up to the working temperatures) that the temperature drop amounted to about 1 °C in one and a half minutes, that is to say in the manner proposed by and later improved by Brunck (15).

In order to ascertain the effect of time lag on the cooled oils, experiments were carried out in which the temperature (working temperature) was kept constant for 10, 15, 30 and up to 90 minutes. Viscosity determinations were carried out. At the same time the effect of time lag was ascertained. When

the working temperature for the viscosity determination was attained, it was kept constant for a certain period of time. After applying the excess pressure by the 600 mm column of water, the time was noted in which the oil rose from mark 3 to mark 4. (Fig.10). This time, multiplied by the constants of the capillaries, gives the absolute viscosity in centipoises.

When examining viscosity variations of the test oils in the Höppler viscometer, the serviceability of the additional equipment, in this case the cold box, was tested. The small compartment of the cooling apparatus used for holding the freezing mixture was charged with carbon dioxide snow and the experimental chamber proper was exposed to the most extreme temperature possible by fully opening the apertures of the intermediate wall. The lowest temperature measured was -35°C. The snow obtained from a carbon dioxide cylinder was inadequate to maintain the temperature over a period of several hours. Experiments made with the solid CO_2, which is obtainable commercially, made it possible to secure a cold-box temperature of -60°C within a short time. The consumption of the solid carbon dioxide was low and the working temperature could be maintained without trouble once a constant value had been attained. The Höppler viscometer, which was connected in the main chamber in the manner already mentioned, was filled with the test oil and the ball "E" was inserted in the drop tube. After the latter has been brought into position required for measuring the viscosity, the time is determined in which the ball falls through the measuring distance between the marks A and B. The time is taken from the moment when the lower edge of the ball appears to touch the upper mark, avoiding any parallax in viewing the latter, until the lowest mark is reached. The third mark C on the drop tube of the precision model used, and which is half way between marks A and B, enables long dropping times to be shortened, and thus facilitates carrying out the experiment at temperature of -20°C and lower. The calculation of absolute viscosity in centipoises is effected in accordance with the formula on page 11.

In the description by Baader of the apparatus for determining the pour viscosity, some information was given as to the experimental details. However, these experiments were ended prematurely since no consistent figures could be obtained.

The method proposed by Vogel, to heat the oil first for 10 minutes at 50°C, was also used in the experiments with the pressure viscometer. At 30°C, the test oil was poured into the 50 cc reservoir and cooled to the working temperature. This temperature was maintained for 1 hour, attention being paid to the fact that, owing to the release of the latent heat of fusion, the cooling process can be considerably delayed. After applying the pressure, the oil is forced through the capillaries into the measuring vessel. The time taken for the measuring vessel to fill was recorded with a stop-watch. On completion of the experiment, the oil was again forced into the reservoir through a second pressure pipeline and the experiment was repeated. The viscosities were calculated in accordance with Poiseuille's law:

$$\eta = \frac{1}{v} \cdot \frac{\pi}{8} \cdot \frac{r^4}{L} \cdot p \cdot \tau \quad \text{where}$$

v = volume of liquid = 25 ccs

r = radius of the capillary = 0.15 cm

l = length of the capillary = 19.6 cms

p = measured pressure difference.

τ = measured time.

Substituting the constants of the apparatus, the formula is simplified to:

$$\eta = 0.4 \cdot p_{atm.} \cdot \tau \text{ sec.}$$

Since the capillary ends in a large liquid-reservoir and the Hagenbach correction (Kohlrausch) is sufficiently small throughout the whole range of measurement, the application of Poiseuille's law in the above form is admissible.

In measuring the starting resistances in the I-G.-apparatus, the test oil was heated in the way described above. After this, the journals and test bearing ring were coated with the oil (which had been cooled to room temperature) and then assembled. In order to obtain a uniform film, the journal was allowed to rotate a few times in the test bearing ring. Excess oil was then removed by moving the ring to and fro during running. In the following experiment axial displacement of the test bearing ring was prevented by a spring. The indicator and impact rod were then set in position, and, by opening the slits of test chamber wall, cooling was commenced. Heating and slit adjustment ensure that the working temperature is kept constant once it has been regulated. After an interval of 1 hour, the motor is started up and the clutch is engaged by pressing the recording stylus to the indicator drum. The "breakaway resistance" is shown by a break in the indicator curve, which rises to a maximum value and then slowly drops. At the end of the experiment the slits are closed and heating is applied at full intensity. The test chamber is heated to + 40°C and kept at this temperature for 30 minutes. The further course of the experiment is evident from the method described above. It is not necessary to prepare the journal and test bearing ring with fresh oil. When the temperature of +40°C has been reached, it suffices to engage the clutch and allow the journal to make a few rotations in the ring.

Calculating the adhesive strength of the oil from the indicator deflection.

Indicator mark: 1 atm = 5 mm for drum of 2.027 cm diameter.

Equivalent force of drum for 1 Kg/sq cm = 5 mm = $\frac{\pi \cdot 2.027^2 \cdot 1}{4}$

= 3.22 Kg.

Deflection: 5 mm = 3.22 Kg., thus 1 mm in the recorded graph = 0.644 Kg.

Lever arm: for all shaft diameters = 6 cm.

Diameter of shaft	40	50	60
Power at the circumference for 1 mm of the recorded graph	0.644x6/2	0.644x6/2.5	0.644x6/3
Area of oil film per 10 mm ring width	12.56	15.70	18.85
Adhesion Kg/sq cm per 1 mm on recorded graph			
Width of Ring 10 mm	0.154	0.0985	0.0684
Width of Ring 20 mm	0.077	0.0493	0.0342
Width of Ring 40 mm	0.0385	0.0256	0.0171

The indicator has a recording height of 70 mm.

The test oils A, B and D were subjected to after-treatment with Fuller's earth. For this purpose, the oils were diluted with high boiling gasoline in the approximate proportion of 1 : 5. The Fuller's earth was added in small quantities until, after shaking for about 15 minutes, the resultant solution was no longer discoloured. After standing for an hour, the mixture was filtered. In order to free the earth completely from any oil adhering to it, the former was washed several times with gasoline until a sample of the filtrate left no residue of oil on evaporation.

IV. EXPERIMENTAL SECTION

A. Examination of Setting Point and Commencement of Flow

The setting point and commencement of flow are given in Tables 1 and 2. As will be seen from the table 1, the time interval had no effect on the commencement of flow. Even cooling from 10°C to 20°C below the expected commencement of flow failed to produce further values.

A relationship between the commencement of flow and the setting point could not be obtained. Except in the case of oil D, the temperature of commencement of flow was generally higher than the setting point. Such was also the case with the refined oils A and B. Furthermore, the effect of previous heat treatment was determined in oil A. The oil whose commencement of flow was being investigated and which had not been previously heated to 50°C, showed a value that was 3.5°C lower than the commencement of flow of the pre-treated original oil. A test, carried out several days after an investigation with the same pre-treated oil specimen, showed a decline in the effect of preliminary heat treatment, since the new value for the commencement of flow approached the figure found for the non-pretreated specimen (See Table 2).

Whereas the effect of previous heat treatment vanishes again after a certain length of time (because this is a reversible process), refining has a permanent influence on the behaviour of mineral oils at low temperatures. Examination of the original oils A and D showed that, in contrast to oil B in which refining had no effect on the setting point, a considerable rise in this setting point occurred after they had been freed from resins. These resins, which are removed from the oils, thus probably exert a protective effect (when present)

which prevents the paraffin wax from being precipitated at low temperatures. (These resins are apparently colloidal in character.)

In evaluating the experimental results of viscosity determination this phenomenon will be discussed in greater detail.

B. Examination of Viscosity

1. By Vogel's Method.

Viscosity determination, using Vogel's apparatus for determining the commencement of flow, were effected at 0°C and -10°C. The viscosities, like the solidification point, are also dependent on the previous treatment of the oils, and and cloudiness caused by the precipitation of solid constituents was also found here. On the whole, this phenomenon is more pronounced with paraffin oils than with oils with a naphthene or asphalt base. It is shown more clearly by the experiments carried out in the Höppler viscometer. This slight cloudiness became more intense as soon as the constant final viscosity figure had been reached.

The viscosities at 0°C determined by Vogel's method were independent of the time interval. On the other hand, at -10°C these time intervals had a considerable effect on the viscosities of the two oils A and D, but a very much smaller effect on the viscosities of oils B and C which solidify at lower temperatures (Table 3). The reason for this is probably the fact that oils with a higher setting point exhibit a greater tendency to precipitate paraffin wax at a temperature of -10°C.

Investigations carried out with oil D, which had been freed from its resins with Fuller's earth, already showed lack of agreement at 0°C. It is assumed that the cause of this is the extraction of the resin, because if this was the case the precipitation of the paraffin-wax crystals takes place at even higher temperatures.

2. By the Höppler Viscometer.

In determining the viscosity at 0°C by Höppler's method, the figures for all the experimental oils were almost twice as high as the viscosities determined by Vogel's apparatus or by extrapolation. It would therefore appear that the viscosity differences are to be attributed to the "thermal history" of the oils. The oils examined in the Höppler viscometer were not subjected to any special preliminary heat treatment, as was the case with the samples examined by Vogel's method. However diesel fuels, which will form the subject of a subsequent report, on being examined in the Höppler viscometer, did not give any differences in the final values, whether they were pre-treated or not. In order to avoid any lack of clarity, oil D was tested, after pre-treatment, in a further series of experiments.

The viscosities of the oils A, B, C and D, and the refined oils A and B, which were determined with stricter temperature control, are shown in Tables 4 and 4a and Figures 13 to 16.

After the oils had been brought to the working temperature, measurements were initiated at, or shortly after, the attainment of this temperature. A characteristic shown by all the oils examined was a tendency of their viscosities to increase, as shown by the shape of the plotted viscosity curves, whose

angle with the abscissa became increasingly steeper the lower the working temperature. Whereas the naphthene-base compounded oil C did not vary in viscosity at 0°C and at -5°C from the beginning to the end of the experiment (Fig 15), the paraffin-base oils A(Fig.13) and B(Fig. 14) and the naphthene-base oil D (Fig.16) showed a slight tendency to increase in viscosity even at 0°C. The curves for -10°C to -20°C show this particularly clearly. Until a constant dropping-time had been reached, a shorter or longer period of cooling was necessary. With a short cooling period, uncompounded oils (A, B and D) show a uniform rise of the curve, which, however, presently passes into a straight line parallel with the abscissa; the compounded oil, on the other hand, takes very much longer to reach a constant dropping-time of this kind. Owing to variations in the times of dropping, the curve undulates before finally becoming a horizontal straight line. It might be assumed from these apparently surprising changes in the dropping-times (treated as a function of temperature), which occurred with some degree of regularity and in which the oil only reached constant temperature after a certain period, that aggregates of various structures have been formed and are broken down by the uniform fall of the sphere. If the oil is allowed to stand (i.e. if the procedure of dropping the sphere is interrupted for a prolonged period) the oils will be found to have a higher viscosity than before.

The longer the procedure of dropping the sphere is interrupted, the higher will be these maximum values. (See Figs. 13 and 15). Thus, for instance, in the case of oil C, the measurement was interrupted <u>before</u> a constant dropping was reached and the oil was allowed to stand for almost two hours. Here too, a sudden increase in the viscosity could be observed. The viscosity determined <u>after</u> the "maximum figure" had been reached was very considerably lower and agreed with the figures of the subsequent measurements. The explanation of this "higher viscosity" value obtained is that the solid constituents suspended in the oil were able to coalesce and form more compact aggregates and thus offered greater resistance (flow resistance) to the dropping of the ball. After streamline flow has been restored (i.e. after the break up of the whole structure) the resulting viscosity figure must approach or actually reach a final value.

Similar processes to the one just described were repeated in the examination of the pre-treated sample of oil D which was carried out at 0°C and -10°C. By comparing the viscosities of these oil samples with the figures of the untreated oil, differences (which at -10°C amount to almost 25%) will be found in the initial figures and, after reaching the stable state, in the final figures (Cf. Table 4 with Table 4a). Moreover, the viscosities ascertained at 0°C and -10°C were even higher. These facts dispose of the possibility of explaining the differences in the viscosities, given by the Vogel and Höppler viscometers, by their dependence on previous heat treatment; indeed, the discrepancies between the viscosity figures obtained with the various types of apparatus used are probably caused by certain still unexplained peculiarities of the apparatus, especially of the Höppler viscometer.

In contrast to the reduction in the viscosities of colloid solutions, which solidify in the form of gels, the dropping-times in oils A to D increase considerably. The phenomenon of the gel formation, occuring in some colloid solutions when they are allowed to stand, is a characteristic property. The

flow resistance is dependent on the existing gel condition. A change in viscosity, caused by disturbance from applied pressure or the dropping of the sphere and brought about by the increased shearing force, is noticeable by the variations in the consecutive times of falling in the case of albumens examined in the Höppler viscometer. At high concentrations and with consecutive dropping of the sphere, albumens, which are a typical example of colloids, give very much shorter fall times compared with the multi-component mixtures A to D. It may therefore be assumed that a process of crystallisation takes place in the oils. The question previously referred to, as to whether gel or crystal formation occurs, would be decided in favour of crystal formation in this case.

Of course, the final crystal lattice which first forms is broken up by the ball-drop, which is started shortly after a constant temperature has been reached. The prolonged intervals between two measurements at a fixed working temperature cause further growth and coalescence of the crystalline substances floating about in the oil. As already stated, these impede the dropping of the sphere and cause a decrease in the falling times until a state of equilibrium is reached as expressed by constant times of falling.

It was furthermore ascertained at the DVL that, in the case of oil having a high content of oxidation products, the consecutive times of dropping were less. With unused oils containing no oxidation products (hard and soft asphalt = 0), this decrease in dropping time did not occur. It may therefore be inferred that the oxidation products are colloidal in character.

If one compares the results of the work carried out by M. Jordachescu (see Fig. 8) with the experimental results given by the Höppler viscometer (see Figs. 17 and 18), it will not be very difficult to draw a parallel between the two methods. However, the simpler operation of the Höppler viscometer is to be preferred to the rather troublesome pressure apparatus. The cooling apparatus in its improved form offers no difficulties for maintaining constant temperature over any length of time and at working temperatures down to -60°C. In both viscometers the shearing forces are the factors used in measuring the viscosity, whether it is a falling sphere or the applied pressure that breaks down the structure aggregates formed in the cooled oil. We find that similar viscosity anomalies occur, and come to the conclusion that the precipitation of the crystal nuclei, a definite number of which are to be found in the oil, can be brought about in a brief space of time, viz. by continually moving the ball in the oil. The value of the final viscosity thus determined should also be the final value of the same oil after being treated for several weeks in the pressure apparatus. This deduction is only of theoretical value, however, as in practice, as we have seen, the oils are stabilised (under the same conditions) giving quite different final figures.

The experimental results show that a longer or shorter interval between two measurements resulted in viscosity figures of varying magnitude, which, however, with a steady ball drop approached the final result and finally remained constant at the figure already determined.

The investigation carried out to determine whether a state of rest has any effect on the viscosities of the unused oils A to D, was also extended to Oil B treated with Fuller's earth. In

this oil too, a rise in viscosity was observed. The oils contain on an average three per cent mineral oil resins. These are oxidised polycyclic compounds. If the viscosities of the resin-free oils are determined in the Höppler viscometer or in Vogel's apparatus, the values found will be considerably lower, providing that paraffin-wax separation has not taken place as in the original oils. If separation of paraffin-wax has already occurred, the viscosity at the same temperatures is very much higher than in the original oils. This phenomenon is attributed to the fact that the resins act as a kind of protective colloid which prevents the paraffin from separating out at low temperatures. Thus, resins tend to lower the setting point.

The increase in viscosity as a function of time and the decrease after leaving the oil A to stand at a temperature of 5°C below the working temperature, is shown in Fig.17. Fig. 18 shows the same process in the case of the refined oil A. On concluding a series of experiments, the oil was cooled from -20°C to -25°C. Drop-time measurements could not, however, be carried out at this temperature. Measurements could only be resumed after heating to -20°C, but at first they gave higher viscosities than previously obtained by cooling to -20°C. The figures fell steadily with regular ball-drop until the state of equilibrium was reached; the viscosities then measured were equal in value to those obtained by cooling to -20°C.

Each pair of curves exhibits the same characteristics, viz. the curves meet at a point (final viscosity figure) and their further course runs parallel to the abscissa. In both cases, the oil which has been normally cooled to the working temperature reaches the final viscosity figure more quickly than when the process is reversed. In any case, the refined oil A, which was brought to a temperature of -15°C, reached the stable state much earlier than the fresh oil examined at -20°C (See Tables 6 and 7).

It has already been mentioned that the viscosity anomalies are to be attributed to the separation of a certain portion of the paraffin-wax crystals in the oil. From the curves in Fig. 17 and 18, it can be stated that the crystals which separate on cooling below the working temperature, will pass into solution on heating until an equilibrium concentration has been attained; i.e. the amount of crystals precipitated at the normal speed of cooling equals the amount formed when the process is reversed.

Nevertheless, the measurements were made on the same day. After the experiments had been repeated several times with the untreated oil-samples, it was found that the viscosity alteration of an oil does not always proceed in the same way if observed on different days, even when carried out under the same experimental conditions. There was no hope, however, of always reaching identical final figures in this manner. In practice, the viscosities fluctuate to the same extent.

The information put forward by Erk from microscopic investigation of oils with low setting points shows that, after overcoming the difficulties caused by the nature of the temperature range, microscopic research methods can be a valuable aid in examining the crystal-forming processes in the oils A to D which have high setting points and are exposed to low temperatures. Finally, in many cases, this method of investigation provides an explanation for phenomena that have long been known

but have remained unexplained. The oil preparations having low setting points used by Erk show the presence of crystal nuclei even at high temperatures. The first traces of the crystal formation grew, on cooling, into a fairly cohesive lattice. Since the quantities of oil used in the microscopic examination were very small, they cooled relatively fast and showed rapid crystal formation.

In the case of an oil in the drop tube of the Höppler viscometer (about 30-40 ccs), crystallisation is very much slower, possibly as the result of supercooling and the high viscosity of the oil. The latter also brings about the slow rate of growth of the crystals. If, for instance, castor oil is cooled to -80°C., the oil remains unchanged. If it is again heated to a temperature at which viscosity is sufficiently low so that the growth of crystals can take place, the oil solidifies into a waxy mass. Through the continuous dropping of the ball, supercooling must be stopped for some time and the crystals are precipitated thus causing an increase in the viscosity. Since the rate of cooling has a very powerful effect on the size of the crystals precipitated, the oils were cooled to the working temperatures so that the temperature drop was 1°C in 1½ minutes in order to ensure a fixed size relationship.

Fig. 19 shows for the oils examined (according to their origin) breaks in the curve which are caused by increases in viscosity. This should show that the state of equilibrium of the system is altered by the separation of the hydrocarbons. This fact agrees with the results of examining the effect of time on viscosity at low temperatures.

The viscosity figures plotted in Fig. 19 are those obtained when the stable state was reached, i.e. the "plasticity" and the flow resistance caused by this plastic state were destroyed by the constant movement of the test ball. The stable state is similar to the flow resistance which, on breaking down the crystal lattice, exerts an influence on the viscosity behaviour. It has already been stated that the alteration of an oil up to the stable condition only proceeds in the same manner in the rarest cases. It is therefore impossible to obtain a curve with well-defined breaks in the low temperature range.

No significance can be attached to the formulae employed by various workers or to the extrapolation of viscosity figures obtained at high temperatures, for the temperature range below 0°C. Although the use of formulae eliminates the drawback of lengthy individual measurements, these formulae are nevertheless only applicable to a temperature range above 0°C and do not permit the mathematical determination of the behaviour of oils at low temperatures.

3. By the Vogel-Ossag viscometer.

The viscosity anomalies observed when using the Höppler viscometer suggested that comparative measurements should be carried out with a gravity-flow viscometer.

The Vogel-Ossag viscometer appeared to be the most suitable for this purpose and viscosity measurements were made at a constant working temperature of 0°C, using a wide-bore capillary. A Dewar vessel filled with melting ice was used for maintaining constant temperature. The figures obtained with this viscometer showed the same irregularities in viscosity as were found in the dropping-sphere and pressure

viscometers. Oils A, B and D, which had not been pre-treated, showed a tendency to increase in viscosity. With oils A and C, viscosity rose only slightly during a period of 4½ or 7 hours (the oil being continually drawn into the bulb and immediately allowing flow to take place), while the viscosity of oil D rose in about 7 hours from 10,680 centipoises to 11,230 centipoises. The figures for the oil D which had previously been heated to 50°C, were appreciably higher than those for the untreated oil: i.e. a rise in viscosity from 11,460 centipoises to 12,310 centipoises within 3 hours. The rate and duration of cooling also showed considerable influence here, inasmuch as when the test oils were suddenly cooled with ice, they showed different figures from the oils that were cooled down to the working temperature by the normal procedure.

The formation of paraffin-wax crystals, which coalesce in the oil to form a lattice structure, is also assumed here. By breaking up the structure aggregates formed in the oil in the reservoir and in the oil-sample after it has been drawn into the bulb, both the sucking-up process and the flowing back caused by gravity are of considerable influence. The crystal lattice, broken by the sucking-up process can reform in the bulb, since the constant viscosity value had not been reached and a very long time was required for the viscosity measurement.

4. By the pressure viscometer.

In the literature section of this report, detailed references have already been made to the viscosity anomalies, while in the experimental section the results of our own experiments have been discussed, all of which show the peculiar characteristics of viscosity changes which occur in the various pieces of apparatus and also at low pressures. These characteristics could not be observed in the apparatus developed by the DVL. The viscosities, insofar as they were measured above 0.5 atm. excess pressure, did not change after the tests had been repeated several times. With regard to the "starting values" (Anlaufwerte), the measurements of which are regularly too high, the explanation given by Yusiti Nisizawa is quite plausible: viz. at the start of the measurement, the true meniscus of the moving liquid (Stromprofil) and regular flow form have not been completely attained. The result of the experiments, which were carried out at different pressures, showed that the viscosity measurement gave the same value when calculated from Poiseuille's formula whether an excess pressure of 2 atm. or 10 atm. was applied (the latter being maximum pressure for the glass capillary). Whereas, in the case of the solidified oil the separated crystals form a connected network, in the interstices of which the liquid component is held as in a sponge, the viscosity figure calculated by Poiseuille's formula is a measure of the resistance exerted after the breakdown of the oil structure and crystal mass. It is not, however, possible to characterise sufficiently the behaviour of the lubricants at low temperatures by one factor, namely: the "flow resistance" already mentioned by Erk. The transfer of the oil into the measuring vessel at low temperatures and high pressures immediately destroys its plastic state (destruction of flow resistance after overcoming the resistance of the crystal structure), so that after exceeding the "flow limit", a broken crystal structure remains, whose pulpy consistency undergoes no further change when the tests are carried out at a determined working temperature. The force required to break up the crystalline structure is not produced in the

apparatus, since even when the measurements are repeated several times (as mentioned above) they give results which remain constant among themselves. An attempt was therefore made to establish a relationship between the results obtained in the pressure viscometer, and those produced by the I.G. apparatus which will be described below. Nevertheless, it was not found possible to establish such a relationship. In starting up an engine from cold, a certain "stickiness" has to be overcome. The I.G. has provided us with the means of ascertaining this energy factor with sufficient accuracy. The flow resistance which comes into play after the "breakaway" cannot, however, be measured by this method. (Note: owing to the heat of friction, the power required to keep the engine in motion drops steadily without reaching a definite end-point). Since further details of the measurement of the "breakaway resistances" have been given in another section, we shall merely state that the two pieces of apparatus supplement each other very well in characterising the oils as regards low temperature behaviour and in operation, as they enable the technical requirements of engines to be satisfied to a very large extent.

The experimental apparatus makes it possible to measure the flow resistance with a sufficient degree of accuracy (i.e. the flow resistance which opposes the "pressure" of the precipitated crystals.) The values shown in the curves in Figures 22 to 27 are end-values and lie on a straight line. The measurement of the flow resistance is fixed as an exactly definable quantity. It must not be imagined that, in viscosity determinations under pressure (in so far as the latter exceeds a given limit), special attention must be paid to rate of cooling. In investigations with the oils mentioned in this article, no influence could be observed. When a determined pressure was exceeded (thus in the case of oil A, 3 atm. excess pressure was sufficient), it was found that the oils were not more flow-resistant even in a fairly wide range below their setting points. The fact that no definite determination of the flow resistance could be made in this investigation, was probably mainly due to the small capacity of the container used for experiments below the setting-point. With suitable apparatus, however, all the difficulties should be eliminated and it should be possible to carry out an ideal determination of the flow resistance. To what extent the various oils are dependent on the applied pressure above their setting points, will be reported elsewhere on completion of the modified apparatus. It will merely be stated here that the oil 170/37 with a setting point of 0°C, which was also later on included in the series of experiments as test oil "E", exhibited peculiar behaviour. This oil was considerably liquified at a working temperature of -10°C and at 1 atm, excess pressure, so that it was not possible to determine the time required for filling the measuring bulb.

At certain temperatures the curve given in Fig. 28 shows a number of breaks which, as already mentioned, are to be attributed to the fact that precipitation occurs with falling temperatures and this brings about disturbance in the equilibrium system. This precipitation may be attributed to the formation of crystals, the quantity of which is dependent on the temperature, a process which persists until the state of equilibrium has been reached: i.e. the "saturation limit". The pressure applied prevents the crystals from coalescing to form a crystalline structure.

To examine this "structural viscosity", investigations were carried out with a test oil "E" mixed with 20% flaked graphite, and in another series of experiments using 5% lamp black. As will be seen from Fig, 26, the hopes of determining some deviation of viscosity were not realised. All the values lay on a straight line. A deformation of the suspension (which had been assumed to possess a certain strength) was complete even on applying the lowest possible excess pressure of 0.5 atm. in the pressure apparatus; i.e. the resistance limit was exceeded. Structural viscosity was certainly present in a range below 0.5 atm excess pressure, but it is impossible to cover this range accurately with the DVL pressure apparatus, as the manometer does not function with the required degree of precision over this range. In order to illustrate the possible structural viscosity (16), the flow curve of a suspension of 5% lamp black in castor oil has been included in this report (cf. Fig.26a). This curve clearly shows that a suspension possesses a certain flow resistance; to overcome this, a fixed pressure must be applied.

C. Examination of the breakaway resistance

1. I.G. apparatus.

Whereas the DVL pressure viscometer is an instrument which must be regarded more or less as a laboratory test apparatus, the I.G. apparatus is an instrument which has been designed with close regard to actual engine conditions. A clear distinguishing characteristic is given by rating the various oils by means of the position of a curve maximum. The curves shown in Figs. 31 to 35 were prepared at different working temperatures and on different days, and present a similar form throughout. Fig. 34 shows curves which were directly recorded by the apparatus on the recording strip of the indicator, and the similarity of the shape of the curve (the curves are plotted together for the sake of clarity) makes it possible to draw conclusions as to the accuracy of the measuring method. Fig. 36 shows the stickiness of the oil in relation to temperature. The resistance caused by the breakaway of the crystalline "cement" formed on the engine parts as a result of low temperature treatment rises rapidly to a maximum, and then gradually falls, owing to a temperature increase of the oil film caused by friction. The setting point stops the oil flow as a result of its density; it is of no consequence here. The resistance to breakage of the crystal structure formed by low temperature treatment, is easily determined by the apparatus; on the other hand, on attaining a maximum, the flow resistance exerted by the oil-crystal mass, which is an important factor in determining thefurther behaviour, cannot be measured with this apparatus.

In this article, detailed regard has been paid to the theme "The value of viscosity determinations in the low temperature range and also the viscosities extrapolated from high temperatures by various methods". As the viscosity at the beginning of a determination differs essentially from that measured on attaining the stable state, no reliance can be placed on the dependence of an extrapolated viscosity (e.g. by Walther) on the stickiness.

V. SUMMARISED DISCUSSION OF THE EXPERIMENTAL RESULTS AND CRITICISM OF THE METHODS.

The usual test methods applied for estimating the low-temperature behaviour of lubricating oils are inadequate. The behaviour at fixed, more or less low temperatures differed from that calculated from the position of the viscosity curve, or predetermined by certain methods. These methods were inadequate in so far as they omitted part of the engine requirements. The present investigation is therefore devoted to the resistance of the oils to the commencement of flow and to the flow itself. The former occurs in practice when cold engines are started and the latter during the subsequent operation.

1. Resistance to the commencement of flow.

The duration of cooling has no influence on the commencement of flow. Preheating to +50°C causes the commencement of flow to drop temporarily by 3.5°C, while refining by eliminating the resins increases it permanently, because, before refining, the crystallisation of the paraffin was delayed by the protective colloidal action of the resins. There is no relationship between setting point and commencement of flow.

It is possible to measure the starting resistances with the I.G. Farben-Industrie apparatus by suitably modifying the experimental procedure, since the curve maximum represents the peak point of the breakaway force and the transition of the solid system to an oil-crystal mass.

Investigations carried out in the Baader apparatus for determining "setting viscosity" (Stockzähigkeit) were prematurely concluded, since comparative results could not be obtained.

2. Resistance to flow proper.

The final results of all the work on viscosity necessitates a classification under the following three headings:

(a) Cause of the anomalies.

Viscosity measurements in three viscometers which operated at low shear strength, produced widely divergent figures and gave rise to viscosity anomalies. Even when the procedure was modified in the Höppler viscometer (preliminary heat treatment of the oils), no change in these anomalies was produced, although the conditions of reproducibility were improved. This is attributed to a disturbance of the internal structure owing to destruction of the flow resistance.

(b) Final viscosity due to low and high shearing forces.

It was found that measurements immediately following one another produced final viscosity figures which deviated from the initial value by up to 90%, and which varied on different days. A final viscosity which became stable after a certain period, was only determined in viscometers working with a low shear pressure. For this reason, and also because in practice various conditions depending on the method of cooling and the operational procedure are attained, it is impossible to obtain serviceable results with viscometers of this type. Better figures were those obtained with a pressure viscometer designed by the D.V.L., because here the viscosity variation was eliminated. Since the behaviour of engine oils in the

low temperature range (with regard to resistance to flow) depends on their flow resistance, and the characteristic high shear pressure of this apparatus immediately destroys the plastic state of the oil, the measurements by this apparatus of the flow resistance (which is exerted by the oil and crystal mass) provides the factor which characterises the behaviour in operation.

(c) Practical standardisation of viscosity.

The investigations have shown that, at low temperatures, too much importance should not be attributed to experimental viscosity data if the final viscosity is not known and the series of experiments has not been pursued to the end. Until the final state has been reached, the viscosity is only "approximate or apparent". The actual viscosity measurements can therefore only be carried out at temperatures above 0°C. The extrapolation of viscosity from this range to low temperatures cannot be applied to engine oils. The breaks in the viscosity curves, met with in estimating the final viscosities, are a characteristic of the crystallising out of paraffin-waxes and are not covered by extrapolation. Even when a high pressure is used (up to 10 atm excess press.), extrapolation is not possible, since breaks in the curves are also shown when using this apparatus.

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TABLE 1A

Oil	A	B	C	D
Specific gravity at 20°C	0,890	0,884	0,902	0,909
Viscosity in cps at:				
100°C	19,6	20,3	19,9	16,3
50°C	160,0	162,0	147,0	137,2
100°F	307,0	341,0	306,0	297,5
20°F	1024	1260	1134	1182
Refractive Index	1,4921	1,4887	1,4987	1,5024
Solid Foreign Matter	0	0	0	0
Setting Point °C	-18,0	-22,0	-23,0	-13,5
Flash Point °C	277	282	238	230
Ignition Point	317	334	291	285
Neutralisation No mg KOH	0	0,028	0	0,04
Sap. value mg KOH	0,1	0,28	4,84	0,14
Ash	0,001	0,0	0,004	0,0
Mol-weight	715	748	570	612

TABLE I

TIME INTERVAL (Mins)	10	15	30	60	90
Commencement of Flow (^{o}C) of:					
Oil A	-	-14.1	-	-14.1	-
Oil B	-	-17.0	-	-	-17.0
Oil C	-	-21.5	-21.5	-21.5	-
Oil D	-15.0	-15.0	-	-15.0	-
Oil A (de-resinated)	-	-14.5	-	-14.5	-
Oil B (do)	-	-20.0	-	-20.0	-
Oil D (do)	-	-12.5	-12.5	-	-

TABLE 2

Engine Oils

Determination of Commencement of Flow

Type of Oil	D_{20}^{o}	Setting Point ^{o}C	Commencement of flow ^{o}C	Mean Value ^{o}C	Temp. of cooled oil ^{o}C	Rate of cooling ^{o}C/min	Time Interval
A	0.890	-18.0	-17.5 **)	-17.5 **)	-30	1.5	15
		-18.0	-15.5 **)		-30		15
			-14.0 o)	-14.0 o)	-25		15
			-14.0 o)		-25		60
			-16.5 +)		-25		15
A (de-resinated)	0.882	-15.5	-14.5	-14.5	-30	1.5	15
			-14.0		-30		
B	0.884	-22.0	-17.0	-17.0	-30	1.5	15
			-17.0		-30		90
B (de-resinated)	0.882	-22.0	-20.0	-20.0	-40	1.5	15
			-20.0		-40		60
C	0.902	-23.0	-21.5	-21.5	-30	1.5	15
			-21.5		-30		60
D	0.909	-13.5	-15.0	-15.0	-30	1.5	10
			-15.0		-30		60
D (de-resinated)	0.900	-9.5	-12.5	-12.5	-25	1.5	15
			-12.5		-25		30

**) Value for the non-treated oil

o) Value of the heat-treated oil

+) Value after disappearance of heat effect

TABLE 3

Viscosities obtained by Vogel's Method.

Type of Oil	Viscosities (in cps) at:				
	0° extrap.	Measured at 0°C.	Storage Period (Mins)	Measured at -10°C	Storage Period (Mins)
A	7729	7895	10	37449	10
		7895	15	42180	20
		7895	20	46227	30
B	8930	7667	15	26121	10
		7667	15	26648	20
		7667	20		
B (de-resinated)	-	-	-	21900	10
	-	-	-	22230	30
C	7420	7524	5	26554	10
		7524	15	26591	30
		7524	20		
D	9692	10232	10	61475	10
		10289	10	67475	10
		10289	15	70395	
				77007	15
D (de-resinated)	-	8614	15	150636	15
		8760	30	185706	120
		9636	60	224437	240
				159592	360
				198930	480

TABLE 4

Viscosity of Oil D with the Höppler Viscometer at 0°C.

Storage Period in Mins.	Stop-watch reading	Centipoises.	Centistokes.
15	13,4"	18599	20194
18	13,4"		
20	13,6"		
25	13,9"		
30	14,0"		
33	14,2"		
40	14,4"		
45	14,4"		
50	14,4"		
55	14,6"		
60	14,6"	20713	22440
65	14,6"		
70	14,6"		
75	14,6"		
80	14,6"		
85	14,6"		
90	14,6"		
95	14,6"		
100	14,6"		
110	14,6"		
120	14,6"		
	at -5°C		
15	28,3"	39273	42503
20	28,5"		
25	28.6"		
30	28.9"		
35	29.1"		
40	29,3"		
45	29,5"		
50	29,7"		
55	29,8"		
60	29,9"		
65	30,0"	41623	44901
70	30,0"		
75	30,0"		
80	30,0"		
85	30,0"		
90	30,0"		
95	30,0"		
100	30,0"		
105	30,0"		
110	30,0"		
120	30,0"		
130	30,0"		

CONTINUATION OF TABLE 4.

Viscosity of Oil D with the Höppler Viscometer at -10°C

Storage Period in Mins.	Stop-watch reading.	Centipoises.	Centistokes.
15	1' 14,0"	102651	110735
20	1' 14,2"		
25	1' 14,8"		
32	1' 15,9"		
37	1' 16,2"		
45	1' 16,6"		
50	1' 16,8"	106555	114613
55	1' 16,8"		
61	1' 16,8"		
68	1' 16,8"		
75	1' 16,8"		
81	1' 16,8"		
88	1' 16,8"		
94	1' 16,8"		
100	1' 16 8"		
105	1' 16 8"		
110	1' 16,8"		
115	1' 16 8"		
120	1' 16,8"		
125	1' 16,8"		
130	1' 16,8"		

TABLE 4a

Viscosity of Pre-treated Oil D (Heated for 10 mins. at 50°C) at 0°C

15	9,2"	12768	13833
16	10,5"		
17	11,0"		
18	11,6"		
19	12,2"		
20	12,7"		
21	13,2"		
22	13,5"		
23	13,7"		
24	13,9"		
25	14,2"		
26	14,3"		
27	14,5"		
28	14,5"		
30	14,5"		
32	14,5"		
34	14,5"		
36	14,7"		
37	14,7"		
38	15,1"	20956	22704
40	15,1"		
45	15,1"		
55	15,1"		
56	15,1"		

CONTINUATION OF TABLE 4a

Viscosity of Pre-treated Oil D (Heated for 10 min at 50°C)

at -10°C

Storage Period in Mins.	Stop-watch reading.	Centipoises.	Centistokes.
20	59,3"	82060	88237
24	1' 12,7"		
28	1' 18,1"		
32	1' 23,2"		
37	1' 25,7"		
42	1' 28,6"		
46	1' 28,9"		
53	1' 29,2"		
65	1' 31,7"		
70	1' 32,6"		
76	1' 33,5"		
82	1' 33,9"		
89	1' 35,5"	132237	142290
94	1' 35,5"		
99	1' 35,4"		
101	1' 35,5"		
107	1' 35,4"		
117	1' 35,4"		
124	1' 35,4"		
134	1' 35,4"		
145	1' 35,4"		

at -15°C

20	3' 22,8"	281250	302419
30	3' 32,2"		
40	3' 37,3"		
50	3' 42,8"		
60	3' 47,7"		
75	3' 53,5"		
90	3' 56,3"	327709	350858
100	3' 56,3"		
115	3' 56,3"		
125	3' 56,3"		
140	3' 56,3"		
150	3' 56,3"		
165	3' 56,3"		
175	3' 56,3"		
190	3' 56,3"		
205	3' 56,3"		
220	3' 56,3"		

at -20°C

Time for the sphere to fall through 1/8 of the measuring distance was 240 mins. The measurement was therefore discontinued.

TABLE 5

Equilibrium reached after .... minutes cooling

Temperature	± 0°C	-5°C	-10°C	-15°C	-20°C
Oil A	35	10	35	60	120
Oil B	25	75	85	185	90
Oil C	immediately	immediately	195	470	415
Oil D	55	65	50	90	-
Oil A (de-resinated)	-	-	95	110	-
Oil B (de-resinated	20	20	30	75	240

TABLE 6

Viscosity of Oil A @ -20°C with rising temperature (Half distance of fall)

Duration of Cooling in Mins.	Stop-watch reading	Centipoises.	Centistokes.
20	6'55.8"		
47	6'14.5"		
72	6' 5.3"		
95	6' 3.4"		
117	5'53.0"	Final value of the constant dropping time obtained with falling temperature	
140	5'37.8"		
160	5'41.8"		
210	5'36.5"		
232	5'33.5"		
253	5'32.0"	5' 18.7"	
275	5'30.2"		
297	5'26.6"		
325	5'20.4"		
355	5'18.9"		

TABLE 7

Viscosity of Oil A (de-resinated) at -15°C with rising temperature (Full distance of fall)

Duration of Cooling in Mins.	Stop-watch reading	Centipoises.	Centistokes.
5	3'34.8"	298465	330526
15	3' 0.6"		
25	2'43.4"		
33	2'38.4"		
41	2'34.6"		
63	2'26.5"		
72	2'19.8"		
79	2'16.8"		
85	2'16.6"		
95	2'16.6"		
110	2'16,6"		

Final value of constant dropping time obtained with falling temp: 2'16.6"

TABLE 8

Flow Resistance of Various Oils. (Every individual determination carried out several times)

Type of Oil	Temp. °C	Vogel-Ossag Viscosity (extrapol.)	Flow resistance in centipoises at various pressures (DVL method) Pressure in atm. 2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0
A	0	6,420	7,000	7,000	6,970	-	-	-	-	-
	-5	10,900	-	15,900	-	15,600	15,200	-	15,200	-
	-10	19,590	-	31,400	31,700	31,000	-	-	-	31,000
B	0	9,070	8,150	-	8,050	-	-	-	-	-
	-5	16,690	15,800	-	15,800	-	15,800	-	-	-
	-10	32,580	-	-	34,100	-	34,000	-	34,000	-
C	0	8,240	-	7,400	-	7,210	7,400	-	-	-
	-5	15,370	14,700	14,700	14,700	-	-	-	-	-
	-10	29,540	-	29,200	28,900	28,700	28,800	-	-	-
D	0	10,000	10,100	-	10,000	9,850	-	-	-	-
	-5	19,930	-	-	20,800	20,000	20,000	-	-	-
	-10	39,525	-	-	50,600	-	48,300	50,000	-	-

FIG.1. Flow resistance and solidification characteristics of 5 different oils and castor oil.

FIG.1a. Isotropic - Nematic - Smectic - Crystalline
Illustrations of phase changes up to crystallisation. (From: Annales de l'Office National des.Comb.Liq., year 12, No.3, 37.)

MICROPHOTOGRAPHS OF VARIOUS OILS USING TRANSMITTED POLARISED LIGHT.

FIG.2. Oil heated to 50°C and slowly cooled to 20°C.

FIG.3. Oil at 40°C after previous heating to 45°C.

FIG.4. Oil heated to 50°C then suddenly cooled to 20°C.

FIG.5. Oil heated to 50°C then slowly cooled to 14°C.

FIG.6. Oil broken down at 0° C.

FIG.7. Oil broken down at -15°C.

FIG.8. Variation of the viscosity of an oil with time.

FIG.9. Curves for discharge quantity against pressure.

FIG.10. Apparatus for determining the commencement of flow.
A = cooling bath
D = U-tube with side tube to pressure source.
G = Dewar vessel
M = Measuring marks
R = Air stirrer
T = Thermometer

FIG.11. Precision model of the Höppler viscometer.

FIG.12. Refrigerator with Höppler viscometer.

FIG.13. Viscosity anomalies determined with the Höppler viscometer. (Oil A)

FIG.14. Viscosity anomalies determined with the Höppler viscometer. (Oil B)

FIG.15. Viscosity anomalies determined with the Höppler viscometer. (Oil C)

FIG.16. Viscosity anomalies determined with the Höppler viscometer. (Oil D)

FIG.17. Variation of viscosity of an unused oil with time (obtained with the Höppler viscometer)

FIG.18. Variation of viscosity of a de-resinated oil with time (obtained in Höppler viscometer)

FIG.19. End values of viscosities obtained by the Höppler apparatus. (Oils A, B, C, D, A de-resinated and B de-resinated)

FIG.20.

FIG.21. The DVL Pressure viscosimeter.

FD2876,46lt69

F.D. 4841/45

Report FB 1150

German Aeronautical Research Institute (D.V.L.)
by
Lichtenberger

Measureing Knocking by the D.V.L. Pressure Acceleration Method

Summary: The D.V.L. pressure acceleration method and its application are described in detail, in the discussion of the theoretical basis of the process, the state of development of the more important knock-measuring methods is described.

In the series of tests on the C.F.R. and B.M.W. 132 single-cylinder engines, in which the influence of numerous working conditions on knock behaviour was investigated, it was shown that there was a similar behaviour with similar fuels when the d^2p/dt^2 was measured.

The knock limit curves of four fuels, of different chemical composition, which were found aurally by the D.V.L. supercharge test method, were established with greater certainty by the d^2p/dt^2 measurement. The D.V.L. pressure acceleration method is thus a fulfilment of the long-cherished desire to measure the onset of knocking objectively, that is to say, without the uncertainty of the aural method.

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