

1942 YEAR BOOK OF GERMAN AVIATION RESEARCHVOL. II, pps. 170-178.Laboratory Method for Testing the Ageing ofLubricating Oils.

by

Dr. Mayer Bugström, Berlin.Report by the German Aeronautical ResearchEstablishment, Institute for Fuels and Oils.

The ageing of motor oils takes effect in three ways: piston ring-sticking, formation of sludge in the crank-case, and formation of deposits on the pistons and valves. According to the test conditions, the method of ageing may involve more particularly one or the other of these processes. The object of this work is to group the different ageing methods according to these different aspects, to discuss briefly those which are usual for aero-engine oils, and to discuss the results obtained with them.

CONTENTS.

- I. Principles of laboratory ageing in a test apparatus.
- II. Oxidative change and ring-sticking.
- III. Oxidative change and sludge formation.
- IV. Oxidative change and deposit formation.
- V. Conclusion.
- VI. Literature.

I. Principles of laboratory ageing in a test apparatus.

Table 1 shows the test conditions to which the oils are subjected in different ageing methods. Comparing these with the conditions to which the oils are subjected when working in an engine, great differences are observed. Above all, the ageing temperatures are generally much lower than the temperatures prevailing at the piston. There is naturally no effect of pure oxygen on the oils in practice, nor of air in the form in which it is used in various oxidation tests in which air bubbles are passed upwards into the heated oil. Also, in operation the oil only comes into contact with metals, whereas the ageing tests generally use glass vessels. The individual methods differ also considerably as regards test conditions, even if there is a certain relationship, such as that between time and temperature. Thus, the three tests which make use of oxidising agents, arranged in order of rising test temperature and reduced time of test are:- the French, English, and DVL (or WAC) tests. It is true that the Sligh test is made at the same temperature as that used in the (British) Air Ministry

test, but owing to the fact that it works in an atmosphere of oxygen it requires a much shorter test time. In the methods of Evens and Schmidt, the time of oxidation and the temperature are even lower than in the Slight test; but then the test not only uses atmosphere of oxygen, but also spreads the oils out thinly over a catalyst. Thus the different conditions of oxidation are partly cancelled out between the different methods. But, of course, this does not mean to say that the oils when oxidised by these different methods will show anything like the same properties. On the contrary, it is repeatedly stated that even a slight alteration in the working conditions can substantially alter the resistance to oxidation. An example given by Mander (10) shows (see Fig. 1) how the rating of an oil may be changed by altering the test conditions, even if the same method is used. Here the comparative asphalt resin values of the oils investigated under varied conditions are shown, and the resin + asphalt values obtained by oxidising under similar conditions are connected together. The resulting curves for individual test methods are in no case parallel or proportional to each other. But not only the oxidising conditions, but also the further stages in the treatment (duration of cooling, interval between the conclusion of the oxidation process and the determination of the oxidation products) have a great influence on the changes taking place in the oil, as was demonstrated by Seufert (11) also on the basis of the Woack process. Fig. 2 (according to Seufert) shows how the content of oxidation products may change after the oxidised oils have stood for varying lengths of time. It is, therefore, necessary to lay down an exact procedure.

Estimates of the correct oxidising temperature differ by as much as several 100°C, as can be seen from the few methods whose results are shown in Table 1. Suida (12) approximates the oxidising conditions as near as possible to those in practice. Where the practical conditions cannot be exactly imitated, Suida would like to see them exaggerated as much as possible. Baader (13) takes the opposite view, saying that if the conditions are intensified in this way (use of oxygen instead of air, increased temperatures), the conclusions reached may be erroneous. A better plan than that of Suida is perhaps the one chosen by Marder (14) who would like conditions which, while not exaggerated, are still the most extreme which occur in the engine, for ageing those oils, such as aero-engine oils, which have to fulfil the most difficult requirements. It must be borne in mind, however, that many oils which were rated very low under these extreme conditions behave much better under the conditions normally prevailing in the engine. Therefore, Marder also makes allowance for the case where it is not a question of a test under exceptional conditions, by making the conditions maintained under laboratory oxidation conform to those found in practice, and by carrying out the oxidation test in such a way that the nature and amount of the products of oxidation correspond to what is found in practice. But it is necessary here to make a distinction between the total amount of oil in circulation, and that part of it which is locally over-loaded.

According to Kadmer (15) mineral oils which have been artificially aged at temperatures above 125°C, can no longer be regenerated, in contrast to oils which have been exposed to oxidising conditions in practice, since they appear to have undergone a chemical change throughout their whole mass, while in practice overheating only occurs locally, for instance, in the piston ring grooves. Accordingly, nearly all the oxidation tests give too high a figure for the content of oxidation products compared to the total amount of oil in circulation, while only those methods which use similar temperatures can be used for comparison with the local over-heating. To determine more exactly the oxidation behaviour of the oils, it would be necessary to determine the effects of temperature on each one of them. This has been mentioned before in various papers (V. Philippovich (16), Marder (14)), but owing to the complications involved it has not yet been attempted.

If the laboratory methods by which the changes in the oil are measured are grouped according to their relationship to engine criteria, then the division suggested by Philippovich appears a reasonable one; it is the one which is carried out in this work:-

Engine Criteria.Laboratory Tests.

Piston-ring sticking.

Sludge formation in the crank-case.

Formation of deposits on pistons and valves.

Oxidation (formation of asphalt and measurement of volatility, ability to form suspensions, solubility of asphalt).
 Oxidation tests and ability to form suspensions, also coking tests.
 Coking tests (also reactive capacity, or adhesive capacity).

II. Oxidation Change and Ring-sticking.

Ring-sticking is caused in the first instance, at least in aero-engines, by products of change of the oil, but not of the fuel. The oil gets from the crank case into the combustion chamber, is there oxidised, and carries the products of oxidation, partly in solution, and partly in the oil in the form of sludge, to the piston ring grooves, where they gradually form deposits (16.) This interpretation is confirmed by the fact that ring-sticking is delayed by an increase in the flow of fresh oil to the grooves (increased consumption).

That the oxidation mainly occurs in the combustion chamber is proved by the large quantities of oxygen which were found in the combustion chamber deposits (see Table 2, Tests by DVL). Also, Weiss and Maillard (19) are of the opinion that the temperature in the crank case is too low and the atmosphere too poor in O₂ for any appreciable degree of oxidation to occur there.

TABLE 1.Test conditions in the oil oxidation tests.

Process	Quantity used g cm	Time of Test. Hours.	Temperature °C	Oxidising Agent	Metal	Characteristics Found.
Method of the English Air Ministry (1, 2)	- 40	2.6	-200	15 Air/h	-	Increase in specific gravity, viscosity, and carbon formation.
Method of the French Air Ministry (3.)	- 200	120	140	Air current over moving oil.	Copper strips	The same, also, increase in asphalt content.
Indiana test. (4)	- 300		172	10 Air/h	-	Time taken to form 0.1 and 1% asphalt, and for viscosity to increase by 25%
Seigh Test(5)	10 -	2 $\frac{1}{2}$	200	Oxygen	-	Asphalt.
Evens and Schmidt(6)	15.5 -	1 h. 40 m.	100	Oxygen	Heavy metal oxide on Silica Gel.	Oxygen consumption; increase in acid number, saponification number, asphalt content.
DVL Cup Test (7,8)	10 -	4	285 (uncorrected 275)	Air	-	Fluidity; asphalt in residual oil.
WAC Method(9)	10.35 -	5	288 (uncorrected).	Air	Aluminum cup.	Substances insoluble in gasoline and asphalt (soluble in chloroform).

TABLE 2.

Composition of the combustion chamber deposits,
the interior of the piston, and the ring grooves.

	H %	O %	O %	Ash %	S %
1 Top of piston (lead-free runs)	2.52	70.0	27.48	8.42	0.0
	2.5	73.6	23.9	4.9	0.8
	2.5	75.5	22.0	6.9	0.0
	1.7	71.3	27.0	4.6	0.0
	3.2	75.4	21.4	14.04	-
2 Interior of piston	4.60	77.8	17.77	8.83	
3 Oil in circulation (centrifuged).	4.47	77.8	17.73	40.94	
	2.6	82.8	14.55	3.1	
4 Ring Grooves					
Groove 1	3.35	75.51	21.14	8.96	
2	3.61	75.29	21.10	6.51	
3	3.59	75.03	21.38	14.27	
4	4.38	75.31	20.31	11.14	

On the other hand, pronounced oxidation occurs in the combustion chamber in addition to thermal decomposition. Incomplete combustion causes hard carbon deposits.

The passage of the partially oxidized oils from the combustion chamber to the ring grooves can be traced clearly in the DVL tests (17) from the quantities of lead found in the ring grooves (when fuels with a lead content are burned). These show the volumes of lead in descending order. The circulation oil also contains lead, which was evidently carried there with the residual oil.

The question is, to what extent the products of conversion of the fuel are involved in the process of ring-sticking. Weiss and Maillard investigated this problem and found that products of the incomplete combustion of the fuel are dissolved in the oil, being unsaturated compounds and acids, such as formic and acetic acid, and also phenols and aldehydes. On account of their tendency to resinification, these substances, it is true, are partly responsible for ring-sticking, but are not the main cause of it, mainly because they only form a very small part of the insoluble substances. Tests with hydrogen, household gas, and gasoline as fuels show that the majority of the precipitates had their origin in the oxidation of the oil, and not in the products of incomplete fuel combustion. Admittedly, there are those who hold that the fuel has a much greater influence on the formation of deposits. Thus Kadmer (20, 21) thinks that this is predominantly due to the incomplete combustion of the fuel, and that the asphalt and carbon which form are a function of the C : H - ratio of the fuel.

In the oxidation tests in the laboratory, the fuel is excluded as a factor. But in order to test the tendency of the oil to ring-sticking it will be necessary to select the test conditions so that they agree as far as possible with the conditions at the piston ring. The best guide to the changes in the oil which lead to ring-sticking under these conditions is the formation of asphalt. Here it must be remembered that the amount of asphalt is determined in the laboratory by solubility tests with naphtha, and this includes that which is soluble in oil. But from the point of view of ring-sticking, only that asphalt is important which remains undissolved or suspended in the piston ring groove. The capacity of the oils to dissolve asphalt is therefore important, and that not only at one temperature, but at several, since the temperature of the oil

falls on its way from the combustion chamber to the crank case, and thus, according to the dependence on temperature of the capacity to dissolve asphalt, greater or less volumes of asphalt can separate out. Tests on the capacity to dissolve asphalt have been started at DVL, but so far only on fresh oils. As Fig. 3 shows, asphalt only begins to dissolve on any considerable scale with most oils at 100°C, but the solubility then climbs very rapidly up to the final temperature of 250°C (16). The same is true of the suspension of carbonaceous matter.

It is clear that the oils have very varied suspension capacities. Differences are most clearly seen in this respect in the groups of greases compounded, and pure mineral oils. Here, too, it depends whether the condition of the suspension at the piston ring is stable. The volatility should also be mentioned in this connection, since the concentration of the dissolved products of oxidation depends on it. Speaking generally, it can be said that oils which are less volatile, as also less viscous oils, have less tendency to ring-sticking, conditions being otherwise equal (16). Deposits which have once formed in the grooves can be reduced by mechanical or chemical influences; the latter may be the less important, since the reactive capacity of the carbonaceous matter here is less important than at points where the surrounding air has a higher oxygen content (17).

Among the oxidation tests for lubricating oils there is a series which works in the range of temperatures from 275 to 300°C, i.e. the temperature of the oil on the rings. These are of interest in this connection. The process used by the Wright Aeronautical Corporation (WAC (9)) uses an aluminium cup as an oxidation vessel, which is heated to 315°C. 3.5 ccm of oil are pipetted into it at 10 half-hourly intervals. The oil then reaches temperatures above 288° (uncorrected, therefore still higher). After 5 hours the naphtha insoluble portion is determined, and of this, that quantity soluble in chloroform.

Evidently the test conditions given here are too mild, for according to later reports the temperature is to be raised to 338° and the time to 7½ hours, so that the stable oils are better differentiated. In the DVL process the oxidation is carried out in glass cups. 10 g of oil are spread out in a thin layer, and subjected for 4 hours to a temperature of about 285°C (in the oil). The volatility (loss of weight) and the oxidation products which are insoluble in naphtha and soluble in benzene, are determined. This process is suitable (as is probably also that of the W.A.C.) for plotting temperature curves, because of its short oxidation time, and it was used for this purpose. The basis of another DVL method, on which A.v. Philippovich will report shortly, is the representation of ring-sticking, as far as this can be effected simply on a laboratory scale (without combustion of lubricating oil and fuel). The oil is heated in an aluminium cup to 300°C, and a segmented disc moves against the bottom of the cup with slight play. The oil gradually thickens, and exerts a growing resistance to motion of the disc, which is indicated by the deflection of a pointer on a torque indicator. The main conclusion reached with this test is that the consistency of the asphalt is not adequate evidence on which to base differences in the behaviour of the oil. Weiss and Maillard (22) also fixed their test temperature at 300°C. At this temperature, the proportion of the naphtha insolubles which was insoluble in chloroform was in agreement with what was found in practical tests. The oil is heated in a flask in a flow of air, the volatile products of oxidation are collected, and tested for acid content. As the density of the oils rose the acid content fell, while the volume of asphalt increased. Apart from an initial delay, the absorption of oxygen was in proportion to the time, and reached about 50% of the volume used. Increased air supply, or an extended test time, caused an increase in the insoluble products, without altering their character. Greases and compounded oils gave poor results. The authors do not adduce comparisons with engine results. That they do not consider the test conditions ideal is clear from the fact that it is considered necessary to make a further approximation to practical conditions by the projected development of a test engine.

III. Oxidation Change and Sludge Formation.

By oil sludge is meant a mixture of oil and substances which are deposited in the oil, in so far as these do not form solid bodies.

Table 3 shows the composition of oil sludge (16)

The composition of the solid carbonaceous particles in the sludge and the oil is similar to that of oil coke; thus the oxygen content of the oil coke particles from the sludge is the same as that of the oil deposits from the top of the piston (24), while carbonaceous matter from the oil on the under side of the piston has 4 to 5 % less oxygen. While, according to this, it is hardly probable that the solid particles of sludge come from the crank case, the conditions prevailing in the crank case hardly allow the formation of asphalt products. Laboratory tests were made by DVL (25), in which the oil was made to circulate in an apparatus made out of various kinds of metal, and was finely atomized, without the formation of asphalt after 50 hours at an air temperature of 198°C. Kadmer assumes that in the formation of sludge, as also of carbonaceous deposits (see above) the products of the incomplete combustion of the fuel play a large part, forming acids, saponifiable matter, and asphaltic materials (21).

An important factor in the formation of sludge in the engine is the penetration of water into the lubricating system. As the oxidation of the lubricating oil becomes intensified, its tendency to form emulsions increases, resulting in the formation of extraordinarily stable emulsions of water-in-oil. On this basis, Andreys (26) has evolved an oxidation test, in which the oil, after oxidation (150°C, outside air, copper catalyst), is tested as to its tendency to emulsify with water, and conclusions drawn as to its degree of oxidation. Apart from this case, lubricating oil oxidation tests generally exclude the influence of humidity, which to a certain extent is a contradiction of conditions in practice.

TABLE 3.

Composition of Oil Sludge.

Designation How obtained	A Centrifuge		B Centrifuge		C Centrifuge (laboratory)	
Operating time Engine	200 hrs. BMW 6		94 hrs. BMW 132		35 hrs. SAM 22B (JPEE).	
Water %	1.5		3.0		0.5	
Naphtha solubles %	64.8		84.9		77.6	
Chloroform solubles %	4.2		1.3		11.4	
	(2.6% asphalt soluble in (Ash free) CHCl ₃)		(0.8% asphalt soluble in (Ash CHCl ₃) Free)		(2.3% asphalt soluble in (Ash CHCl ₃) free)	
Carbon %	84.6	84.4	83.1	84.0	83.2	83.2
Hydrogen %	11.8	11.8	8.5	8.6	11.1	11.1
Oxygen + nitrogen %	3.4	3.4	7.4	7.4	5.65	5.7
Ash %	0.2	-	1.0	-	0.05	-
Chloroform insolubles %	29.5	-	10.8	-	10.5	-
Carbon %	38.9	68.9	51.2	66.0	69.6	70.5
Hydrogen %	1.9	3.4	2.1	2.7	3.1	3.1
Oxygen + nitrogen %	15.6	27.7	24.3	31.3	-	26.4
Ash %	43.6	-	22.4	-	1.2	-
<u>Composition of Ash</u>						
SiO ₂ about %	1.3		1.1		0.1	
Fe " %	18.5		14.6		1.0	
Al " %	6.5		1.1		0.1	
Pb " %	17.3		5.6		0.0	

The increase in viscosity, with progressive formation of oxidation products, is used by several tests as an indication of ageing. Such tests are the English Air Ministry test and - for oils with very high resistance to oxidation - the Indiana test. Evan and Kelman (27) heated the oils in Petri dishes in the presence of iron to 180°C assuming thereby that ageing is completed on the hot cylinder walls. The changes in viscosity which occur in this ageing test should be closely related to the behaviour in the engine. At all events, the values obtained agree better than when the oil is aged in a flow of air - at least in the case of oils which contain metallic soaps. Damerell (28) describes a method for measuring viscosity in a glass dish, which serves as an oxidation test (e.g. 2.5 hours, 150°C). The principle of the method is the measurement of the time which the oil takes to flow from one side to the other when the dish is tilted.

Apart from individual cases, such as that which has just been mentioned, there is less emphasis on the determination of the viscosity in the ageing tests, than on the actual identification of the products of oxidation, since the increase in viscosity - and the density - are the result of the formation of these substances, and there is no simple relationship. The determination of viscosity alone is therefore only an emergency measure (as in the Indiana test, if there are no products of oxidation to be identified), but otherwise is done in conjunction with tests for identifying the products of oxidation, either by isolating them by means of solvents, or by initial combination with an absorption agent, as was done by Suida, Pöll, etc.

Tests made by Mardles and Ramsbottom (29) show how great is the influence of temperature on the formation of the products of oxidation. They found that in general mineral oils require not less than 24 hours at 200°C to form one per cent of sludge, while at 225°C they only need a few hours, and at 250°C only a few minutes. The increase in absorption of oxygen as the temperature rises corresponds to this rapid increase in the formation of sludge. Thus, at 110°C an oil required 300 hours to absorb 1 mg of oxygen per gramme of oil, at 125°C 48 hours, and at 200°C only a few minutes. The authors found similar relationships when oxidation was carried on until the formation of solid substances occurred. But they see no connection between the formation of deposits on the one hand, and sludge formation, increase in viscosity, acid formation, etc., on the other. They therefore demand that oxidation tests which are based on the measurement of the absorption of oxygen should be supplemented by a determination of the products of oxidation. The DVL came to the same conclusion when they investigated the Evens and Schmidt test (30).

It appears that one should not at once generalize about the great influence of the increase in temperature on the formation of oxidation products. Thus, Marder (10) found that the increase in oxidation products caused by the increase in the test temperature from 250°C to 275°C is only a fraction of the increase which occurs when the temperature is raised from 200 to 250° (see Fig. 1); he draws the conclusion, that the logarithmic relationship between the temperature and the speed of reaction, of which van t'Hoff claimed the existence, was invalid for the reactions which take place in the ageing of oil.

The temperatures at which there is active destruction of the oil, accompanied by external evidences of decomposition, are in the region of 250°C (Mardless and Ramsbottom (29), Suida (31)). The methods which work in this temperature range have already been mentioned in connection with piston ring sticking. These methods are more concerned with discovering the tendency to formation of sludge, but also attempt to find the relationship to ring-sticking.

In the same way, Barnard (32) found, in his investigations into the Indiana test, that the connection with ring-sticking is only a general one, and concluded that this was a function of other properties of the oil in addition to the tendency to the formation of sludge. On the other hand, he found that there was a large measure of agreement between the tendency to sludge formation in the Indiana Test and in the engine, as also in the increase in the viscosity of the oils. According to Ramaya and Waldmann (33), the Indiana test

reproduces fairly accurately the behaviour of the oil in the engine, while the Air Ministry and Sligh Tests are unsatisfactory in this respect. Jostes and Hann (34), while they made no comparative engine tests, nevertheless find that the Indiana Test is satisfactory for comparative tests and for classifying lubricating oils. The fault of most of the customary oxidation tests, as they see it, is that they fix the time of oxidation arbitrarily, and at the same figure for all the oils investigated, without considering ^{that} the oxidation of an oil is not a linear function of time. This leads to the production of lubricating oils in different stages of oxidation, and to a greater dependence on the test conditions. This disadvantage is avoided by using as the standard of comparison the oxidation time required by the oils under test to reach the same or a similar state of oxidation. The Indiana Test fulfils this requirement; a modified form of it, (with only 20m³ of initial oil) will be described later. Tests, made on 10 oils, showed that the rating was to a large extent independent of external conditions (temperature, and the volume of air).

These advantages of the Indiana test do not manifest themselves in oils with a very slight tendency to form asphalts such as many synthetic oils and aero-engine oils with a mineral oil base. Many such oils produced no asphalt in the DVL tests, even after 400 hours running time. Jostes and Hann, and also Kadmer (35) made the same findings with synthetic oils. Kadmer draws attention to the pronounced thickening and pronounced formation of acidic and saponifiable products of the synthetic oil, which thus contrasts with other light oils. It must also be noticed that the reduction in the volume of oil caused by the repeated taking of samples, is a disadvantage of the Indiana test, especially with stable oils. This defect can be circumvented, if the inception of the formation of asphalt is determined by an optical method, using a small volume of oil. In this connection, mention should be made of a method of Weiland (36), who measured the coloration of an oxidised oil (154°C, 5 minutes under a flow of air), and found that the results were reproducible, and were in agreement with the Indiana Test. According to Weiland, the oxidation of oil is, within certain limits, an exponential function of the temperature.

Apart from the Indiana test, the most widely used test is the English (Air Ministry) process (1). According to tests by DVL, the limits placed on the Ramsbottom carbon values (maximum of 1 for the carbon value of the fresh oil, maximum of 0.70 for the increase in the carbon value) are somewhat too stringent, whilst the maximum increase in viscosity (at the most 100%) can be met by the ordinary aero-engine oils, apart from the compounded and synthetic ones. A variation of this test is also carried out by IG; a comparative test is made in nitrogen, and the thickening of the oil when oxidised in air is compared with it, so that the influence of the vaporisation loss can be eliminated. The efficacy of the Air Ministry test is shown by the tests of Mielnikowa and Dzielowski (37), who obtained comparable results from tests made on a Jupiter engine and by the Air Ministry laboratory method. The number of oils tested was, however, small. On the other hand, Redgrove (38) found that it is better to rate an oil by the Indiana test than by the Air Ministry test. Auld (39) recommends that the Air Ministry oxidation be carried out at a higher temperature (250 instead of 200°C).

The same tendency in the direction of higher temperatures is observed in the methods which Damian worked out for the French Air Ministry. By this method, the oils are subjected for 120 hours at 140°C to a swinging movement in gently moving air, so that they move over strips of copper (3). Damian's object in adding the copper strips was to temper the strictness of the conditions of selection as far as possible to the requirements of working safety (40). Actually, the French ageing process - according to DVL tests (25) - puts a greater strain on the oils than the English one. Of the observations made by Damian (41), those oils which behave well in an engine give less than 0.2 % of separation and an increase in the Conradson carbon value of less than 200 %. Only the former was confirmed by DVL tests. On the other hand, the increase in the Conradson value caused by oxidation was more than 200% in some oils which otherwise behaved well. That the Damian process in the form given above has proved unsatisfactory is shown by the opinion of Martinet (42), who thinks that

the values found by this means do not agree with the state of lubrication in the cylinder. Another method of Damian's will be mentioned in connection with the estimation of carbon values.

Various comparisons between these and other oil oxidation methods have been made in various quarters, with generally very little agreement. It must be remembered here which changes in the properties of the oils are being compared, and to which group of oils the comparison applies. According to tests at DVL (25), the rating agreed better when the individual test data (increase in viscosity and carbon value) were compared with each other than when the same individual results are compared in different methods (increase in viscosity in the Air Ministry and Indiana tests). Similar tests were made by Martinet (43) with transformer oils; he was able to distinguish poor oils and those which were satisfactory, but found different orders of rating with the different methods. In the same way Noack rated automotive oils differently according to the method he used, even though in individual cases he obtained agreement between values obtained by different oxidation methods (including one of his own, which agreed well with engine tests). Redgrove, (38) on the basis of his tests, would not use the oxidation method for assessing the behaviour in the engine, but rather as a means of tracing the origin or method of refinement of new oils. Despite these unfavourable opinions, the oxidation tests are still in use for assessing sludge forming tendency on the one hand and on the other hand to obtain material on which to base the choice of method, and improvements on them.

IV. Oxidation Change, and Formation of Deposits.

Owing to the high temperature and the presence of oxygen in the engine, part of the oil is lost by vaporisation and combustion. Insoluble oxidation products form in the remaining oil, and these are given the collective names of "carbonaceous matter (or coke)" and asphalt; where these products of oxidation separate from the oil and form more or less permanent layers on parts of the machinery, they are known as "deposits".

The place where these deposits mainly form is the combustion chamber, since it is there that the greatest oxygen content and the highest temperatures are found. The piston ring and the crank case (including underside of the piston) are only involved to a secondary extent (8, 19). The fuel may also be a contributory cause of coke formation, if it is of such a nature or the conditions of combustion are such, as to encourage it; but most opinions about the origin of coke are to the effect that the part played by the fuel is insignificant compared with that of oil (8).

Generally, the carbon tests are used for measuring the deposit. Mention should also be made of a proposal by Bahlke and colleagues (45) for using the vapourisation (90% point at 1mm Hg) to measure the formation of deposit; low vapourisation in their opinion enhances the formation of deposit. Similarly, there is a certain relationship between the viscosity and the formation of deposit, in that very viscous mineral lubricating oils, such as Brightstocks and cylinder oils, have much higher carbon values than the fluid oils (46). The structure of the oil also has an influence on coking; thus, paraffin-base oils (unless enriched by refining with solvents so as to form iso-paraffins) have higher carbon values than asphalt-base oils of the same viscosity. Special importance as regards the formation of deposits attaches to the capacity to undergo reactions of the carbonaceous matter formed. The structure of the oils has an influence here, as was shown by tests at DVL (16). These tests, which showed the amount of coke which burns away at various temperatures, proved that the capacity of the coke to react is in the following order, according as they come from the following types of oil: paraffinic, compounded, naphthenic, and fatty oils (see Fig. 4).

Other factors besides the structure of the lubricating oil influence the reactive capacity. Such are the composition of the fuel, the operating conditions (temperature, running time) and the type of engine.

How far coke which has once formed disappears owing to combustion or peeling away is a question of the reaction capacity and the adhesion capacity. The volume of coke which forms is thus determined, on the one hand by the dependence on temperature of the amount of coke which forms, and on the other hand, on the reaction and adhesion capacity (16).

The carbon tests can be looked at from various points of view. Perhaps it is most practical to distinguish between tests which work by excluding air or limiting the air flow and those which work in an unrestricted flow of air. To begin with, we should discuss those tests which do not heat the oil right up to the formation of carbon, but still heat it to the point at which cracking occurs and distillation products form, which can then be investigated. Such are the cracking tests evolved by Koetschan (47) (heating 300 grammes of oil for two hours to 380°C in a glass retort, investigation of the deposits and distillates), also tests by Maillard (48), who found decomposition temperatures (under atmosphere pressure) for mineral oils of 380 to 400°C, for castor oil of 250°C, and a DVL process for determining the thermal stability of aero-engine oils (49). In the last mentioned case, 150 grammes of oil are heated in a glass flask for 6 hours in nitrogen to 400°C, and then tested for changes in properties (specific gravity, viscosity, bromine number, molecular weight). The greatest thermal stability was possessed by a naphthenic-base oil, followed by paraffin-base oils, and finally synthetic oils.

The remarkable thing was that, in spite of their better behaviour as regards ageing and engine performance, the synthetic aero-engine oils had a lower thermal stability.

The carbon tests which operate with air excluded, are the familiar ones of Conradson (50) and Ramsbottom (7). These two methods burn the oils at such high temperatures, that the vapours ignite outside the vessel, so that the weight of the deposit is related to the quantity of oil weighed in. Little is known about how well these tests agree with the results found in practice although a series of tests made at DVL (51) produced good agreement at least for the Conradson test. The oils were rated for carbon, and sludge formation in the engine, by this method with more accuracy than by several other oxidation tests currently in use (Fig. 5). But because of the small number of oils tested, no generalisation can be made from this result. If the tests are applied to used oils, it must be remembered that foreign matter and asphalt increase the weight of deposit, so that the Conradson value of used oils differs from that of fresh oils by the weight of these substances. The carbon tests carry the artificial ageing of the oils to its completion; the Ramsbottom test specified in the (English) Air Ministry Oxidation Test, may be mentioned in this respect. Jentzsch (52) has patented a method, in which the oil, which has been treated with oxygen at temperatures between 200°C and the point of self-ignition, is subjected to coking temperatures, e.g. 500°, and the carbon deposits determined. In the apparatus evolved by Damian (53), the oil, pre-heated to 100°, drops into a crucible whose temperature can be adjusted between 200 and 550°C. It is there heated without a flame, and, is kept at the test temperature for 15 minutes after the last drops of oil have fallen. After treatment with petroleum ether, the chloroform soluble and insolubles are determined. By this means the lubrication conditions prevailing in the cylinder are reproduced; rapid, extreme fluctuations in the oil temperature, heating without flame in an atmosphere which is poor in oxygen, formation of thin layers and flow of heat to the static oil when the engine is stationary (reproduced by the dropping of the oil, followed by heating), and the formation of insoluble substances in the hot oil (insoluble in chloroform). The assessment is made by plotting temperature curves, showing the temperatures when the deposits first appear and at which they reach a maximum, and the amount of these deposits (Fig. 6). After the maximum has been reached, the amount of deposit falls sharply, finally approaching the Conradson value (which should correspond to the deposits in the combustion chamber and at the top of the piston). With poor oils, the maximum value for the portion insoluble in chloroform (8%) was reached at 300°C. The used or aged oil was also tested in this way; the less the differences in the values compared with fresh oil, the better the assessment of the oil.

The two last-named methods work in a limited flow of air, thus leading up to the methods in which the oil is heated in abundant air until coke forms. They thus imitate the formation of coke in the engine, as far as this occurs in air. To these methods, which are based on oxidative coking, must be added another, described by DVL as early as 1933, in which the oil is allowed to drop from a burette into a V₂A crucible which is heated, and has air playing round it (51). At temperatures of 400°C and above, self ignition invariably took place. The deposit from the coked or burned oil is weighed before and after extraction with benzene (Fig. 7). The method does not appear to produce results differing substantially from the Conradson and Ramsbottom tests (see also Fig. 5). It is possible that too little account has been taken of the movement of the oil during the process of oxidation in this and similar processes. Later tests by DVL cause the oil to drop on to a heated metal strip which is tilted in a certain way, so that the oil flows down it. A carbon-like coating is left, which can be weighed. The amounts of deposit left on strips of different metals at temperatures between 250 and 400°C can be shown by curves (see Fig. 8).

A differently constructed apparatus of the Standard Oil Development Co. (Thwaites (54)) has a metal funnel, with a spiral on the inside over which the oil flows slowly. The funnel is heated to temperatures from 250° to 350°, and the amount of deposit is estimated from the increase in the weight of the funnel. Thwaites found that the results agreed to a certain extent with engine tests (Fig. 9).

The latter methods are very closely related to those discussed in the section on piston-ring sticking, and indeed their most important purpose is measuring the tendency of oils to ring-sticking, for ring-sticking is to a great extent a function of the formation of deposit. Therefore, there is no hard and fast line dividing methods for measuring the tendency to ring-sticking and those which are for measuring the formation of other deposits.

CONCLUSION.

The formation of deposits in the combustion chamber is an important factor in piston-ring sticking and the tendency to form sludge. The processes which are used for assessing these properties should thus not deviate too much from the conditions in which deposits are formed.

Thus, it is not the average change in the whole of the oil, but that in the part of it which is subjected to excessive stress, which is measured. But many of the oxidation tests work under conditions which, while they change the total oil to a greater extent than in practice, affect to a lesser degree that proportion of the oil which would be overstrained in practice.

Taking this fact into account, we should try and get as close as possible to practical conditions. Since there is a certain amount of scope here, it will appear best, at least as far as aero-engine oils are concerned, to choose for laboratory tests the most stringent conditions prevailing in the engine, without, however, going to extremes.

The oxidation test conforms to practical conditions on the following points:-

1. Temperature. There is a tendency to fix the temperature higher than was previously the custom. A temperature of 275 to 300°C (as in the DVL or WAC processes), is required in order to imitate the processes in the ring grooves, and a higher one still for the combustion chamber (see coking processes). By raising the temperature in stages it is possible to get nearer to the conditions obtaining in practice (Damian). The same is true of the plotting of the curves (DVL coking by drops, Thwaites, Damian).

2. Air. Here, too, it is necessary to distinguish between the ring grooves and the combustion chamber. In the first case the air is poor in oxygen (Damian), in the second case it is richer (DVL, Thwaites, WAC). The customary carbon

tests depart from practical conditions in that, while the very high temperature imitates the conditions in the combustion chamber, the exclusion of oxygen does not. The complete exclusion of air gives a false impression - as the thermal treatment of synthetic oils shows, and the use of oxygen instead of air is excluded because it is not in accordance with practical conditions.

3. The Vessel. Ageing in glass vessels does not correspond to practical conditions. Metal vessels are better (WAC), or metal strips can be used (Damian). DVL have already tried to approximate more closely to practical conditions by using several metals. It would be desirable to make further tests on these lines.

4. Movement of the oil during oxidation. In this respect the individual processes differ very greatly, according as the greater emphasis is laid on the development of thin, highly-heated layers (a) or thorough mixing with air (b).

Under (a) can be reckoned:-

The DVL dish process, in which the oils are kept motionless during the test;

The WAC and the Damian dropping processes, which introduce the oil into the oxidation vessel gradually. Damian continues the heating of the stationary oil for some time, in order to imitate the heat flow when the engine is at rest, and when there is no cooling by oil, water, or air;

The methods in which the oil flows down over a heated plate (Thwaites, DVL), or is in the form of a thin layer between metal discs. (DVL).

Under (b) are included all those methods in which air is blown into the oil (Air Ministry, Indiana, Weiss, and Maillard).

An intermediate position between (a) and (b) is occupied by those tests which keep the oil in a state of motion by pumping or shaking (copper strip process of Davian, and DVL-Turbine).

It is recommended to combine the measurement of volatility with the actual oxidation test, and to determine other properties which influence the changing of the oil in the engine, such as capacity to dissolve asphalt and to form suspensions, and reaction capacity, in special tests.

There appear to be good prospects for determining the oxidation tendency by measuring the time taken to reach a certain state of oxidation. Of such methods, only the Indiana test has so far got into wider use. Tests should be made to see if this principle can be applied to other methods employing more stringent conditions, especially in respect of aero-engine oils which have high resistance to the formation of asphalt.

The tests in which the oxidation time is arbitrarily laid down require very exact test conditions during oxidation and consumption if the reproducibility is to be improved. It is particularly necessary with used oils to distinguish between the end of oxidation and the beginning of consumption.

BIBLIOGRAPHY.

1. Air Ministry General Specification No. DTD 109.
2. F.H. Garner, C.J. Kelly and J.L. Taylor: The British Air Ministry Oxydation Test for Lubricating Oils. World Petroleum Congress, Proceedings II (1933) p. 448 to 457.
3. Norme Air 1093 of 16.11.1933.
4. T.H. Rogers and B.H. Shoemaker: Ind. Eng. Chem., Anal. Ed.-6 (1934) pp. 419 to 420.
5. ASTM Standards on Petroleum Products and Lubricants (1935) p. 9.
6. F. Evers and R. Schmidt: Die künstliche Alterung von Mineralölen. Erdöl u. Teer vol. 9 (1933) pp. 11, 27.
7. M. Richter: Entwicklung eines neuen Oxydations-verfahrens für Schmieröle. Nicht veröffentl. Report (1936).
8. A. v. Philippovich: Über die Beständigkeit von Flugmotorenöl und ihre Prüfung Luftf.-Forsch. Vol.14 (1937) pp. 254/261.
9. A.L.Beall: Auswahl von Ölen für Hochleistungs-Flugmotoren. Vortrag vor der Nat. Product- SAE Meeting (1936)
10. M. Marder u. V. Tolkmitt: Über den Wert von Laboratoriumsmethoden zur Bestimmung der Alterungsneigung von Mineralölen. Öl u. Kohle Vol 14 (1938) p.618.
11. Seufert: Ermittlung der Alterungsneigung von Motorschmierölen. Öl u. Kohle Vol.14 (1938) pp. 239/241
12. H. Suida: Über Alterung von Schmierölen. Öl u. Kohle Vol 13 (1937) p. 205.
13. A. Raader: Über Alterung von Schmierölen. Öl u. Kohle Vol.13 (1937) p. 302.
14. M. Marder u. Tolkmitt: l. c. p.637.
15. E. H. Kadmer: Schmierstoffe u. Maschinenschmierung. Berlin 1940. p.169.
16. A. v. Philippovich: Die Veränderung von Flugmotorenöl im Betrieb und ihre Prüfung. Öl u. Kohle Vol. 13 (1937)pp.1235 to 1245.
17. M. Richter: Die laboratoriumsnahe Prüfung von Schmierölen auf ihre Neigung zum Kolbenringverkleben. DVL-Jahrbuch 1937, pp. 543 to 548.
18. C.G.A.Rosen: Einflüsse auf die Alterung von Dieselschmierölen. Nat. Petr. News 1940, pp. 152/55.
19. H.Weiss u. A. Maillard: Contribution to the study of the changes occurring in lubricating oils in internal combustion engines. J.P.T. Vol. 24 (1938) p. 416.
20. E.H.Kadmer: l.c. pp. 156, 173, 177, 178.
21. E.H.Kadmer: Über die natürliche und künstliche Alterung von Fahrzeugmotorenölen. Öl u. Kohle Vol 13 (1937)pp. 101, 127.
22. H.Weiss u. A. Maillard: l. c. p.419.
23. H. Suida: l. c. p.227.

24. E.A.Evans u. A.L.Kelman: Metallic soaps in lubricants. General Discussion on Lubricants Inst. of Mech. Eng. (London 1937) II, p.285.
25. K. Mayer-Bugström: Prüfung von Alterungsverfahren für Schmieröle. Nicht veröffentl. Bericht 1937.
26. W.O.Andrews: Sludge on deposits in turbine oils. Inst. of Mech. Eng. (London 1937) II pp. 202 to 208.
27. E.A.Evans u. A.L.Kelman: 1. c. p.288.
28. V.R.Damerell: Measuring Oxidation of Lubricants. Inst. Eng. Chem. Anal. Ed.11 (1939) p.265.
29. E.W.J.Mardles u. J.C.Ramsbottom: The oxydation behaviour of internal combustion engine lubricants. Inst. of Mech. Eng. (London 1937) II, pp. 354 to 366.
30. A. v. Philippovich u. K. Mayer-Bugström: Oxydationsbeständigkeit von Schmierölen. Nicht veröffentl. Bericht 1934.
31. H. Suida: 1.c. p.203.
32. D.P. Barnard u. Mitarb.: Causes and effects of sludge formation in motor oils. SAE-Journ. (1934) p.167.
33. K.S. Ramaija u. W.L.Waldman: Alterung von Schmierölen. Petrol.-Ind. (russ. Neftjanoe Chosjaistwo) 1937 No.12 pp. 33/37.
34. F. Jostes u. A.Hann: Die Prüfung der Alterungsneigung von Schmierölen im Laboratorium. Ol u. Kohle Vol. 15 (1939) pp.515, 533.
35. E.H.Kadmer: Über die künstliche Alterung von Kohlenwasserstoffölen. Chem. Zeitung Vol. 68/69 (1938) pp. 611 to 613.
36. W.F.Weiland: Messung der Schlammbildungsneigung von Schmierölen. Oil Gas Journ. Vol.36 No.36, 83 to 86, 93.
37. B. Mielnikowa u. J. Dziewonski: Essais de l'oxydabilite. Sprawozdania (1934) No. 1 (13) pp 39 to 55.
38. E.R.Redgrove: Alterungsversuche an Schmierölen. Petr. Times Vol. 32 (1934) pp. 583 to 585.
39. S.J.M.Auld: The susceptibility of mineral lubricating oils in use. Chem. and Ind. Vol.55 (1936) p.1018; Characteristics of solvent-refined motor oils. J.P.T. 22 (1936) p.57.
40. J. Damian: Influence des actions catalytiques sur le vieillissement des lubrifiants. Chimie et industrie Vol.27 (1932) p.323.
41. J. Damian: Methode d'appréciation des lubrifiants. Publ. scie. et techn. du Min. de l'Air (1932) No.14 p.28.
42. P.Martinet: Technique mod. Vol 28 (1936) pp.472 to 474.
43. P.Martinet: Auswertung der Ergebnisse von Versuchen zur künstlichen Alterung von Mineralölen. Technique mod. Vol 28 (1936) pp.381/85.
44. K.Noack: Über Methoden zur Ermittlung der Alterungsneigung von Schmierölen für Kraftfahrzeuge. Ol u. Kohle Vol 13 (1937) p.965.
45. W.H.Bahlke, D.P.Barnard, J.O.Eisinger u. O. Fitz Simmons: Factors controlling Engine-Carbon Formation. SAE Vol 29 (1931) II p.215.

46. E.H.Kadmer: 1. c. (16)pp. 135, 136.
47. R. Koetschau: Über die thermische Beständigkeit Hochsiedender Mineralöle. Von den Kohlen und den Mineralölen, III Vol. 1930 pp. 110 to 168.
48. A. Maillard: Sur l'alteration des huiles de graissage dans les moteurs a combustion interne. Ann. com. liq. 1936, p.965.
49. M. Richter: Die Bestimmung der thermischen Beständigkeit von verschiedenen Flugmotorenölen. Nicht veröffentl. Bericht 1938.
50. ASTM-Standards on petroleum products and lubricants (1937) p.53.
51. A. v. Philippovich: Neuere Untersuchungsverfahren zur Bestimmung der Rückstandsbildung von Motorenölen. DVL-Jahrbuch 1933, VI, pp.36/42.
52. H. Jentzsch: Bestimmung der Alterungsneigung von Ölen, Fetten, flüssigen Brennstoffen. DRP. 679357 (ausg. 3.8.1939).
53. J. Damian: Contribution au probleme du graissage des moteurs a explosion et a combustin interne. La revue petrolifere (1937) No.726 p.337.
54. Standard Oil Development Co. (übert. von H.L.Thwaites): Method of and apparatus for testing lubricating oils. A.P. 2174021 vom 13.5.1936.

FIGURES.

- Fig. 1. Asphalt and resin content of 10 oils after ageing under various conditions (after Marder).
- Fig. 2. Content of oxidation products after exposure to air for various lengths of time (after Seifert).
- Fig. 3. Asphalt solubility in fresh oil.
- Fig. 4. Reactivity of oil coke.
- Fig. 5. Sludge formation in aviation oils.
- Fig. 6. Coke and sludge formation with temperature, according to Danian.
- Fig. 7. Coke formation in the presence of air (DVL).
- Fig. 8. Drop coke (DVL strips): Oil - Stanavo 100: metals - aluminium, iron, copper.
- Fig. 9. Relationship between sludge formation according to Thwaites and ageing in the CFR engine.