For these curves therefore the mean displacement of the whole range of excess air ratio was inserted in fig. 7. Although there are some objections to this procedure, the figure shows a marked dependence on the aromatic content of the effect of the oil type on the knock limit curve.

For fuels with a B4 basis, in which the aromatic content is limited to 25% (± 1) according to the blending instructions of the RLM group GL/A-M, sheet 4, edition August 1942, it may be seen that the different oils do not cause a displacement sufficient to affect the rating of fuels according to the knock limit curve. The deviations found in the experiments with VT 702 + 0.12 lead which has a B4 basis could only be observed with very exact and specially devised methods. During the normal investigation of fuels according to the DVL supercharge method, the spread of the test points amounted to at least ± 5 mm. Hg boost pressure. The observed deviations due to the kind of oil lie within this range and are therefore immaterial. Similarly for a given control curve one need not expect danger to the engine due to change in lubricating oil in the case of operation of main engines with B4 fuel, so long as the control curve excludes approach to a possible knock region at any operation point.

On the other hand in the case of higher aromatic content it would be advisable to take into account the deviations which are outside the normal range. It is true that fuels of such high aromatic content as the gasoline-benzol blend are unusual. All the same 44% by vol. is permitted for C3 which is used in practice. The knock limit curves obtained for the several oils differ by amounts which may be appreciable, especially in the two extreme cases in fig. 7.

The value of 35 mm Hg boost pressure which has been observed in the above case is outside the range of deviation both for the rating of fuels according to the DVL supercharge method and also for practical main engine operation.

The differences between the individual curves increase with increasing aromatic content and reach about 90 mm. Hg boost pressure at the minimum point for the gasoline-benzol blend. This is the same value that was found in the previous experiments on the air-cooled BMW 132 N under completely different operational conditions.

The results indicate a dependence of the knock rating of a fuel on its aromatic content, differing according to the oil used. On the basis of this result and the fact that the two leaded fuels VT 702 and C3 can be fitted into the suggested framework it may be inferred that there is no effect of the oil on the lead susceptibility.

IV. Summary

The following were the objects of the experiments: first to find out whether the change in the anti-knock value of highly aromatic fuels observed in the air-cooled engine under the conditions of the DVL supercharge method also occurs under different conditions: furthermore to determine the order of magnitude of the knock limit curve deviations from the Aero Shell 100 curve, taken as a reference, as a function of the various oils.

A displacement of the knock limit curve was observed for the gasoline-benzol blend of the same order of magnitude for the same oil as already found on the BMW 132. From this one can conclude than an influence of the lubricating oil on the anti-knock value actually exists independently of the conditions of operation and of the engine used.

The magnitude of the effect of the oil on the knock limit curve depends on the aromatic content of the fuel. An appreciable effect cannot be observed for fuels with a B4 basis. C3 mixtures, as a consequence of their higher aromatic content, begin to show deviations which are outisde the usual experimental deviations. For highly aromatic fuels such as the gasoline-benzol blend the differences, varying with the kind of oil used, in some cases amount to as much as 90 mm. Hg boost pressure.

Changed knock characteristics were shown for leaded as well as unleaded fuels, depending only on the aromatic content . From this it was inferred that the effect of lead addition remains unchanged by the kind of oil used.

Literature

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3. F. Seeber: Testing of fuels of high antiknock value in the aero engine single cylinder. Luftfahrtforschung January 1939.

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Figures

Fig.1 - Knock limit curves of VT 702 + 0.12 lead for various lubricating oils in the DB 601 engine.

DB 601: boost air temperature 130°C: 1900 revs/min.
Compression: 8.0:1, Ignition 35° B.T.C.
Valve overlap: 120° crank angle, fuel: VT 702 + 0.12% TEL
O.N. 92

Fig.2 - Knock limit curves of the VT 706b/707 blend for different lubricating oils in the DB 601 engine.

DB 601: bboost air temperature 130°C, 1900 revs/min.
Compression: 8.0:1, Ignition 35° B.T.C.
Valve overlap: 120° crank angle, fuel: VT 706b/707, O.N. 75

Fig.3 - Knock limit curves of C3 + 0.12 lead for various lubricating oils in the DB 601 engine

DB 601: boost air temperature 130°C, 1900 revs/min.
Compression: 8.0:1, Ignition 35° B.T.C.
Valve overlap 120°, fuel C3 + 0.12% TEL, O.N. 95.

Fig.4 - Knock limit curves of CV2b for various lubricating oils in the DB 601 engine.

DB 601:: boost air temperature 130°C, 1900 revs/min.
Compression 8.0:1, Ignition 35° B.T.C.
Valve overlap 120° crank angle, Fuel CV2b, O.N. 79

Fig.5 - Knock limit curves of the gasoline-benzol blend for various lubricants in the DB 601 engine.

DP 601: boost air temperature 130°C, 1900 revs/min.
Compression 8.0:1, Ignition 35° B.T.C.
Valve overlap 120° crank angle, Fuel Gasoline-Benzol blend, O.N. 88.5

Fig.6 - Knock limit curves of the gasoline-benzol blend for various lubricating oils in the BMW 132 N.

BMW 132-N: boost air temperature 130°C, 1900 revs/min.
Compression 6.5:1, Ignition 30/31 B.T.C.
Valve overlap 41° crank angle, Fuel Gasoline-benzol blend, O.N. 88.5

Fig.7 - Approximate deviations of the knock-limit curves using Rotring and Stanavo 100 from the curve obtained obtained with Aero-Shell 100 as a function of the aromatic content.

DB 601: boost air temperature 130°C, 1300 revs/min.
Compression: 8.0:1, Ignition 35° B.T.C.
Valve overlap 120° crank angle.

Table I

Engine Data

Engine type DB 601

Stroke	160 mm.
Bore	150 mm.
Compression	E = 8.0
Capacity	2.828 litres
Combustion chamber	404 cc.
Valve timing:	
Inlet opens	71° B.T.C.
" closes	53° A.B.C.
Exhaust opens	62° B.B.C.
" closes	49° A.T.C.
Fuel system	Injection: start of delivery 26° A.T.C.
Pump	Bosch PZ 2/1000 V 402 (cam pump)
Nozzle	L'Orange 6/38 9-2029 A
Ignition system:	
Plugs	Bosch W 260 T1
Magneto	Bosch FI 1R 36 Bosch FI 1L 36
Boost air:	
Blower	Klein, Schanzlin + Becker, 1.5 atm. excess 450 m³/h.
Air heater	DVL 24.5 kW.
Coolant	Water
Pump	Machine factory Odessa Type S 30/160 135 l/min.
Exhaust equipment	DVL, through silencer, extraction fan.
Brake equipment	Siemens generator type A 6 247

Table 2

Inspection of Lubricating oils

Supplier	Deutsche Vacuum-Öl A.G., Bremen	Wifo Stassfurt Leopoldshall	Wifo Niedersachswerfen
Grade	Rotring D	Stanavo 100	Aero-Shell 100
Sample No.	423/40	269/41	270/41
Date received	16.12.40	12.8.41	8.8.41
Sp. Gr. @ 20°C	0.8913	0,886	0.8889
Refractive Index	1.4923	1.4918	1.4907
Viscosity; °E			
@ 20°C	120	103	119.2
50°C	18.0	17.3	17.7
100°C	2.82	2.75	2.88
Pole Height	1.88	1.68	1.90
Flash Point °C	272	259	270
Fire Point °C	323	303	317
Setting Point °C	-16	-16	-17
Neut. No. mg KOH	0.04	0	0.02
Sap. No. " "	0.19	0.09	0.1
Asphalt %	0	0	0
Ash %	0	0	0

Table 3

Inspection of Fuels

Grade	75% VT 706b 25% VT 707	CV 2b	25% unleaded gasoline 75% aviation benzol	VT 702 + 0.12 TEL	C3 + 0.12 TEL
Sample No.	240/41	157/42	120/41	405/40	189/42
Supplied by	mixed by DVL	Wifo, Coswig	Mixed by Olex	Ammoniakwerk Merseburg	Wifo, Schäferhof
Sp.Gr. @ 20°C	0.7760	0.8023	0.8265	0.7206	0.7642
Refractive Index n_{D20}	1.4358	1.4537	1.4696	1.4021	1.4307
Water solubility %	0	0	0	0	0
Reid vapour pressure atm.	0.525	0.335	0.215	0.435	0.425
Distillation: °C,					
I.B.P. %	50	48.5	58	48	50
10 % @ °C.	71	80	72	64	74
20	80	90	80	70	83.5
30	86.5	98.5	81.5	76	92
40	92.5	106	84	83	99
50	99	113.5	87	90	108
60	108	122	89	97	118.5
70	115	130	93	103	132
80	128.5	140	100	112.5	147.5
90	142	151.5	119	123	166
F.B.P. %/°C	99/160	97.5/166	98/146	98/144	98/183
Corrosive properties, Cu, Al-rivets 3 hrs., 50°C	unchanged	unchanged	unchanged	unchanged	unchanged
Gum, mg/100 cm³	1.2	1.0	9.8	2.4	6.6
Crystallization point °C	under -60 (slightly cloudy)	under -60	-19	under -60	under -60
TEL by iodine method	0	0	0	0.12	0.12
Iodine No. (Hanus)	1.90	3.61	2.60	5.2	4.25
Aniline point II °C	51.0	48.0	58.4	60.2	58.0
Arom. & Unsats., wt.% (Kattwinkel)	44	53.7	85.3	22	44.8 (1)
Naphthene %	35.4	33.9	5.7	25.5	18.4 (1)
Paraffin %	20.6	12.4	9.0	52.5	36.8 (1)
C content %	87.78	88.3	90.38	85.20	87 (2)
H_2 content %	12.35	11.3	9.58	14.73	13 (2)
O_2 content %	0	0	0	0	0
C/H ratio 1 :	7.11	7.8	9.54	5.78	6.7
Theoretical air requirement kg/kg	14.3	14.0	13.7	14.85	14.4
Lower calorific value	10105	9991	9849	10457	10250 (2)
Octane No. (M.M.)	75	79	88.5	92	95

(1) of 254/41 (figures obtained from Drugehnen depot)
(2) calculated from specific gravity.

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Ref. ZwB. FB 1859

DEUTSCHE LUFTFAHRFORSCHUNG
Research report No. 1859.

Extension of the FKFS rapid method for determining the lead tetraethyl content of fuels.

Widmaier.

Synopsis: It has been pointed out repeatedly that difficulties are experienced when the FKFS method of determining the lead content is applied to fuels which contain unsaturated compounds, peroxides and resins. Although such fuels cannot be used for aviation it is important that it should be possible to make a quick TEL determination on captured fuels which are wanted for use at the front.

Detailed experiments with various fuels have recently been carried out at the Institute for this purpose. These experiments will be described below. They show that the FKFS method of determining lead may be generally applied - particularly in the laboratory at the front.

Index:

1. Introduction

At the beginning of the war the Reichluftfahrtministerium made an urgent request for the development of a rapid method of determining the content of lead tetraethyl in fuels. The institute has complied with the request; and already in the spring of 1940 they were able to issue such a method. This method gave accurate values for the lead content of the usual fuels. The range of variation for some types of gasoline, however, was still too large; these types include hydrocarbons which are unsaturated and which tend to gumming.

This range of variation is due to the fact that, as is well known, the iodine reacts not only with lead tetraethyl but to some extent also with unsaturated hydrocarbons.

One can understand these reactions if for example, one considers the chemical properties of olefins and the general reactions of the halogens. Whereas chlorine and bromine add smoothly on to ethylene hydrocarbons, iodine only adds on partially. The following reaction occurs here, the halogens being denoted by X:

$$C_nH_{2n+1}\ CH = CH_2 + X_2 \rightarrow C_nH_{2n+1}\ CHX\ CH_2X$$

When iodine adds in this way the observed lead values will be too high.

If potassium iodide is added to an n/10 solution of iodine in ethyl alcohol till iodine - potassium iodide (potassium tri-iodide) is formed this will have the effect of slowing down side reactions and eliminating them in most cases. The enlargement of the iodine molecule to the iodine-potassium iodide molecule has the effect of a steric hindrance on the reaction with unsaturated hydrocarbons; this favours the addition of iodine to lead tetraethyl.

Conversely, lead values may also turn out too low; this may happen in the presence of substances which can act as oxidixing agents e.g. hydrogen peroxide or organic peroxides. These oxidizing agents liberate iodine from the potassium iodide contained in the alcoholic solution of iodine.

In order to ascertain and eliminate all possible sources of error in the determination of lead in the various fuels which occur at the front, all the possible factors influencing the accuracy of the lead determination according to the FKFS method were examined; a new set of directions was worked out which takes these possibilities into account.

2. Extraction of iodine- sensitive components by means of sulphuric acid.

Any olefins and aromatics which are contained in the fuel and which would falsify the FKFS. iodine method are separated off by means of concentrated sulphuric acid; the iodine will then add on only to the lead tetraethyl. It is also possible however that in the reaction with olefines and aromatics some lead tetraethyl may be transformed into lead sulphate.

Numerous experiments were carried out with sulphuric acid of various concentrations. It was found that sulphuric acid at concentrations up to 70% has no noticeable effect on the lead tetraethyl if it is in contact for only a short time. The experiments described below were then carried out with 70% H_2SO_4.

a). The effect of the time of contact of sulphuric acid on the lead tetraethyl in the fuel.

The fuels were treated with 70% H_2SO_4 for 15, 30 and 120 secs. in order to find out the most suitable time of contact. The values of lead tetraethyl found in this way were compared with the values found according to Ulrich's sulphate method. Table 1 shows that for a shaking time of 30 secs. the sulphuric acid forms no,or a negligible amount of, lead sulphate. A shaking time of 20 secs. was therefore adopted.

b) Assimilation of iodine by base fuels after they have been treated with sulphuric acid.

The assimilation of iodine was determined for a number of fuels both before and after treatment with sulphuric acid in order to find out the effectiveness of the 70% sulphuric acid. Table 2 shows that the effect of sulphuric acid is particularly clear in the case of Roumanian gasoline and cracked gasoline. In general only certain resin constituents and the higher molecular olefins are removed by the 70% sulphuric acid; this produces only a very slight volume change in the fuel. This volume change need not be taken into account since it was shown by later experiments that some lead tetraethyl is destroyed in step with the decreasing quantity of fuel. It is remarkable that the olefins which are added to the Leuna gasoline, viz. caprylene and hexylene are not seperated off by the 70% sulphuric acid; they do notassimilate any iodine either and therefore do not affect the lead determination. It must thus be assumed that only the resin consituents and the high molecular olefins take up any iodine.

The more or less strong effect of the sulphuric acid gives an immediate indication of the iodine sensitivity of the fuels shown by the intensity of the brown coloration. If the brown coloration is slight one uses 10 cc of 70% sulphuric acid and 50 cc if the coloration is intense.

3. Effect of the water content of the fuel.

Fuels have varying capacities of absorbing water, depending on their chemical compositions; this fact has to be considered especially for the following fuels; heavy gasoline, Roumanian gasoline, synthetic gasoline and cracked gasoline. If this is ommitted the lead tetraethyl contennt of the fuel is almost always determined too low; this may be seen from table 3. It is therefore necessary to dry the fuel to be analysed with sodium sulphate after the treatment with sulphuric acid and water. After the fuel has been dried the content of lead tetraethyl will be determined correctly. The different effect of water in the various fuels may also be seen from table 3.

4. Effect of potassium iodide in the alcoholic solution of iodine.

A solution of iodine in ethyl alcohol saturated with potassium iodide is prescribed in the old directions for the FKFS method of determining lead. Now it was investigated what was the minimum amount of potassium iodide in the alcoholic solution of iodine which would effect a complete conversion of the lead tetraethyl in the prescribed time.

Table 4 shows that without potassium iodide the alcoholic solution of iodine gives lead tetraethyl values which are much too high. Solutions of iodine containing 0.1, 0.5 and 1.0 per cent by wt. of potassium iodide still give lead tetraethyl values which are too high. Only when 1.5% by wt. of KI is added to the iodine solution does one obtain good values for the lead tetraethyl; 1.25% by wt. would however have been sufficient, since there was 0.25% by wt. residue of potassium iodide. Larger amounts of potassium iodide have no bad effect on the determination of lead tetraethyl.

5. Effect of the experimental conditions on the chemical reactions between lead tetraethyl and iodine.

Although iodine generally reacts slowly in organic solvents and although the reaction with lead tetraethyl can be accelerated by shaking it has been shown that the lead tetraethyl combines with iodine quantitatively in a short time by simply allowing the reaction mixture to stand. The experimental results are summarized in table 5.

Apart from greater simplicity, allowing the mixture to stand entails a higher accuracy in the case of fuels which are particularly sensitive to iodine. This may be demonstrated particularly well for the samples of Roumanian gasoline and cracked gasoline. Whereas on shaking the values for the two gasolines vary from 0.0974 to 0.1019% by vol. and from 0.0972 to 0.1009% by vol. respectively, the values only vary between 0.0997 and 0.1002, and 0.0989 and 0.0996 respectively when one allows the mixture to stand. Even if after the treatment with 70% sulphuric acid the basic gasoline still takes up some iodine, the limit of variation of the lead values is low for one and the same concentration of lead.

6. The influence of temperature on the reaction of iodine with lead tetraethyl

The regulations and constency of the temperature at which the addition of iodine to the lead tetraethyl occurs merits special attention. The temperature must lie between 15 and 20°.

Table 6 shows that the lead values are too low when the temperature is below 10°C, the values are too high when the temperature is above 20°C.

7. Special Characteristics of the FKFS lead determination

In the course of the many lead determinations that have been carried out it has emerged that the starch which is added during the titration causes small differences in some of the fuels. These are probably due to the capacity of iodine to be adsorbed by colloids. For this reason the titration has recently been carried out without starch. The time of titration must also be kept as low as possible since some more iodine might add onto the basic gasoline during the titration.

Summarizing shortly, one has to pay attention to the following points:

a) The temperature of the fuel should lie between 15 and 20°C.
b) The 70% sulphuric acid should not be in contact with the fuel for more than 20 secs.
c) The alcoholic solution of iodine should not contain less than 1.25% by wt. of K.I.
d) The iodine solution should be in contact with the fuel for exactly 6 mins. without shaking and in the dark.
e) One should, if possible, titrate without starch.
f) The titration should be carried out as quickly as possible.

8. Working directions for the general application of the FKFS method of determining lead.

a) Alcohol-free aviation fuels A3, B4 and C3.

The fuel to be analysed is brought to between 15 and 20°C; 25 cc of the fuel are measured out with a pipette and transferred into an iodine number flask with a capacity of 100 cc. 5 cc of the N/10 alcoholic iodine - potassium iodide solution, standardized by a blank determination, are then added (12.7 gm analytically pure iodine and 12.5 gm analytically pure potassium iodide are dissolved in 1 litre of anhydrous ethyl alcohol). The mixture is left standing in the dark for exactly 6 mins. The iodine excess is then back titrated with a microburette against n/10 sodium thiosulphate as quickly as possible, without the use of starch.

The content of lead tetraethyl in volume per cent is then given by the amount of N/10 alcoholic iodine solution that had been used after multiplication by 0.0391.

b) Alcohol free fuels with an iodine number greater than 10.

50 cc of the fuel to be analyzed are shaken vigorously with 20% sulphuric acid for 20 secs. The amount of sulphuric acid depends on the intensity of the brown colour of the fuel; it varies from 10 cc to 50cc: 10 cc are used if the coloration is slight; 50 cc if the coloration is intense. As soon as the layers have separated the sulphuric acid is run off; the fuel is washed with water twice; the ground seat in the shaking vessel is also freed of sulphuric acid with water. The water in the fuel is removed by adding anhydrous sodium sulphate into the shaking vessel; the drying is often complete only after vigorous shaking. The fuel which is now perfectly anhydrous is now tested according to a).

c) Fuels containing alcohols

Fuels containing alcohols have first to be freed of the alcohols by washing with water. They can then be treated according to a) or b) respectively.

9. Summary

The first step in the general application of the EKFS method to all practical fuels is the treatment of the fuel with 70% sulphuric acid. After thorough washing with water it is then dried well with anhydrous sodium sulphate. The reaction between iodine and lead tetraethyl is then allowed to proceed without shaking.

This new method has the particular merit of making the EKFS method of determining lead suitable for mobile laboratories at the front employed in analysing captured fuels. Although the method has been extended one lead determination only takes 15 mins.

(Table 1 on next page.)

TABLE I

Effect of the time of contact of 70% sulphuric acid on the lead tetraethyl (TEL) in the fuel

Denomination of fuel	Amt. of TEL meas. out in vol. %	TEL content acc. to Ulrich vol. %	Shaking time 15 secs. with		Shaking time 30 secs. with		Shaking time 120 secs. with	
			10 cc.	50 cc.	10 cc.	50 cc.	10 cc.	50 cc.
Roumanian gasoline	0.1	0.0995	0.1065	0.0988	0.1009	0.0982	0.0985	0.0919
Synthetic gasoline	0.1	0.1002	0.100	0.1022	0.10256	0.1028	0.0950	0.0945
Iso-octane	0.1	0.0993	0.1001	0.0978	0.0997	0.0979	0.0982	0.0919
Automotive gasoline	-	0.0224	0.0242	0.0227	0.0235	0.0215	0.0219	0.0199
Leuna gasoline	0.1	0.0989	0.0985	0.0989	0.0985	0.0985	0.0980	0.0977
Alkylate gasoline	0.1	0.1001	0.1005	0.1001	0.1001	0.0979	0.0997	0.0970
Hydrogenated gasoline	0.1	0.1002	0.1017	0.1017	0.1024	0.1015	0.1017	0.1001
B4 fuel	-	0.1205	0.1205	0.1197	0.1205	0.1189	0.1210	0.1183
C3 fuel	-	0.1230	0.1228	0.1225	0.1232	0.1220	0.1224	0.1208

Table 2

Effect of 7 0% sulphuric acid on the assimilation of iodine by the fuel.

Gasoline sample	Amount of H_2SO_4 used cc	Assimilation of n/10 iodine solution before treatment with H_2SO_4 cc	after treatment with H_2SO_4 cc
Roumanian gasoline	50	0.61	0.05
Cracked gasoline	50	0.10	0.03
Synthetic gasoline	10	0.13	0.06
Leuna gasoline	10	0.06	0.02
Alkylate-gasoline	20	0.01	0.00
Z-fuel		0.00	0.00
Hydrogenated gasoline	10	0.07	0.00

Table 3

Effect of water in the fuel on the determination of lead tetraethyl

Denomination of fuel	Theoretical content of TEL Vol. %	Observed content of TEL in fuel sat. with H_2O	fuel dried with Na_2SO_4
Iso-octane	0.1	0.0993	0.0989
Heavy Gasoline	0.1	0.0903	0.0978
Roumanian Gasoline	0.1	0.0919	0.1024
Leuna Gasoline	0.1	0.0966	0.0985
Synthetic Gasoline	0.1	0.0809	0.1028
Cracked Gasoline	0.022	0.0172	0.0215
Automotive gasoline	0.0224	0.0160	0.0192

Table 4

Effect of potassium iodide in the alcoholic solution of iodine on the determination of T. E. L.

Denomination of fuel	Theoretical content of TEL vol. %	Observed TE L content in vol. % Solution of I_2 used, contains:-				
		0.1%by wt. KI	0.25% by wt. KI	0.5% by wt. KI	1.0% by wt. KI	1.5% by wt. KI
Roumanian Gasoline	0.1	0.1294	0.1242	0.1056	0.1036	0.1009
Iso-octane	0.1	0.1067	0.1045	0.1001	0.0999	0.0985
Synthetic Gasoline	0.1	0.1142	0.1094	0.1024 0.1020	0.0985	0.0989
Leuna-Gasoline	0.1	0.1067	0.1048	0.0993	0.0989	0.0989

Table 5

Determination of TEL under various experimental conditions.

Determination of fuel	Theoretical content of TEL vol. %	Temp. °C.	Observed content of TEL vol.% Shaking time 5 min.	Standing 6 min.
Iso-octane	0.1	20	0.0985	0.1002
" "	0.1	20	0.0999	0.0998
" "	0.1	20	0.1009	0.0998
Roumanian Gasoline	0.1	20	0.1019	0.1002
" "	0.1	20	0.0989	0.0997
" "	0.1	20	0.0974	0.0997
Leuna Gasoline	0.1	20	0.0989	0.0995
" "	0.1	20	0.0975	0.0995
" "	0.1	20	0.0993	0.0992
Cracked Gasoline	0.1	20	0.0972	0.0996
" "	0.1	20	0.1009	0.0989
" "	0.1	20	0.0992	0.0989
Synthetic Gasoline	0.1	20	0.1003	0.1004
" "	0.1	20	0.1009	0.1008
" "	0.1	20	0.0996	0.1005

Table 6

Effect of temperature on the determination of lead.

Denomination of fuel	Theoretical content of TEL vol.%	Temperature °C.	Observed content of TEL vol. %
Roumanian Gasoline	0.1	-20	0.0891
" "	0.1	-20	0.0946
" "	0.1	-20	0.0848
" "	0.1	0	0.0962
" "	0.1	0	0.0970
" "	0.1	+10	
" "	0.1	+20	0.0999
" "	0.1	+20	0.1008
" "	0.1	+30	0.1028
" "	0.1	+30	0.1036
Leuna Aviation Gas.	0.1	-20	0.0661
" "	0.1	-20	0.0630
" "	0.1	0	0.0825
" "	0.1	0	0.0837
" "	0.1	+10	0.0954
" "	0.1	+10	0.0950
" "	0.1	+20	0.0982
" "	0.1	+20	0.0987
" "	0.1	+30	0.0985
" "	0.1	+30	0.0993

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DIFFERENT KNOCK BEHAVIOUR OF FUELS OF DIFFERENT CHEMICAL STRUCTURE IN THE ENGINES BMW 132 N and DB 601E

SYNOPSIS:

Tests had shown that the knock behaviour of fuels does not only depend upon the temperature of the unburnt residual mixture and upon the resulting chain introducing reactions but that it is also determined by peroxides which may already be formed on unvaporized fuel particles during the mixture formation in the compression stroke. These peroxides influence the knock process considerably. A knock limit curve with its minimum in the region of $\lambda = 1.05$ shows the first kind of reaction clearly. The second kind has its lowest anti-knock value in the rich region, according to the temperature of the engine and the type of fuel; and from this minimum in the rich region the curves show a progressive increase of the anti-knock value. Since aero-engine fuels in the BMW 132 N engine - when tested according to the DVL supercharge method - showed knock limit curves which had their minima at $\lambda = 1.05$, it was necessary to find out whether correlation could be obtained with fuel ratings from knock limit curves having their minima in the rich region. Numerous fuels of extremely different chemical constitution and of different anti-knock values were tested in the engines BMW 132N, BD 601A and DB 601E. These fuels differed considerably as regards their absolute anti-knock values and also in their order of rating. The effect of these results on the fuel rating according to the DVL supercharge method is discussed and the need pointed out for fundamental knock tests in an engine which gives knock-limit curves with minima in the rich region.

CONTENTS

INTRODUCTION:

The constantly progressing developments in aero-engine design and the endeavour to obtain maximum output from a given cylinder capacity among other measures led to an increase of the valve overlap. By this means the residual gases are scavenged and an increase in volumetric efficiency is achieved. Furthermore, the flow of scavenge air during the overlap period has a cooling effect on valves, piston and combustion chamber walls, so that, in spite of the fact that a higher power is obtained from the same cylinder capacity, the overall thermal condition of the cylinder is reduced.

However, the knock behaviour of the engine was affected in an unusual way. The relatively cooler state of the engine at certain mixture strengths is detrimental to the vaporization of the fuel. This led to pre-reactions of the non-vaporized fuel particles, so influencing fundamentally the knock behaviour, and the shape of the knock limit curve differed from the usual type. The testing of aero-engine fuels according to the DVL supercharge method is based on the well known type of knock limit curves with their minima at $\lambda = 1.05$. The rating is done according to the absolute height of this point in comparison with other fuels. It was to be assumed that in engines which show different types of knock limit curve the ratings and the absolute anti-knock values would not give good correlation.

Fuels as chemically different as possible and with different anti-knock values were tested by the DVL supercharge method with a BMW 132N cylinder.

The same fuels were then tested in an engine which gave knock limit curves with minima in the rich region as well as curves with minima at $\lambda = 1.05$. Thus it was possible to determine whether the variations in the fuel rating are due to different engines or to the different shapes of the knock limit curves. The conclusions reached should then show whether the DVL supercharge method with the BMW 132 N engine is sufficient for the rating of fuels or whether it is necessary to carry out tests on another engine type.

II. General Remarks on Knock Behaviour and Knock Limit Curves.

Tests on liquid cooled engines undertaken to establish their knock behaviour under various operational conditions and with various fuels, resulted in a number of knock limit curves which were totally different from the usual ones. The opinion generally held that the knock limit curves had only one shape in any circumstances, independent of the fuel and operating conditions, could no longer be entertained in the light of these tests. The knock limit curves which hitherto obtained in engines had the characteristic feature that their minima were always in the region of the excess air ratio $\lambda = 1.05$. From this point the anti-knock value of the fuel increased more or less sharply, and thus gave the well known form of knock limit curve. Both the position of the minimum and the increase of the anti-knock value could be explained by the theories and discussions which try to interpret knock behaviour.

From all the various theories which were put forward to explain the knocking combustion of more or less large mixture residues the "compression theory" proved to be best. According to this the flame front originating from the sparking plug is propagated with a velocity depending upon the quality of the mixture formation, the pressure, the temperature, the excess-air and finally the turbulence. This flame-front increases the pressure and the temperature of the unburnt mixture. This leads to reactions in the residual mixture. These reactions produce unstable products and so have a chain starting effect and lead to a rapid reaction. The resulting sudden pressure rise and its expansion in the combustion chamber produce the characteristic knocking noises when the gases strike the cylinder walls and the piston.

According to the compression theory the start of knocking is due to the thermo dynamic condition of the unburnt fuel air mixture. The factors affecting the temperature limit which causes the self-ignition of the fuel in the unburnt mixture are:- the compression and its time variation, the temperature and its variation in time and place as well as the mixture composition and its variation. Under given operating conditions, e.g. when plotting a so-called fuel loop, alteration of the mixture composition under suitable conditions can change the engine from the knock free region to the knock region and vice versa. The mixture composition influences the knock behaviour through the different end temperatures of the unburnt residual mixture. The difference in the end temperature is caused by the alteration of the quotient C_p/C_v and by the differences in the combustion temperature itself. Jost and his colleagues calculated the values of the temperature and their variations. For a gasoline of mean molecular weight 100 and composition $(CH_2)_n$ they considered the dissociation of the combustion gases and expressed the exact course of the specific heat in terms of the air ratio. Then they found the values of the end temperature of the unburnt residual mixture as shown in fig. 1. The highest temperature of the unburnt mixture is in the region of λ 1.05. In agreement with this fact a fuel loop plotted in the same diagram shows the start of knocking in this region when operating conditions favourable for the onset of knocking are reached and the knock itself is only conditioned by the processes in the unburnt mixture.

We can imagine that the well known knock limit curves obtained according to the DVL supercharge method are obtained thus:- From a number of fuel loops at different constant boost pressure the points at which knocking begins and ends are plotted against the excess air ratio. The minimum is at $\lambda = 1.05$. Then with the earlier onset of knocking at higher boost pressures, in accordance with the fuel and the other working conditions, the curve rises on both sides of the minimum and shows the well known form of a knock limit curve.

A different shape of knock limit curve could be obtained with a minimum in the extreme rich region and showing an almost linear rise of the anti-knock value over the whole region of the excess air-ratio. Extensive tests with various fuels and under different operating conditions gave a complete explanation for the causes of this difference from the normal knock-behaviour. It was found that, apart from the chemical constitution of the fuel, the thermal state of the engine was solely responsible. This type of knock limit is not necessarily a characteristic of the liquid cooled engine. Liquid cooled engines of older type or under special conditions of high thermal loading give knock limit curves with their minima in the region of $\lambda = 1.05$, and there are also air cooled engines which give curves with their minima in the extreme rich region. The droplet theory of Callendar was used to explain this behaviour. It is not possible to explain here all the factors influencing the knock limit curves which have their minima in the rich region nor can the theory of Callendar be presented in detail. Only those points will be mentioned which have a bearing on the phenomenon with which we are dealing.

Callendar was able to show that in the presence of non-vaporised fuel droplets the formation of peroxides increased. After a large number of tests it became clear that this was the main factor responsible for the alteration of the shape of knock limit curve. Fig. 2 shows two knock limit curves which were obtained from engines of a similar design, and could be compared directly. One of the knock limit curves comes from the DB 612 sleeve valve engine and shows the well known behaviour with the minimum in the region of $\lambda = 1.05$. The DB 601E differed from the preceding type only in the design of valve gear and in the valve overlap. Its knock limit curve in the lean region was almost the same under suitable operating conditions, and its anti-knock value in mm. Hg. boost pressure coincided with that of the DB 612 sleeve valve engine in the region $\lambda = 1.05$. But whilst the sleeve valve engine with the fall in temperature of the unburnt residual mixture shows from its minimum onwards a rise of the anti-knock value, the anti-knock value of the DB 601E falls continuosly from this point and reaches its minimum in the region of $\lambda = 0.7$. It is clear that the two similar branches of the knock limit curve in the lean region are due to the same causes in the engine. Of course different boost air temperatures must be selected according to the different thermal conditions and the different valve-gear. But when the two curves separate, conditions are fundamentally different. The normal rise of the anti-knock value of the sleeve valve engine in the rich region is due to the temperature drop of the unburnt mixture, this being due to the enrichment of the mixture. This normal rise of the anti-knock value in the rich region contrasts with the continuous decline of the curve of the conventional engine with greater valve overlap. This large valve overlap of 120° crank angle results, through the complete scavenging of residual gases and the additional cooling effect of the scavenging air , in the whole thermal condition of the engine being reduced. The fuel entering the cylinder during the injection process has therefore no opportunity to vaporise com-pletely. Part of the fuel, depending on the degree of mixture enrichment and on the operating conditions does not vaporize but remains as droplets. These unvaporized fuel particles form peroxides during the compression stroke according to the theory of Callendar. These peroxides are the unstable prod-ucts which are the main cause of the onset of knocking. Knocking therefore starts much earlier in an engine which forms knock producing unstable products not only during the flame travel in the combustion chamber but also during the compression stroke. Fig.2 shows for the DB 601E that this state of affairs becomes more evident in the rich mixture region. For by increasing the quantity of the injected fuel the temperature of the mixture is still further reduced by vaporization, and there is a larger number of non-vaporized fuel particles and peroxides. The consequence is that the boost pressure must be reduced in order to counteract the knock producing effect of the peroxides.

Turning now to fig. 2 and considering the effects of such pre-reactions in the mixture during the compression stroke on the absolute position of knock limit curves, the following appears. As mentioned previously the curves of different type with approximately equal height in the region of $\lambda = 1.05$ could be obtained only at different boost air temperatures. The knock limit curve of the sleeve valve engine was plotted at 130°C boost air temperature, while the curve of the conventional engine had the same form and almost the same absolute anti-knock value in the lean region at 80° boost air temperature. This difference in the boost air temperature necessary to obtain the same anti-knock value, is due to the fact that engines with sleeve valves for the same design of the combustion chamber have a higher anti-knock value than engines with a conventional valve system, in spite of the higher thermal level of the sleeve valve engine. From the point of equal knock behaviour of the two engines in the lean region the area between the two curves from $\lambda = 1.05$ onwards must be considered as a loss in anti-knock value due to the peroxides on unvaporized fuel particles.

Considering now the knock limit curve of the DB 601E engine at 130° boost air temperature also plotted in fig. 2. First of all there is an increase of the anti-knock value when the boost air temperature rises. The loss in anti-knock value represented by the shaded area is thus reduced But it appears to be completely inexplicable at first sight why there is suddenly an increase of the anti-knock value when the boost air temperature rises. This phenomenon does not agree with the compression theory of knock. But further consideration of the factorsdetermining the knock limit curve with a minimum in the rich region make this knock behaviour understandable. Since the vaporization of the fuel improves with increasing boost air temperature the proportion of unvaporized particles and also the proportion of the peroxides decreases. Thus the boost pressure may be increased at the same mixture strength for the same knock intensity.

A consequence of this reversed temperature senstivity of fuels may be mentioned. In order to increase both the power and the maximum power altitude of aero engines blower speeds have been increased more and more to obtain the necessary pressure ratio. This also increased the boost air temperatures. As a counter measure inter-coolers were proposed because an engine with normal knock behaviour can enter the knock region when the boost air temperature rises. An engine having knock limit curves with minima in the rich region will act quite differently, since such knock behaviour does not necessitate the reduction of the boost pressure with an increasing boost air temperature. Extensive tests showed that with a number of suitably selected fuels the boost pressure may be increased so much that the reduction in volumetric efficiency due to the boost air temperature rise is balanced and the same power is obtained.

The fact that engines showed a fundamentally different knock behaviour necessitated further study of the fuel rating by the DVL supercharge method. It is quite possible that, because of the fundamental difference in the knock limit curves differences in the absolute anti-knock value may occur between fuels tested according to the DVL supercharge method in the BMW 132 engine and the same fuels used in the actual engine; moreover the order of the fuel ratings may change. There may be differences in anti-knock value due to the fact that the temperature sensitivity of fuels is opposite for the two forms of knock limit curve. Whilst fuels, tested according to the DVL supercharge method in the BMW 132, show with increasing boost air temperature a reduction of the anti-knock value, the same fuels tested in the DB 601E engine, show an increase of limiting boost pressure. For the same reason the rating of fuels, which is determined from the relative positions of the minima may be altered. With a favourable selection of the operating conditions during the test procedure, particularly with a suitable boost air temperature, it may be possible to obtain a nearly consistent rating of fuels. But the conditions thus found are never of any use in practice when the operating conditions of the main engine are very different from those of the test engine, particularly as regards the boost air temperature or the valve overlap and when the test engine is characterised by a knock behaviour with a minimum at $\lambda = 1.05$, whilst the main engine perhaps gives knock limit curves with decreasing anti-knock values up to the rich region.

Other methods used for the testing of fuels should show values comparable with the behaviour in the actual engine only under particularly favourable operating conditions. The octane number in the CFR or I.G. engine is determined by adjusting for maximum knock in the region of $\lambda = 1.05$, the fuel is rated by comparing it with blends of the same knock behaviour. Even with the available results of the DVL supercharge method the results of the octane number rating did not agree particularly well with the practical values. It can hardly be expected that they will improve if this method is adopted for engines with knock limits which have their minima in the rich region. As regards fuel ratings according to the Oppau method comparable results are not available but the same will probably apply. This test method is also based on knock limit curves with minima at $\lambda = 1.05$. Therefore the results obtained by this method can be applied to engines with a different type of knock behaviour only with reservations. In order to find out the deviations of the various ratings a great number of fuels were tested of very different chemical constitution and of different knock behaviour by the DVL supercharge method in the two engines. In the following section a description is given of the fuels and of the test conditions under which these tests were carried out.

III. Test Procedure.

The problem itself made it clear which engines to use and what test conditions to apply. For the fuel rating according to the DVL supercharge method the BMW 132N cylinder was used on a full scale radical crankcase under the well known conditions. The latter are given in the engine data in Table I.

For comparison a liquid cooled cylinder of the DB 601 type was used, fitted on a DVL single cylinder test stand. By selecting suitable operating conditions this engine gave knock limit curves which had their minima in the rich region. For this purpose the valve overlap was increased to 120° crank angle and so the thermal state of the engine was low in spite of the fact that the boost air temperature was 130°C. In order to avoid an excessive increase of absolute boost pressures the compression ratio was raised by a small amount to $\varepsilon = 7.2$. This permitted the plotting of sufficient points even for high anti-knock fuels.

From tests carried out in the DVL, no considerable difference in the rating of fuels was anticipated through this small increase of the compression ratio. It was desired to test the behaviour of the liquid cooled engine not only as regards its knock behaviour with the minimum in the rich region but also with the normal position of the minimum at $\lambda = 1.05$. For this purpose the valve overlap was reduced and thus the temperature level raised, other operating conditions remaining the same. With a valve overlap of 40° crank angle all the knock limit curves were obtained with the minimum at $\lambda = 1.05$.

All other data relating to the DB 601 engine are given in the engine data Table I.

The fuels were selected to be chemically as different as possible and of different anti-knock values. Table II shows the fuels which selected being partly pure substances partly blends of two or more components, and the main analysis data are also shown.

IV. Test Results

The fuels shown in Table II were used in the engines according to the conditions described in the section. "Test Procedure". The knock limit curves were plotted in the following graphs which show a particular group of fuels in each diagram. In order to facilitate the comparison each graph contains the same group of fuels for one of the different engine types. Thus in Fig.3 are the knock limit curves plotted as mm Hg boost pressure against excess air ratio for the homogeneous fuels and the BS mixtures in the BMW 132N engine with 40° crank angle valve overlap and in the DB 601 engine with 40° and 120° valve overlap. Fig. 4 shows the results for blends made from two or more single components, all of them with 0.12% by volume TEL content, for the same engine types and plotted in the same manner.

Before discussing the graphs in detail a brief explanation is given of why, in this case, it is best to plot the knock limit curves in mm Hg against the excess air ratio, and also the errors are described which result from the method used for the determination of the excess air ratio.

Previous tests were made to determine the influence of the valve overlap. These tests showed that with knock limit curves which have minima in the rich region, the MEP obtainable at the knock limit is no longer a suitable basis for rating.

For it was found that knock limit curves with these characteristics whenplotted as p_{me} against λ, were not at all affected by the variations of the boost air temperature, but that the knock limit curves coincided for the greater part of that region of the excess air ratio which is here of interest. In this case rating of the fuels from comparison of the curves would have been more difficult if not impossible. With knock limit curves having minima at $\lambda = 1.05$, the absolute heights in relation to the anti-knock values are determined apart from other factors mainly by the more or less strong temperature sensitivity of the fuels irrespective of whether the values are plotted in mm Hg boost pressure or in kg/cm² MEP. This would be the case with the BMW 132 engine and with the DB 601 engine at 40° crank angle valve overlap and at a boost air temperature of 130°C. But knock limit curves of the DB 601 engine at a valve overlap of 120° crank angle are completely insensitive to temperature for fuels of a very low aromatic content when the curves are plotted as p_{me} against λ. Whereas knock limit curves with similar characteristics allow a comparison of fuel ratings without too great difficulty at different boost air temperatures if the engines are not too different, such a comparison is impossible in this case. It could no longer be considered correct to compare the anti-knock value of a fuel which was determined by the temperature and the method of plotting, with a curve of the same fuel having its minimum in the rich region, and which does not depend on the value of the boost air temperature. Even with very small variations of the boost air temperature the order of rating would be different each time. It was for these reasons that for the first time p_{me} values are not plotted in this report.

Although it is very convenient to compare various knock limit curves on the basis of the excess air ratio λ then the values of the calculated air ratio are incorrect. By the present method of calculation the whole air quantity passing through the engine and measured by the air flow meter is related to the measured fuel. But this air quantity contains also a proportion of the scavenging air. This proportion differs not only with the valve overlap and the speed but also with the ratio of boost pressure to exhaust back pressure. When plotting knock limit curves at the different boost pressures which occur, this means that the value calculated for the air ratio is wrong each time by a different amount.

Tests made to obtain the relevant proportion of scavenging air from the available curves and to eliminate it from the total air quantity were not very successful and were abandoned. Until a reliable method is available to determine the combustion air this inadequate method of plotting must suffice.

The following results of the knock behaviour can be considered reliable only when they refer to a rating for a real minimum at $\lambda = 1.05$. The points may even contain wrongly calculated λ values but by virtue of their unmistakable position they can well be compared. The values obtained from curves with minima in the rich region and taken at $\lambda = 1.05$ can no longer be considered completely reliable. This must be taken into account in discussing the diagrams which follow.

First of all in fig. 5 the real minima of the two engines are related to each other. In this case one axis shows the anti-knock values at $\lambda = 1.05$ for the BMW 132N engine whilst the other axis shows the minima obtained from the DB 601 engine with a 40° valve overlap. Superficially it appears that the ratings in the two engines agree quite well. Apart from a few exceptions all points are on one curve; some fuels are outside the curve, and it would be worth while to investigate the cause of those irregularities, and to find out why some fuels disturb the regularity. But first the results of the BMW 132N and the DB 601E engines will be discussed. Fig 6 shows the anti-knock values obtained in the region of $\lambda = 1.05$ by an analogous method of comparison, it must be pointed out that the BMW 132N engine has a minimum in the region of the Stoichiometric air ratio, whereas the DB 601 E engine does not show a minimum at $\lambda = 1.05$ with a boost air temperature of 130°C because of the peculiar shape of the knock limit curve. Irrespective of the fact that it is impossible to find the exact points for $\lambda = 1.05$ with knock limit curves which have minima in the rich region, the values obtained should show whether a comparison of the values obtained from the two engines is permissible. A glance at fig.6 shows again that almost all the points obtained are on one curve, and only a few fuels fall outside. The fuels which do fall outside are different from those in fig. 5. There the fuel blends M.131 and M.132 are rated quite high in the BMW engine and very low in the DB 601. In fig. 6 we see that these two blends lie well on the curve but the gasoline benzol mixture and C 3 reference fuel are rated quite highly in the DB 601 compared with the BMW 132 engine and are far outside the curve. An exact explanation necessitates making suitable tests; but we may anticipate that the reason for the fact that only the two fuels with aromatic content viz. the gasoline benzol and the C3 mixture - lie outside the curve is their temperature sensitivity. As a liquid cooled engine of a more recent design, the DB 601 has undoubtedly a lower overall temperature at otherwise the same operating conditions, which explains in a sufficiently satisfactory manner the fact that the highly tmperature sensitive aromatic fuels are off the curve. There is, however, a fact which needs further discussion. Comparing fig. 6 with fig. 5 the slope of the curve has completely changed. For the results obtained from the two engines to agree completely we should theoretically obtain a straight line which should have a gradient of 45° and should pass through the origin. Fig 5 shows deviations. The straight line first of all does not go through the origin which no doubt is due to different fuel rating in the two engines consequent on the differences in design. By a suitable selection of the operating conditions an approximately similar behaviour of the reference fuel "Eich B4" could be obtained in the BMW 132N, DB 601A and DB 601E. Therefore there is only a very small deviation of the straight line from the theoretical. The BMW 132 cylinder fig. 5, gives the fuels a more favourable rating and it is understandable that in this case where, at relatively low boost pressures, agreement on the reference fuel was unobtainable deviations of the other fuels with increasing boost persisted or increased. This would explain the different slope of the curve obtained compared to the theoretical curve. For the behaviour of fuels in the two engines in regard to the minimum knock rating a constant factor should serve to convert the values found in one engine to those in the other. This simple method is at once ruled out when fig. 6 is examined, in which the curve does not go through the origin and showed this time a deviation to the other side, i.e. the DB 601E cylinder gives the more favourable rating of the fuels. This could beexplained by the fact that the temperature level of the cylinder is lower because of the high valve overlap. The other very important fact is the alteration of the angle of the curve obtained when compared to the theoretical curve (45°). The alteration of the gradient is such that this time the DB 601 cylinder at 120° valve overlap gives a more favourable evaluation of the knock behaviour of the fuels. Since the λ 1.05 minima were taken from the knock limit curves of the BMW 132N engine and were really the lowest values of the knock limit curve, irrespective of the fact that the air ratio might be incorrect, whereas the DB 601E engine has no minimum in the region of the stoichiometric mixture ratio under the present operating conditions the points were taken from the calculated λ = 1.05 values. It is probable that this affected the gradient of the curve in fig. 6. Assuming that an error of 10% was made in the determination of λ and plotting the new values in fig. 6. a curve is obtained which is less inclined, but it is still considerably steeper than the curve in fig. 5, and the conversion of the results to the BMW 132 values would be possible only by means of another constant.

In an attempt to relate the real minima of the two engines, in fig.7 the lowest anti-knock values taken from the knock limit curves of the BMW 132N engine at λ = 1.05 plotted in mm Hg. are plotted against the minima in the rich region of the knock limit curves on the DB 601E engine. The curve obtained this time passes almost through the origin and comes very near to the required theoretical slope of 45°. Compared with fig. 5 and fig. 6 this means yet another deviation, another constant is obtained for the conversion of the anti-knock value of the fuels in the two engines. It can therefore be stated that the fuel rating by determining the abolsute anti-knock values according to the DVL supercharge method in the BMW 132N engine, cannot be used for engines with knock limit curves of different characteristics, since this method which uses a conversion factor is not satisfactory. The causes of knocking in the two engines are different, and therefore it is impossible to obtain complete agreement of the ratings. The fact that fig. 5 to fig. 7 partly allow a favourable interpretation is misleading as will be shown in the following paragraphs.

It must be remembered that the compression theory says that knocking is caused mainly by the thermo-dynamic condition of the unburnt residual fuel air mixture. Knock limit curves with a minimum at λ = 1.05 are obtained, mainly due to reactions in the residual mixture. The temperature limit causing the knocking reaction of the residual mixture is reached earlier when the boost air temperature is increased. In other words an increase of the boost air temperature requires a reduction of the boost pressure in order to obtain the same thermo dynamic state of the residual mixture. According to the hypothesis concerning the influence of fuel droplets, the amount of these fuel droplets decreases with the amount of unvaporized fuel, i.e. with increase in boost air temperature. In order to obtain the same condition of the residual mixture residue resulting in a reaction at the knock limit an increase of boost pressure is necessary in spite of the fact that the boost air temperature is raised at the same time

There are thus two types of engine. One of them shows a knock behaviour which is already familiar i.e. the anti-knock performance of the fuel falls with increasing boost air temperature. The other engine type behaves differently, its anti-knock value rising with increasing boost air temperature. It is difficult to compare the knock behaviour of the same fuel in the two engines. Consider the testing of any one fuel in the two engines at a relatively low boost air temperature, e.g. 50°C. This value is quite common for the main engine during practical operation. In this case the fuel will be rated quite well in an engine with normal knock behaviour whilst the anti-knock value of the same fuel expressed in mm Hg will probably be lower in the other engine.

A number of fuels with different anti-knock values rated in these two engines will give us a curve with a considerably flatter inclination than the theoretical curve with a slope of 45°. Testing the same fuels at a high boost air temperature, e.g. 160°C, which value can also be obtained in main engines, the engine with the normal knock behaviour will now give the fuel a very poor anti-knock value because of the high boost temperature, whilst the engine giving pre-reactions in conjunction with unvaporized fuel particles during the mixture formation gives quite a good anti-knock value in comparison because of reduction in the number of fuel droplets at the high boost air temperature. From tests with various fuels a correlation curve is obtained with a greater slope than that of the theoretical curve. With a suitably selected intermediate boost air temperature it may happen that the curve obtained from comparative tests will have the theoretical slope. This is, however, an isolated case which applies only to the particular boost air temperature. Under no circumstances can it be assumed that this isolated agreement i.e. the equal slopes of the theoretical and of the test curves, permits applying the fuel rating in an engine with knock limit curves having minima at λ = 1.05 to another engine with knock limit curves having the minima in the rich region.

A final series of tests with various fuels confirmed completely these ideas and a short commentary is given in the following passages:- Fig.8 shows the knock limit curves for a wider range of boost air temperatures for the engine BMW 132N and for the fuels C1, C3 and VT 702. Fig.9 shows the same fuels in the engine DB 601 with a valve overlap of 120°. Comparison of the two graphs shows that the knock limit curves of all fuel have the minimum at λ 1.05 in the BMW 132N engine. Therefore a reduction of the anti-knock value occurs with increasing boost air temperature. In Fig. 9 however the minimum moves into the rich region and the anti-knock value of all fuels rises with increasing boost air temperature. For the region of the stoichiometric fuel air ratio the values of the boost pressure in mm Hg from the knock limit curves were compared in Fig. 10. The corresponding points for the same boost air temperature can be joined by a curve, which, however, has a different slope for each boost air temperature. The curve drawn through the points for 130°C agrees almost with the theoretical curve. The points of the other boost air temperatures give a larger or smaller slope than the theoretical. The angles made with the theoretical curve give some guidance as to the difference in the temperature effect for the same fuel in the two engines. Fig. 10 shows clearly that the boost air temperature of 130°C in the DVL supercharge method gives quite accidentally a more or less good agreement between the anti-knock values in the various engines so long as only the minima are considered. Any higher or lower boost air temperature gives deviations which become greater the more the boost air temperature differs from the test temperature of 130°C.

As regards the possibility of continuing to use the DVL supercharge method in its present form, the following can be said: If only a general idea of the anti-knock value is required the present form of the supercharge method may be used. The DVL supercharge method in the BMW 132N cylinder gives an indication of the anti-knock value although the difference in the rating of a fuel might be considerable in different engines and there might be even a contrasting temperature effect in the different cylinders. A determination of the rating of fuels according to their knock behaviour in another engine giving knock limit curves with minima in the rich region is partly possible by means of the results of the DVL supercharge method, but with the following reservations:- Substances with small aromatic content do not alter their order of rating as shown by fig. 5 to fig. 7 irrespective of whether they are tested in the BMW or DB cylinder. Differences can be considerable with highly aromatic fuels. Evidence for this fact is given by fig.5 to fig.7, where the C3 reference fuel, the gasoline benzol blend and the two isopropylbenzene blends M 131 and M 132 are completely outside the curve. Some explanation is required for this behaviour of fuels C3 and the gasoline benzol blend, since their exceedingly favourable anti-knock value is due to the temperature sensitivity associated with their aromatic content. The engines BMW 132 N and DB 601A have approximately the same temperature level and give almost the same anti-knock values as shown in fig. 5, and the decrease of the thermal internal stress in the DB 601E gives the increase of the anti-knock value of these temperature sensitive fuels in this engine. This appears from fig. 6 and fig. 7. No explanation is available for the behaviour of the mixtures M.131 and M.132. Fig. 5 shows that they are rated quite favourably in the BMW engine, but do not, however, show an increase of anti-knock value in the cooler DB 601E cylinder, which should result from their temperature sensitivity. The DVL supercharge method underrates the gasoline benzol and the C3 mixture which makes the determination a safe one. But the mixtures with a high content of isopropylbenzene were rated too favourably. This may lead to troubles in the DB 601 engine. Further tests must show whether similar phenomena will occur with other fuels. Substances which are likely to show such deviations can be eliminated by a simple chemical determination of the aromatic content in advance. Their anti-knock values obtained from the knock limit curves in the BMW 132N cylinder must no longer be used to determine the order of rating.

The rating must not be confused with the absolute anti-knock values. And this is one of the points where the application of results of the supercharge method in the BMW cylinder becomes uncertain. Aero engines are nowadays designed and developed for maximum performance. Since all kinds of adjustments are involved their control curves are often critically near a knock region; therefore anti-knock values are very doubtful when they are merely derived from the results of the supercharge method. In this case it is essential that fuel tests on knock behaviour should be carried out on the engine type in question. Finally it is entirely impossible to draw any conclusions from the temperature characteristics of a fuel in a BMW cylinder as to the temperature characteristics in other engines which - because of a smaller thermal internal stress - have different types of knock limit curves. Therefore all questions which concern the temperature characteristics and the range of the knock region for the two forms of knock limit curve necessitate a fuel test in a cylinder of another engine type which gives for the whole operating range knock limit curves of a similar kind.

V. Summary:

The knock limit curves which are formed according to the compression theory of the phenomenon of knocking, have their minima at the temperature peak of the unburnt residual mixture, which occurs in the region of the stoichiometric mixture ratio. But at a low temperature level of the cylinder knock limit curves are obtained which, because of the peroxide formation with unvaporized fuel particles especially in the region of air deficiency, shift their minima into the rich region. The two kinds of knock limit curves show contrasting temperature characteristics. Knock limit curves with minima at $\lambda = 1.05$ show with increasing boost air temperature a decrease of the anti-knock value, whereas knock limit curves with minima in the rich region show with increasing boost air temperature an increase of the anti-knock value.

The DVL supercharge method for the testing of aero engine fuels rates these fuels according to their knock behaviour by means of knock limit curves with minima at $\lambda = 1.05$, obtained in the BMW 132N engine. But recent liquid cooled aero-engines with high valve overlap have a very low temperature level and give mostly knock limit curves with minima in the rich region. It was attempted to find out whether the fuel rating according to the DVL supercharge method in the BMW cylinder can be used for liquid cooled engines.

A great number of very different fuels was tested in a BMW 132 N and in a DB 601 cylinder. The result was that it is possible to use the above method for the rating of the anti-knock value of fuels with low aromatic content. Fuels with a higher aromatic content are often quite considerably outside the curve and do not give clear results as regards their order of rating. Corresponding experimental anti-knock values were plotted in one diagram and could be joined by a straight line. Generally speaking rating is valid if the experimental values are well on the straight line; but this straight line is only a criterion for equal knock behaviour in the two engines if the gradient equals that of a theoretical curve of 45° or less.

Final tests with some typical fuels at various boost air temperatures permitted interpretation of the significance of the various gradients of the curve , and the steepness of the curves served as an indication of whether the fuels were over or underrated in the engine. At a suitable boost air temperature e.g. 130°C with the DVL supercharge method, good agreement was obtained but deviations occur at higher or lower boost air temperatures.

The DVL supercharge method with the BMW 132N cylinder may be used in its present form at 130°C boost air temperature for the general evaluation of anti-knock value of any fuel. A determination of the order of rating from the results of the BMW 132N cylinder for engines with different knock limit curves is permissible as far as fuels are concerned which have a small aromatic content, but this method fails when dealing with fuels of a higher aromatic content. Fundamental tests on the extent of the knock region of a fuel and its temperature sensitivity when used in an engine with a low temperature level, should be carried out in a suitable engine cylinder, of another type if necessary, since the results of the DVL supercharge method in the BMW 132 cylinder are not valid in this case. To establish a control curve, related to knock behaviour tests in the corresponding (identical) cylinder are required. Because of the mutual influence of the cylinders in in-line engines and because of the displacement of the dead centre in radial engines due to the kinematics of the crank drive and also on account of the different cooling systems tests with the main engine can hardly be avoided.

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TABLE I

ENGINE DATA AND SPECIFICATION

Engine Type:-		BMW 132N	DB 601
Data:	Stroke	162 mm	160 mm
	Bore	155.5 mm	150 mm
	Compression ratio	ε = 6.5	ε = 7.2
	Capacity	3.076 Ltr.	2.828 Ltr.
	Compression volume	559 cm³	456 cm³

Valve Timing:		Valve overlap: 40°	120°
Inlet opens:	18° before TDC	24° before TDC	71° before TDC
Inlet closes:	78° after BDC	56° after BDC	56° after BDC
Exhaust opens:	72° before BDC	52° before BDC	69° before BDC
Exhaust closes:	22° after TDC	16° after TDC	49° after TDC

TABLE II.

No.	Fuel	Initial Fuel composition of the Mixture % vol.			Receipt No.	Specific Gravity.	Refraction	Ratio C/H	Lo Theoretical Air	Mean Octane	% Weight of Arom.	T.E.L. %
1	Eich I4	-	-	-	215/43	0.714	1.4011	5.71	14.87	89.3	12.6	0.12
2	Eich C3 IE	-	-	-	133/43	0,791	1.4419	7.54	14.14	92.8	44.8	0,12
3	Captured Fuel	-	-	-	284/43	0.716	1.4050	5.71	14.86	99.4	18.2	0.10
4.	BS 2	75%ET100	25%VT707	-	121/41	0.707	1.4023	5.45	15.0	88.7	5.9	-
5.	BS 3	75%VT302	25%VT702	-	262/42	0,829	1.4691	9.20	13.7	88.9	82.3	-
6.	BS 4	47%Ethanol	53%VT702	-	264/42	0.750	1,3825	4.98	12.08	89.7	11.8	-
7.	ET 110	-	-	-	236/42	0.704	1.3998	5.53	14.95	97	2.0	-
8.	ET 120	-	-	-	273/43	0.707	1.4013	5.62	14.92	95.6	4.8	-
9.	M130+0.12 T.E.L.	20%ET110	70%VT702	10%VT303	136/42 104/43 194/43	0.730	1.4138	5.94	14.74	95.7	20.0	0.12
10.	M131+0.12 T.E.L.	20%ET110	40%VT702	40% Isopropyl Benzene	236/43 104/43 271/43	0.770	1.4409	6,87	24.36	118	49.1	0.12
11,	M132+0.12 T.E.L.	20%ET110	50%VT702	30% " "	"	0.761	1.4333	6.63	14.45	113	39.8	0,12
12.	M133+0.12 T.E.L.	20%ET110	60%VT702	20% " "	"	0.743	1.4226	6.24	14.62	97.9	30.1	0.12
13.	M134+0.12 T.E.L.	20%ET110	70%VT702	10% " "	"	0.727	1.4135	5.90	14.77	95.8	20.1	0.12
14.	M135+0.12 T.E.L.	70%VT810	30%DHDVT340	-	274/43 237/42	0.732	1.4158	6.02	14.72	91.2	31.8	0.12
15.	M136+C.12 T.E.L.	80%VT810	20%DHDVT340	-	237/42 237/42	0.731	1.4132	5.99	14.73	89.4	26.9	0.12
16.	M137+0.12 T.E.L.	80%DHD VT340	20%ET120	-	237/42 273/43	0.746	1.4372	6.30	14.59	95.6	52.7	0.12
17.	M138+C.12 T.E.L.	80%DHD VT340	20%ET110	-	237/42 236/42	0.752	1.4378	6.40	14.54	97.0	52.7	0.12
18.	M139+C.12 T.E.L.	80%DHD VT340	20% French Iso-Octane	-	221/43 300/43	0.764	1.4375	6.69	14.42	96.8	52.7	0.12

Fig.1 Relationship between the end temperature of the unburnt residual mixture and the first onset of knocking at $\lambda = 1,05$

Fig.2 Increase of the knock region at rich mixtures from $\lambda = 1,05$ onwards due to pre-reactions during the mixture formation.

Fig.3 Knock limit curves of various fuels in the engines BMW 132N, DB 601A and DB 601E

Fig.4 Knock limit curves of various fuels in the engines BMW 132N, DB 601A and DB 601E

Fig.5 Comparison of the Anti-Knock values of various fuels at the minimum point ($\lambda = 1,05$) in the engines BMW 132N and DB 601A

Fig.6 Comparison of the anti-knock values of various fuels at an excess air ratio of 1,05 in the engines BMW 132N and DB 601E

Fig.7 Comparison of the anti-knock value of various fuels at the respective minima of their knock limit curves in the engines BMW 132N and DB 601E

Fig.8 Knock limit curves of the fuels C1, C3 and VT 702 in the BMW 132N at various boost air temperatures

Fig.9 Knock limit curves of the fuels C1, C3 and VT 702 in the DB 601E at various boost air temperatures.

Fig.10 Different rating of the anti-knock value of some fuels in terms of the boost air temperature.

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GERMAN AERONAUTICAL RESEARCH

Research Report No. 1905

The Rating of Fuels on their tendency to vapour-lock.

by Widmaier

SYNOPSIS.

Engine troubles due to vapour locking occur in the use of fuels of a certain composition and volatility. These troubles are caused by the fuel itself as well as by other factors, mainly dependent on the condition of the engine and of the surrounding air.

No standard test method has so far been devised for experimentally determining the tendency of fuels to vapour-lock. The boiling behaviour and the vapour pressure are usually used as a measure of it. In the determination of Reid vapour pressure there are certain difficulties in handling the apparatus and the method is not very accurate.

The apparatus described here gives a quick and sufficiently accurate determination of the absolute vapour pressure of fuels. Another simple instrument is used to test vapour-lock in relation to flying altitude.

CONTENTS.

Work by: O. Widmaier. Stuttgart 10.2.44.

I. Causes of vapour-lock.

Vapour-lock can completely or partially stop flow in the fuel system and thus the fuel feed of the engine. It is mainly due to the fuel containing low boiling point fractions which are vaporized in the fuel pipe or in the carburettor by the heat of the engine. Moreover vapour-lock is affected by the air pressure, which varies with the flying altitude.

Three factors which are important in vapour-lock are:

1) The vapour pressure of the fuel or of its components,

2) The external pressure on the fuel,

3) The fuel temperature.

The complete control of these three variables would enable vapour-locking to be prevented at any altitude. In addition to selection of suitable fuel, vapour-lock can be countered by the following measures:

1) Pressurizing the fuel tank,

2) Cooling the fuel,

3) Insulating the fuel lines exposed to heat radiation,

4) Preventing the formation of vapour pockets in the fuel system,

5) Reducing to a minimum the pressure drop within the fuel system,

6) Pressure feed instead of suction feed.

As vapour-lock is a function of the vapour pressure, the tendency of a fuel to vapour-lock is usually still measured by the Reid vapour pressure. This method however does not always give reliable results, as the determination is done in the presence of air, with the result that the expansion of the air has to be considered. Also, as already stated, vapour-lock depends on other factors and experiments have been done to discover as far as possible all the factors involved. The various methods for the determination of vapour-lock and vapour pressure are briefly reviewed here.

II. Present stage of the evaluation methods.

1) Lab. determination of vapour-lock.

A.W. Schmidt (1) has developed an apparatus which attempts a very close reproduction of practical conditions. It consists of a vessel in which a suitable copper fuel pipe is fitted. The water filled container is heated to test temperature and the flow rate of the fuel under test is set at 120 cu.cm/hr. The time taken by the gasoline to form 10 cu.cm. of vapour is measured. The shorter this time, the higher the tendency to vapour-lock.

Hammerich (2) describes an apparatus which reproduces the engine conditions and determines the so called "relative break-off temperature", i.e. the temperature at which the regular fuel feed to the engine is interrupted. While investigating the relation between this break-off temperature and the fuel properties, Hammerich found a practical rating basis in the mean of those sections of the boiling curve up to 50° and 70°C. This quantity was called the volatility of the fuel.

Fig. 1 shows the relationship between volatility and relative break-off temperature for various fuels. As will be seen, the values for fuels of equal vapour pressure lie on a straight line. If $tg\alpha$ represents the slope of the lines, according to Hammerich, the following equation can be formulated for the relationship between relative break-off temperature (rel.AT), Reid vapour pressure and volatility (Fl.):

$$\text{Rel. A.T.} = \frac{30 - \text{Fl.}}{tg\alpha} + 48$$

Using Hammerich's apparatus, Koch (3) proved volumetrically that the amount of fuel fed through a jet decreases with increase of temperature, and that at a temperature characteristic of each fuel, which he called the true break-off temperature, it tends to a zero value. Koch considers this temperature to be decisive for vapour-lock in the engine and proves by tests that it agrees well with the temperature at which a fuel attains a vapour pressure of 0.96 to 1 atm. Consequently Koch recommends adjustment of the fuel vapour pressure to 1 atm. below 50°C for winter use, and not below 60°C for summer use.

The method suggested by Koch has the drawback that the fuel is again evaluated according to its boiling behaviour at one point. Experience shows however that the operating conditions of the engine have a considerable influence on the vapour-lock of the fuel. F. Schaub and H. Velde (4) therefore started by carrying out engine tests. They proved that the break-off temperatures are primarily affected by the fuel consumption and the engine speed.

Laboratory tests were therefore based on an apparatus designed to test the fuel under conditions similar to those prevailing in the engine. Fig. 2 shows Schaub and Velde's apparatus for measuring break-off temperature. The fuel is pumped from tank a through heating coil b and thence into the carburettor d, in which the fuel level can be observed through a window e. From there the fuel flows through the throttle f and the flowmeter g to the overflow. The temperature at which the fuel level falls as a result of insufficient feed is taken as break-off temperature.

These tests showed that with increasing fuel flow the break-off temperature falls off in varying degreesfor the various fuels.

In extensive tests with this apparatus, Schaub and Velde found widely varied effects for different engine designs. It is therefore impossible to-day to set down directly a criterion for the vapour-locking tendency of a fuel.

2) Determination of the vapour pressure.

While the instruments used for scientific purposes reproduce engine conditions as closely as possible, it is sufficient for inspection purposes to determine the vapour pressure. This is usually determined both in Germany and the U.S.A. in the Reid (5) bomb. This consists of a small container with an air jacket, filled with an accurately measured quantity of fuel and leaving a space full of air. A manometer connected to this container shows the pressure of the fuel vapour resulting when the bomb is immersed in a water bath at 37.8°C. The expansion of the air in the container is calculated from the following equation:

$$b = \frac{(P_a - P_t\ (t - 100)}{460 + t} - (P_{100} - P_t)$$

in which: t is the initial temperature of the air chamber in °F, P_t the vapour pressure of water in lbs/sq.in. at t°F, P_{100} the same at

100°F, P_a the barometric pressure in lbs/sq.in. (1 lb/sq inch = 0.0703 Kg/cm²).

W. Dannefelser (6) introduces a new correction formula for the calculation of Reid vapour pressure, viz:

$$b = \frac{(B - P_{t_A})(t_M - t_A)}{273 + t_A} + (P_{tM} + P_{tA})$$

where:

B = the corrected barometric pressure in Kg/sq.cm.

t_A = the initial temperature of the air chamber in °C.

t_M = test temperature in °C.

P_{tA} = saturation pressure of water vapour in Kg/sq.cm.at t_A °C

P_{tM} = saturation pressure of water vapour in Kg/sq.cm. at t_M °C

In contrast to the American formula, Dannefelser's formula always gives a positive correction factor.

Bridgeman and Aldrich (7) give a much more accurate method of vapour pressure determination. The fuel is cooled by liquid air and the air present in and over the fuel is extracted. The vapour pressure of the air free fuel is then measured with a mercury manometer.

A glass tube, 1 m. long and 10 mm. closed at one end, is filled with dry mercury. The tube is then turned upside down under mercury keeping it sealed with a finger. This produces a complete vacuum in the tube and the absolute vapour pressure of the fuel introduced into the vacuum space by means of a pipette can be measured. The liquid vaporises and depresses the mercury head by the vapour pressure of the fuel in question. The only corrections to be applied are for the height of the liquid level, and at higher temperatures, the vapour pressure of the mercury.

L. Hurel (8) describes an apparatus for the measurement of the vapour pressure; it is made of pyrex glass and is based on the static test method. In contrast to the Reid bomb, which allows measurements only up to a volume ratio vapour:liquid = 4, it permits measurements for ratios up to 10,000. Modifications allow operation either under vacuum or at atmospheric pressure.

Renato Salmoni's (9) method should also be mentioned. He does not measure the vapour pressure, but the change in volume due to vaporisation at atmospheric pressure and calculates the vapour pressure from the equation:

$$p = (1 - V_1/V_2)$$

where V_1 is the air volume at atmospheric pressure and V_2 the volume after vaporising the fuel.

A recent work by Halla (10) shows that the vapour pressure can also be determined from the volatility of fuels. The vapour pressure and the vapour density g_o per litre of saturated gas are related as follows:

$$P_{atm} = g_o \cdot 0.08213\ (t + 273)/M$$

where t is the temperature and M the molecular weight. The general use of this equation is difficult because the molecular weight of fuels can vary within wide limits.

3) Conclusions based on present knowledge.

Criticisms of known methods of measuring vapour pressure and vapour-lock can be summed up as follows:

1) The results of the various methods do not agree.
2) The apparatus used is often very elaborate.
3) The working conditions for aviation fuels cannot be easily reproduced.
4) Even the determination of the absolute vapour pressure in relation to the temperature is not easy.

All the same endeavours should be continued to characterise the tendency of fuels to vapour-lock troubles by physical or analytical data. This will not be easy as these data cannot take into account the varied relationship between engine and fuel. As regards the fuel however vapour pressure is a decisive factor in the danger of vapour-lock. As said before, the Reid vapour pressure determination gives no absolute values, as the test is carried out in the presence of air. Each measurement requires therefore a correction, which may lead to errors.

The relationship between engine and fuel as regards vapour-lock can be determined experimentally only in a circumstantial way; it is therefore necessary for the time being to stick to one quantity, the absolute vapour pressure, and thus exclude sources of error as far as possible. Attempts have therefore been made to develop an extremely simple device for the determination of absolute pressure.

III. Description of a new apparatus for the determination of absolute vapour pressure.

The equipment consists (Fig. 3) of the vapour pressure vessel proper with thermostat and of a high-vacuum oil pump. Figs.4 and 5 show details of the vessel. It is made of brass and has four leads, a, b, c and d.- a leads to a vacuum manometer e - b carries a +60°C, -60°C. mercury thermometer, and c the glass funnel g containing the fuel. The lead l is from d to the vacuum pump. The vessel is placed in the thermostatic bath h, consisting of glass vessels i and k.

For the determination of the vapour pressure at different temperatures the fuel sample and the pressure chamber were cooled at -50°C in an alcohol-dry ice mixture. The pressure chamber is then evacuated as completely as possible and isolated by means of the clip l on the pump lead. A cooled 200 cc. fuel sample is poured into the separating funnel g and carefully run into the pressure chamber; the vapour pressure at the required test temperature is then read off on the manometer in mm.Hg.

There is a small error due to residual air in the vessel and that dissolved in the fuel, but this is negligible compared with errors in the reading of the manometer.

It is important to use sufficient fuel to ensure that all the fractions contributing to the vapour pressure are all present in the liquid phase.

IV. Test results on vapour pressure determination at different temperatures.

The accuracy attainable with this vapour pressure apparatus was investigated by tests with pure organic liquids (chloroform, ethyl alcohol, carbon tetrachloride and benzene). Table 1 and Fig. 6 show the vapour pressures obtained in relation to the temperature. All the vapour pressures are rather too high as the liquids in question contained air; still they agree well with those published in the literature.

Very low pressures are not accurately measured by the manometer, but these are of little importance.

The vapour pressures of five different fuels were likewise determined at -40°C to + 50°C. Fig. 7 shows that between -40° and 0° C the vapour pressures of the various gasolines differ but little, but that vapour pressure differences, sometimes considerable, appear between 0° and +50°C. As already mentioned, the accuracy of manometer readings is unsatisfactory at very low vapour pressures; from 100 mm.Hg onwards it is however good, as corroborated by the tests on organic liquids, Fig. 6. In comparison with the Reid bomb, the new apparatus has the advantage of operation at different temperatures allowing quick determination of vapour pressure curves.

V. Tests on vapour-lock in relation to flying altitude.

Present day aviation fuels have a boiling range of 40° to 180°C at a pressure of about 750 mm.Hg. As pressure falls with altitude, boiling begins earlier. This change of initial boiling point favours vapour-lock to a degree depending on the altitude.

The relation between vapour-lock and altitude can be checked by the apparatus shown in Fig. 8. The fuel under test is cooled to -50°C and poured through the funnel b into the 250 cu.cm. Erlenmeyer flask a up to the bottom edge of the rubber stopper. The fuel is then warmed in a bath c to the temperature at which its vapour-locking tendency is to be determined, and the temperature read off on the thermometer e. The fuel fractions vapourising are condensed in the cold trap f maintained at -60°C by means of the refrigerant (alcohol and dry ice) contained in flask g. The altitude i.e. the pressure drop at which vapour-locking commences, is then determined by connecting the tubing h to a vacuum pump and slowly throttling the air intake i, causing bubbles of vapour to rise up the lead d. The depression is read off on manometer k giving a comparative value for the tendency of the fuel to vapour-lock at the particular altitude considered.

Vapour-lock actually starts in flask a at a lower depression than that measured. It can however only be determined with a comparatively large error, as it depends on the corners and irregularities of the fuel contained. If the boiling delay is taken into account reproducible values are obtained.

Figs. 9 and 10 show the results of vapour-lock determination for fuels B 4 and C 3 with and without a pentane addition. They show that at lower temperatures both fuels present no danger of vapour-locking even at great altitudes. If however the fuel is heated to between 20 and 40°C a considerable amount of vapour-locking can appear. A 10% addition of pentane has a negative effect particularly at high temperatures, as also shown in Figs. 9 and 10.

VI. Summary.

The critical investigation of methods for the experimental determination of vapour-lock and vapour pressure shows that the results of the various methods do not yet agree satisfactorily. Further, for a thorough investigation of fuel vapour-lock under actual working conditions extensive apparatus is necessary.

For inspection purposes, knowledge of the vapour pressure must suffice. Apparatus was therefore developed to determine the vapour pressure at various temperatures more quickly and accurately than in the Reid bomb. This apparatus consists of a pressure chamber with thermostat. It is evacuated as completely as possible, the fuel admitted, and the vapour pressure obtained by direct reading on a manometer.

Another apparatus was produced to test vapour-lock in relation to the flying altitude; at various fuel temperatures it indicates the degree of vacuum at which vapour-lock appears. The pressure drop is produced by a vacuum oil pump and is read off on a mercury manometer.

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Table 1.

Vapour pressure of organic liquids at various temperatures.

		Effective vapour pressure mm.Hg.	Vapour pressure reading mm.Hg.
Chloroform at	- 40°C	-	10
" "	- 20 "	20	27
" "	+ 0 "	61	70
" "	+ 20 "	160	174
" "	+ 40 "	369	370
Ethyl Alcohol at	- 40°C	0.39	10
" " "	- 20 "	2.5	15
" " "	+ 0 "	12	28
" " "	+ 20 "	44	55
" " "	+ 40 "	133	135
Carbon tetrachloride at	- 40°C	-	-
" "	- 20 "	10	15
" "	+ 0 "	33	40
" "	+ 20 "	91	100
" "	+ 40 "	215	222
Benzene at	- 40°C	-	-
" "	- 20 "	6	15
" "	+ 0 "	27	35
" "	+ 20 "	75	85
" "	+ 40 "	181	185

Fig. 1	- Volatility in relation to the relative break off temperature.
Fig. 2	- Schaub and Velde Apparatus for the determination of vapour-lock.
Fig. 3	- Apparatus for vapour pressure determination for fuels.
Fig. 4 & 5	- Pressure bomb for vapour pressure determination - Section and plan view.
Fig. 6	- Vapour pressure of organic liquids in relation to temperature.
Fig. 7	- Vapour pressure of fuels at various temperatures.
Fig. 8	- Equipment for the determination of vapour-locks in fuels.
Fig. 9 & 10	- Vapour-lock in fuels at various pressures and temperatures.

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NID 24-PG 25402

DVL Report on the conference on knock characteristics and storage of fuels (pp65-75)
16, 17 June 1941

Experiments on liquid-cooled cylinders.

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It has emerged very clearly, from the papers of Messrs. Dr. Seeber and Witschakowski, that much remains to be done before knock tests will be reproducible or uniform results will be obtained from different test stands. However, after painstaking work, at times with the help of Dr. Seeber, we reached a relatively good agreement with the DVL. Values obtained at other stations which are concerned with the distribution of high power fuels differ appreciably from ours and those of the DVL.

For the cause one may first note the considerable influence of apparently irrelevant deviations in the test stand construction. This has been brought very much to our notice since we have discarded our old test stands and installed engines in sound proof rooms.

We are under the impression that the existing directions are still insufficient and that the overall construction must be much more closely defined. It is not possible, however, to make all the necessary modifications because the redesign is very costly.

A further reason for the deviations of engines and for the day to day variations in the results may lie in the thermal loading of the cylinder, which is bound to be high. It is already apparent that with small engines the thermal state of the cylinder is of great importance for the knock characteristics. The thermal load on larger cylinder is much greater and small irregularities, as for instance in the sealing of the exhaust valve, may have a very marked effect on the knocking.

The technical testing station Oppau therefore started working with liquid cooled engines, this method of cooling being less sensitive to overloading. It was also desired to find out how the fuels in question behaved in the engines in which they were used. The DB 601 was therefore taken into consideration first, its single-cylinder version being designated DB 6001. The I.G. experimental engine fitted with this cylinder is shown in fig. 12. The camshaft used was that of the series E which has about 40° valve overlap. Another liquid cooled engine was the single-cylinder Jumo 211 constructed out of main engine components, fig. 13. The construction of the cylinder head may be seen from fig. 14. The operation of a liquid cooled engine is much easier than that of an air cooled cylinder. Not only is the cooling fan eliminated but also the extrator if this is not used for the exhaust gases. Further the necessary regulation of temperature of the cooling air for accurate tests becomes superfluous.

All three constructional types i.e. BMW 132, DB 6001 and Jumo 211 were now examined with different fuels under conditions as nearly equal as possible.

The conditions of the experiments were:

Compression ratio	1:8
Boost air temperature	130°C
Engine speed	n= 2000/min
Oil outlet	70°C
Coolant outlet	80°C
Exhaust gas extractor depression, with 1500 mm Hg boost pressure.	3-400 mm WS

The fuels used were B 4, CV 2b - RLM and ET 100.

The so-called engine characteristics at 760 mm Hg boost pressure and temperature of boost air 80°C were taken so as to investigate the behaviour of the three engine-types at the same boost. (Fig.15.). The lower performance of the BMW is obviously due to a smaller volumetric efficiency. Fig. 16, shows the reproducibility of the knock limit curves of the three fuels in the DB 6001. The corresponding curves in the BMW 132 N (fig. 17) in which the error limit ± 2% has been exceeded are inserted for comparison. It may thus be seen that by using liquid cooling smaller variations may be expected.

The knock limit curves were now arranged according to different fuels. (Fig. 18 and 19). From these one sees that the different engine types evaluated the fuels rather differently. The positive or negative differences in performance of the DB and Jumo in comparison with the BMW cylinder have been represented in fig. 20 in order to show this effect more clearly. The DB permits much higher powers than the BMW 132, and evaluates especially favorable the aromatic fuels. On the other hand, the Jumo surprisingly could only be supercharged a little; the inverted order of the fuels shows that the cause of this must be sought in higher cylinder temperatures. (Footnote: It must be mentioned that the initial observations giving a lower rating for the Jumo-cylinder must not on any account be construed as a judgment of the value of this type, because the water cooling in the single cylinder constructed by the Technical Test Station differed considerably from that in the main engine. The experiments were later repeated with improved head cooling. The result was a considerable upwards displacement of the knock limit curves for B 4 and CV 2b fuels; they then differed but little from the curves of the DB 6001. One can see from this how much insufficient cooling may falsify the knock characteristics of a watercooled cylinder. see fig. 20).
This example shows that much may be done on the engine side to suppress the knock tendency; obviously it is a better plan first to exhaust the improvements attainable by varying the engine rather than to make higher demands on the fuel. The example chosen here further shows how much information may be gained from experiments with different fuels; they may uncover faults which even long-term temperature measurements may not detect.

Fig. 20 showed that efficient cooling of the cylinder has a very favorable effect, especially in combination with aromatic fuels. A few preliminary experiments with increased valve overlap (fig. 21) showed that considerable variation in fuel rating may result in this way. From fig. 22 it is apparent that the knock limit curves for the DB 6001 may in general be raised by increasing the valve overlap especially with aromatic fuels. The cause of this is to be attributed to improved cooling of the cylinder by increased scavenging. The lowering of the knock limit curves in the rich region which has been observed elsewhere as a result of high valve overlap was not observed to the same extent. This surprising phenomenon requires study by further investigations. It should be left to the designers of engines to find out whether it is justifiable to build engines of such valve timings.

This is another indirect example of how knock characteristics may be influenced by constructional factors. It could be shown that in a main engine the tendency to dilution of the lubricating oil was considerably reduced by replacing the usual injection nozzle by one of different design. Greater freedom of choice for the upper end of the boiling curve was achieved in this way;

and allowed of an improvement in the anti-knock value of the fuel by the addition of special anti-knock components. Since the improvement in injection attained by changing the injection nozzle will have a favorable influence on the overall behaviour of the engine, we have thus shown again that investigations of this kind can lead to improvement in the engine as well as the fuel.

In a later paper we shall show that routine examination of fuels as to their knock behaviour under supercharged conditions may also be carried out in the I.G. test engine. The operational conditions for this engine have been adjusted to give agreement with the results for the usual BMW 132 N. It will always be necessary however to watch the constents of this equation and to alter them from time to time when progress in the engine constructional field so demands. In especially important cases it will also be necessary to carry out comparison tests on the fuel in the large cylinder. The above investigations have shown that constructional features may have a very large influence on the knock behaviour. In order to be able to define the course of development of fuels it is absolutely essential that these questions should be thoroughly investigated in a single cylinder test engine.

Nowadays our test-stands are erected in sound proof rooms and controlled from a switchboard. This has been recognised as essential, since with continuous operation the noise of the engine has bad effect on human health. This does however raise the question of how to observe the detonation. The simplest way is this. A wire, 3 mm thick is attached to the cylinder and led outside through the wall and ends in a small sheet iron plate. For a single cylinder this makes the knocking sufficiently audible.

Since knock tests on main engines are not yet available, we investigated other methods of observing knocking by elimination of the normal engine noise. The condition was that no indicator drilling should be made in the cylinder. The problem was solved quite satisfactorily by means of a magnetic pick-up which reacts to the vibrations of the whole engine. Our experiments have led to an arrangement similar to that used by Prof. A.W. Schmidt. (Footnote: Compare A.W. Schmidt, Investigations on the knock characteristics of fuels on the test stand and under operational conditions, Oel und Kohle 34, (1940) No. 37, p 350.)
A peculiarity of our arrangement perhaps consists in the pick-up being connected with the engine only by one longish thin steel wire.

It has not proved practical simply to view the picture on a cathode ray tube; where the knock impulses are visible as shown in fig. 23. It is much more practical to listen in to the knock noise on a loud speaker or head phones. Without being bound by the observations of an instrument, the investigator is in this way always aware of the operational condition of the engine. The knocking vibration which is recorded by this instrument is clear and distinct from any other lesser noises. It enables one to make a better determination of knock on the single cylinder test stand than is possible by means of the wire telephone mentioned above. It may be expected that this instrument would also be useful for listening to detonation in the main engine.

DVL Report on the Knock Characteristics
and Storage of fuels 16,17 June 1941
(pp 83 - 84)

Knock behaviour in engines having large valve overlap and with the DVL - injection method with divided injection.

By

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As compared to the engine without large valve overlap on which the DVL supercharge test method for fuels is based, more recent developments in engines have brought about changes which influence the shape of the knock limit to a considerable extent. The adoption of engines with large valve overlap results in an increased performance and a relatively smaller thermal load on the engine, on account of the filling of the dead space and cooling of the combustion chamber. By altered valve timing an appreciable different shape of the knock limit curve is produced due to the change in the influence of the residual gas and the temperature distribution in the combustion chamber, which are probably different from that in an engine without or with only little valve overlap. In general the knock limit curve in an engine with large valve overlap is flatter than without valve overlap. Especially with lower boost air temperatures and with fuels which have naturally a flat characteristic, the flattening of the knock limit curve may go so far that it shows throughout a declining tendency with increasing richness of the mixture. Fuels with a very steep characteristic i.e. especially aromatic fuels, also show a considerably flatter course but in this case it remains of similar form with a minimum at a slight air excess (λ about 1.1). Especially in connection with the rise of fuels which are rich in aromatic compounds, engines with large overlap show a somewhat more favorable knock characteristic. Difficulties with respect to knocking may only occur under conditions in which the engine is throttled down; when the pressure after the engine exceeds the pressure before the engine and higher boost air temperatures are caused by the additional heating due to residual exhaust gases. These conditions of operation however are not very likely to occur in actual engine operation.

Another method of operation developed in the DVL, the method of divided injection aims at a reduction in the knocking tendency of gasoline engines.

Investigations on spontaneous ignition and knock phenomena were carried out at the DVL Institute for engine operating methods and thermodynamics and the following results were deduced. A certain initial time is necessary for spontaneous ignition, its magnitude depending on an exponential function of the temperature and a power of the pressure of the unburnt gaseous mixture in the combustion chamber. Furthermore in the gasoline engine the knock process depends on the composition of the mixture. With normal formation of the mixture by injection of the fuel during the inlet stroke, the distribution time and the induction period before onset of spontaneous ignition are very quickly reached with increasing boost and detonation then occurs. The formation of the mixture was altered in order to attain knock-free running at higher boosts. Injection in the inlet stroke was restricted to a small amount of fuel so that as a consequence of the large air excess there was little tendency to knock. The second part of the fuel necessary for the attainment of the desired final composition of the mixture was partly injected during the compression stroke and partly during combustion. This reduced the time up to the combustion of the mixture in the cylinder to below the induction period necessary for the occurrence of knocking.

Extensive experiments with different types of engines were carried out. The experiments showed that especially during operation of the engine with excess of air the knock limit is raised by 2-4 kg/cm^2 mean effective pressure, according to type of engine and fuel. The knock limit curve in this method is also considerably flatter than with normal mixture formation.

DVL Report on the Conference on Knock Characteristics and Storage of Fuels. 16,17 June 1941 (pp 85-96).

The supercharge test in the NSU engine of the Ruhrbenzin A.G. Oberhausen-Holten.

By

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Oberhausen-Holten.

The erection of a small-engine supercharge test stand was started at Ruhrbenzin 2½ years ago. This was meant to provide a means of determining the knock limit of fuels with a small laboratory sample. The evaluation should agree with that of the DVL test on the BMW engine, as far as possible, the latter being the standard test in Germany to-day. The supercharge test-stand of the Ruhrbenzin has now been in use for about a year. More than 600 curves have been plotted. A second test stand of the same kind has just been finished.

The construction of these test-stands is essentially the same as that of the DVL the methods of testing also being similar. Our development work on these test-stands, it is true, is not yet completed. All the same, I willingly accede to the request of the DVL to report here on the results obtained so far.

The test engine we chose was the NSU 501 OSL. This is a four-stroke air cooled motorcycle engine with a capacity of 500 cc. The bore is 80 mm, the stroke 99 mm.

The air is led into a compressor through a filter and a gas meter and is then compressed. It then passes through an oil-trap and electric heaters into the engine. A regulating valve connects the pressure and suction sides of the pump. The boost pressure and the amount of air introduced into the engine are controlled by this valve.

The fuel is injected into the inlet pipe. In this respect there is a difference from the BMW 132 in which injection is directly into the cylinder. The method of injection had to be developed first because the engine normally operates with a carburetter. The injection pump and nozzle were delivered by the firm of Bosch. From the satisfactory fuel consumption and air consumption values one can infer that the mixture formation, fuel distribution and efficiency were good.

In the lean region the consumption has between 180 and 190 gm/HP - hr., and with air excess ratios from 1,3 to 1,5 supercharging is still possible.

Experiments with direct injection into the combustion chamber were also carried out with various arrangements of the injection nozzle and various nozzle shapes. Under the most favorable conditions of direct injection into the inlet pipe the knock limit curve was as shown in fig. 1. The knock limit curves for injection into the induction pipe and for direct injection were plotted for five different fuels. The larger spread of results indicated in the fuels H and G correspond to the larger variations which had been found with these substances. With somewhat unfavourable valve and injection timingsthe fuel consumptions, contrary to expectation, were not appreciably lower than when the fuel was injected into the intake pipe. Thus injection into the cylinder did not show any essential advantages. In consideration of the trouble of drilling for the injection nozzle into the finned cylinder head we nowadays prefer injection into the suction tube..

Cooling of the engine is effected by means of a centrifugal blower. The power of the engine is measured by a hydraulic dynamometer in the usual way. In the supercharge test the same method is applied as in the DVL method.

I assume that this method is known, and I shall not go into it further.

Fig. 1. Comparison of the knock limit curves with injection into the intake pipe and injection into the cylinder (BS-Standard-fuels).

During the development of the method, a number of modifications to the engine appeared necessary for supercharged operation. That such alterations might become necessary could be counted on from the start considering that mean effective pressures twice or three times those for which the engine had been intended and developed are used in the test procedures for modern fuels. Apart from efforts to attain sufficiently reliable operation, we worked also on determining the range of variation and on means of reducing it. We also tried to fit the results to those of the BMW 132 cylinder.

The values in fig. 1 already give an idea of the magnitude of these variations, each curve having been plotted from two series of measurements. Deviations in aromatic fuels or those containing alcohols seem to be larger then in paraffinic fuels. As an indication of the limits of deviation I have included fig. 2 where more measurements were available for plotting. Here the range of variation is somewhat wider. It is to be remembered in the consideration of these figures that our experience of the NSU supercharged engine only extends over a short period of time. If to-day the variations in the NSU engine are still somewhat greater than in the BMW -132 cylinder, I still believe that this need not necessarily be the case, fundamentally.

In general the supercharge test will meet with similar difficulties in relation to deviations as those sufficiently well known in knock testing engines. These are probably due to the fact that in the air fuel mixture the pressure and temperature at the end of compression may undergo slight variations without these variations being observable from the outside.

One obvious condition for a narrow range of deviation is that the engine operating conditions should remain sufficiently constant, and also that the mechanical condition of the engine is good. According to our experience the quality of the valve seating must be particularly watched.

Fig. 2. Examples of curves plotted repeatedly under the same conditions for an indication of the range of deviation.

The task of making the ratings of different fuels in the NSU engine coincide with those in another engine, the BMW 132 in our case, meets with special difficulties. From aero-engines we know that the permissible boost and mean effective pressure for different types of fuels are not in the same ratio on different engines; in any engine they also depend on the operating conditions. The assessment in one engine, such as the BMW 132 test engine may thus seem arbitrary at first. The selection of such an engine and of the conditions under which the test is carried out is governed by the requirement of obtaining a fuel as rating which will give a safe and reliable representation of the behaviour of the fuel in the practical flying operation of the main engine. One must be prepared for other test conditions to appear more suitable at some future date in accordance with the developments of fuels and engines. Then different forms of supercharge test must be developed on small-engine.

One requirement in the attempts to fit the NSU engine ratings to those of the BMW-132 cylinder, under the conditions valid at present and also for possible future alterations in those conditions, was that of finding out the influence on the curves of alteration in the operating conditions. Numerous experiments were carried out at the Ruhrbenzin for this purpose. We used a B 4 fuel for a number of preliminary experiments and for the main test programme, five fuels provided by the Institute of fuel research of the DVL and having the following composition:

G) 75% ET 100 + 25% aviation gasoline
H) 75% motor benzol + 25% aviation gasoline

I) 47% Ethanol + 53% aviation gasoline
K) Aviation gasoline + 1.2 cm^3/ litre TEL
L) ET 100, pure

From figs. 3 and 4 may be seen how differently these fuels are affected by intake air temperature, ignition timing and compression ratio.

Fig. 3. Effect on boost pressure of intake air temperature for λ 0.8 and 1.1 (5 BS-Standard fuels).

Here the mean effective pressures for air excess ratios 0.8 and 1.1 of the 5 named fuels have been plotted as in terms of ignition timing compression ratio and intake air temperature. The lines represent mean values of a number of curves. Similar curves for the BMW have been published by the DVL institute of fuel research. It is evident taht the fuels H and I which contain aromatic substances and alcohol are relatively sensitive to a variation of those operational magnitudes; fuels G, K and L which have a more paraffinic nature, seem to be less sensitive.

Fig. 4. Effect on boost pressures of ignition timing and compression ratio for λ = 0.8 and 1.1 (5 BS-Standard fuels).

Apart from the factors mentioned above, cylinder head and exhaust valve cooling and the position of the injection also affect the knock limits of the various fuels differently, although for most fuels their influence is small. Here too the fuels containing arometics and alcohols were more sensitive.

The influence of engine speed and valve overlap were also observed with several types of fuels. Not sufficient data are available, however for establishing their effects precisely.

The injection timing had little effect on the position of the knock limit curve. We injected at the beginning of the inlet stroke, in the neighbourhood of top dead centre. Injection at a much later time increased consumption. Furthermore unfavorable injection timing may result in a loss of fuel through the exhaust valve because of the valve overlap; the supercharge curves would then be mainly displaced horizontally. The boost pressures may be considerably modified by adjustments of the valve overlap, while the mean effective pressures are relatively much less affected. For this reason the mean effective pressure is considered by us to be a much better basis of comparison for the assessment of fuels than the boost pressure.

Work on the influence of operating conditions is still in progress; nothing final can therefore be said as to the degree of approximation of the results to those of another engine. As an example of agreement already established between NSU and BMW engine the supercharge curves of the five named fuels for the NSU engine are compared with those of the BMW in fig. 5. One can see that though the values do not coincide, a similar evaluation is obtained . As a further example I show the supercharge curves of three aviation fuels taken on the BMW engine by the DVL and by ourselves. The conditions under which these values were obtained are compared in the table. The supercharge curves for the NSU engine are more closely together and somewhat flatter in general than those of the BMW engine.

Fig. 5 Comparison of knock limit Curves for 5 BS-Standard fuels in the BMW and the NSU.

The lower maxima of the mean effective pressures in the NSU engine were at first consciously aimed at in order to spare the engine which had been intended for a quite different purpose. With the small alterations of the engine carried out by us, we could run the engine continuously with supercharge for a period of 200 hours without any appreciable engine trouble. Naturally grinding-in of values was required more frequently, namely every 20-30 hrs.

It therefore seems quite possible to run the engine at higher mean pressures,

Fig. 6. Comparison of supercharge curves for 3 aviation fuels.

with the same safety if further constructive measures are taken. Such measures, which must be carried out by the manufacturers, are to be considered, particularly if they might have to be done for a greater number of engines.

Summarizing one can say that the NSU supercharge test stand has fulfilled our requirements in the field of application for which it was intended. The development of synthetic aviation fuels has been considerably advanced by the opportunity offered by the NSU engine to determine the degree to which laboratory specimens could be used for supercharging, when the production of these substances in quantities of 20 to 30 litres as required by the aero-engine single-cylinder would have been practically impossible. Besides the small amount of test sample, 2-3 litres, further advantages over the aero-engine single-cylinder are the low construction cost in our case 10-12000 RM for each test stand, and the simpler manipulation involved in assembling and testing.

Table

Comparison of operational factors in the supercharge test of the BMW 132-(DVL) and the NSU 501 OSL-engine (Ruhrbenzin).

		DVL	RB
Engine		BMW 132	NSU 501 OSL
No. of cylinder		1	1
Bore	mm	155	80
Stroke	mm	160	99
Capacity	Litre	3076	0.494
Compression ratio		1:6	1:7
Cooling		air	air
Mixture formation		injection into cyl.	injection into inlet pipe
Injection Timing		25° A.T.C.	10° crank angle A.T.C. (inlet stroke)
Ignition Timing		variable	constant 22° B.T.C.
R.P.M.		1600	1600
Inlet air temp °C		80	80
Evaluation factors		p_{me} Boost pres. at onset of knock (10 knocks/min)	p_{me} Boost pres. at onset of knock (10 knocks/min)
Reference factor		air excess ratio	air excess ratio
Knock measurement		Aural	Aural

ZWL Report on the Conference on Knock Characteristics and Storage Fuels 16,17 June 1941 (pp 111-112)

Discussion on the lectures of 16.6.1941

General Views

Up to now mainly aromatic fuels have been employed in the production of high power fuels because new installations for the manufacture of Iso-paraffins cannot possibly be built in such a short time. It is true to say that 20% only of the total demand for Iso-paraffins can be produced. The remaining 80% must however be of equally high anti-knock value as Iso-octane if possible. A fundamental drawback of aromatics is their sensitivity to temperature changes which can be explained theoretically. This sensitivity might however be modified by modifying the boiling point curve and the composition of the aromatics. Valve overlap and divided injection offer means which can be used to overcome the disadventages. For this reason it would be necessary to adjust the engine to the practical conditions imposed by the fuel (Pier).

Dup. of P.G. 25492

DEUTSCHE LUFTFAHRTFORSCHUNG

Report on the conference on knock characteristics and storing of fuels. 16th and 17th June 1941. (from page 118)

Practical storage behaviour and its chemical features.

By
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1. Fundamental demands on aviation fuels

The practical importance of the various properties of the fuels is given by the demands made by aviation. Two of these requirements are of very considerable importance in relation to the storage stability, the homogeneous and uniform character of the fuels and the possibility of storage under the most varied practical conditions. The first demand is that the fuels have good storing properties even in mixtures from various production sources and independent of the manner of production. The second demand covers all the conditions of operation under which fuels may be used. Testing of the fuels must thus be carried out under the most unfavorable conditions in order to obtain a real guarantee against failures.

II. Conditions for carrying out an exact assessment of the storage stability.

Formerly difficulties caused by insufficient storage stability were encountered for unleaded gasolines only in the presence of larger amounts of olefines or particularly the unstable diolefines, (in particular resin formation); saturated hydrocarbons behaved well almost without exception. When leaded gasolines were used the behaviour was different. It appeared that mixtures containing engine benzol or fuels with a high proportion of aromatic substances had worse properties than pure gasolines. The chemistry of the phenomenon was not clear. It was, however probable that the composition of the fuel or the impurities in it cause an accelerated decomposition of the lead tetraethyl and a consequent formation of resin. A number of experiments were carried out at the DVL in order to elucidate the mechanism; these experiments will be reported on below. Here, as also in connection with the properties of combustion one meets the difficulty of applying the experimental results to practical conditions. One way say that for well-defined fuels one can make certain inferences as to the phenomena under practical conditions from the experimental understanding of certain connections in as far as the former are known. Some of these conditions may easily be determined, such as the volume of the liquid or the volume ratio of liquid to vapour in the vessel; others it is difficult to ascertain such as the gas exchange or the nature of the container walls. In addition it often happens that other fuels may be added during storage, under conditions such that the proportion of the added fuel either is not determined or cannot be ascertained. Furthermore one is not clear about the conditions of storage of the gasoline under investigation or even about its actual state. For it will be shown later that the gasoline may alter to such an extent, even in clean tight glassbottles and in the dark, that one cannot even guarantee reproducibility at one and the same test station; so much the less at different laboratories which receive their samples in different vessels and after different periods of time. These facts show that it is possible to make a definite prediction as to how some fuel will behave under one or the other set of conditions of storage only if these conditions are stated unambiguously since this will never be possible one will have to be content with a statement that one fuel will fail under unfavorable conditions where a second fuel will be more satisfactory. It will be left to further laboratory and storage experiments to show whether it is possible to lay down definite limiting values permissible for the storage stability.

It is for this reason that the correlation between bomb ageing and practical storage is so bad; quite apart from the different temperature regions of the processes the overall conditions in practice are milder than the laboratory conditions in one case and more stringent in the other. The difficulty of relating the results of laboratory ageing experiments to practical conditions is not restricted to the bomb test but extends to all laboratory methods. In order to safeguard at the manufacturing stage against undesirable changes in the fuel one has to take into account the worst circumstances. This may be done by suitable refining and by adding inhibitors.

Inhibitors

Inhibitors have already proved themselves in the protection of olefinic fuels against oxydation; they are of no importance in connection with saturated gasolines. The use of inhibitors has again come very much to the fore in connection with leaded fuels, especially those with a greater proportion of aromatic compounds. According to the experiments carried out at the DVL it is evidently possible to increase the stability of gasolines to a large extent by making suitable additions. When one turns one's mind to the use of leaded reference fuels in engine experiments one is impressed by the necessity of adding inhibitors to fuels which are sensitive to storing.

Formation of low volatile substances on storage of aviation fuels.

By

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The storage stability of fuels shall be discussed here; without getting lost in general considerations we mainly want to give a picture of the present state of laboratory tests of the storage stability of leaded fuels. It is expedient to start by briefly touching on the fundamental causes of the lack of stability which leads to the formation of low volatile substances.

One may in general distinguish between two cases which lead to the formation of resinous substances.

1) Changes in the fuels which are directly due to groups already present in the fuels (for normal fuels mainly unsaturated compounds)
2) Changes in the fuel due to the formation of new groups which may either lead to polymerisation or condensation; they may also depress the vapour pressure of some fuel components to such an extent that these are included in the resin estimation.

The T.E.L. in the fuel is itself not changed in the absence of light, oxygen and foreign substances. A leaded fuel enclosed in glass tube under pure nitrogen only shows a minute formation of a triethyl lead compound after heating at 180°C for 5 hours Leaded fuels behave diffarntly when air and light are present.

The influence of light shall not be discussed here since it is of no practical importance. It can be shown by the DVL method that T.E.L. especially in some particular fuels, - is destroyed by oxygen in stages leading over triethyl - diethyl and leadll compounds. Basic lead compounds are the primary products of the reaction; most of these are then converted to the corresponding salts by the carbon dioxide of the air and the acids present in the fuel or being formed in it. This decomposition of the T.E.L. is generally accompanied by a considerable acceleration of the oxidation of the fuel. We are here dealing with a mutual oxidation acceleration. Some fuels are considerably more sensitive to oxygen in the presence of T.E.L. and the formation of resins is thus generally increased. Apart from this there is an undesirable effect of the lead decomposition products as such since they are insoluble in the fuel and have a low volatility.

In addition there is the effect of the walls of the fuel container and the effect of soluble metal salts.

What we are interested in is how one can in advance determine the behaviour of fuels under practical conditions from knowledge gained in the laboratory. One generally employs the bomb method. This method has given valuable indications as to the storing characteristics of unleaded fuels; it was applied unchanged to leaded fuels. Theoretically it is impossible to obtain really satisfactory results for a process which is so complex and in which oxidation, polymerisation and condensation occur, in part at a higher energy level. To quote just one example, at 100°C i.e. the temperature at which ageing proceeds in the bomb, the oxidation velocity may be strongly enhanced at the expense of the velocities of condensation and polymerisation. This means that any groups present or being formed which tend to condense or polymerise are oxidised by the oxygen in such a way that they lose their powers of condensation and polymerisation either partly or completely. As a consequence of this some fuels may be rated relatively high without giving good results in practice. This state of affairs becomes even more obscured by presence of T.E.L.

If one wanted to form a really concise judgment one would have to understand the several phases of the formation of the low volatile substances; this is a task the solution of which is not to be expected in the near future. Another question of importance is the following up of the partial process viz. oxidation by means of substances, which in contradistinction to molecular oxygen are not affected by inhibitors. It is thus proposed to carry out experiments in which fuels are o xidised by substances acting similar to oxygen and such that it would be permitted to work in a homogeneous phase and under arbitrary conditions. The DVL may come back to these results at a suitable time.

The importance of the question of inhibitors is demonstrated by the fact that many of the aviation fuels coming up for examinatio n contain a considerable amount of substances (several tenths of one per cent) which show a certain amount of inhibiting effect. These fuels have a favourable behaviour when tested in the bomb. The properties of the fuel become considerably worse after the inhibitors have been removed (as shown by the ageing in the bomb); this is represented in the Table I.

Table 1

Removal of the inhibitors

No. of exper.	Cont. of vol % TEL	Decomp. TEL in soln. %	Temp. during ageing °C	Resin cont. mg/100 convnl. working up	Cont. by vol % of decomp. TEL			Time of inductn. in mins.
					Total	Dis-solved	Sep-erat-ed out	
1	0.1185	0.0006	100.8	9.4	0.0090	0.0070	0.0020	> 240
2	0.1210	0.0009	100.5	23.1	0.0355	0.0305	0.0050	> 240

The "natural" inhibitors were removed from fuel 2 before the leading. Both fuels were aged directly after leading. If other fuels accidentally do not contain these inhibitors or not enough of them, they will be rejected by the test-station as unsuitable, in accordance with the present-day test methods. The DVL proposed the deliberate addition of small quantities of particularly effective inhibitors already in December 1940; the method is still being tested under practical conditions. This will be discussed later in connection with the subject of inhibitors.

After this short sketch of the general situation we now come to the actual method of performing the bomb test. With the aid of some examples we shall also explain the possible sources of error in the method which give rise to the different results obtained at the various test-stations. According to a suggestion of the R.L.M. ring experiments were commissioned by the DVL in the spring of this year to be carried out at seven stations ; this was supposed to show to what extent one could expect to reach concordant results when testing a fuel leaded at one station. An extended test-method was proposed for the purpose: this made it possible to estimate the resin total, i.e. including that part contained in the lead slime separately from the lead decomposition which occurs; this is advisable because it is very questionable whether the quantity and distribution of the decomposed T.E.L. and of the resinous substances in the lead slime and the fuel agrees in the two cases: bomb test and actual practice. It was possible that the resin determination which is subject to so many variable and hard to control influences might not lead to reproducible values: in that case the lead numbers obtained would also be a measure of the reproducibility of the bomb ageing method.

The principle may be summarized shortly as follows: The fuel from the bomb, containing the lead which has separated out, is divided into two halves. One half is filtered and the lead determination is carried out. This gives the amount of lead compounds remaining in solution. The second half is qauntatively freed from decomposition products of lead tetraethyl in solution by a 0.5% solution of nitric acid; a lead determination is then carried out on this part of the fuel. This gives the quantity of unchanged lead tetraethyl. The difference in the two lead values gives the quantity of decomposed lead tetraethyl in solution; it is mainly in the form of a triethyl-lead compound. Resin estimations were carried out both for the filtered fuel, according to the usual routine, and also for the fuel treated following the suggestion of the DVL, this latter sample containing all the resins and potential resins and no decompound T.E.L.

The result of the ring experiment was not favourable as far as the reproducibility was concerned. The large, differences among the experimental lead numbers established that it could not be a question or not solely a question of an error in the resin estimation. Therefore experiments were also carried out on the factors which might be effective during bomb ageing.

Fig. 1 Effect of the temperature on the bomb treatment of two leaded fuels.

The effect of the temperature is seen in fig. 1. for two synthetic fuels of the same origin but of different deliveries. The temperature differences which may occur in consideration of the difference in altitude and weather amount to from 3 to 4°C They should hardly exceed 1-3°C on the average; the influence of temperature need consequently be considered only in relation to the atmospheric pressure which has to be stated in each case, this has been proposed once before by the DVL.

The suspected influence of the nature and type of the glass insets was only noticeable somewhat for one labile fuel; this may be seen from the table 2 (experiments 5-8).

Table 2

Addition of Various glasses.

No. of exper.	Addition of various glasses	DVL method	Resin content mg/100 convent. method.	Vol.% of decomp. T.E.L. Total	in sol.	sep. out	Time of induction.
1	–	7.8	18.2	0.0215	0.0150	0.0065	> 240
2	Jenaer glas.	9.1	19.2	0.0205	0.0140	0.0065	"
3	Gundelach glas.	8.4	21.8	0.0230	0.0165	0.0065	"
4	Maschinen-glas.	7.9	19.8	0.0230	0.0160	0.0070	"
5	–	10.8+ 3.8	+ 15.9	0.0490	–	–	~ 185
6	Maschinenglas	33.2+ 3.5	– + 16.1	0.0525	–	–	~ "
7	Jenaer-Glas	14.8+ 3.6	– + 16.8	0.0535	–	–	~ 170

Fuel 53/40 with a content of 0.1155% vol. T.E.L. was used for experiments 1,2, and 3 and aged directly after leading.
Fuel 76/40 with a content of 0.1200% vol. T.E.L. was used for the experiments 5,6 and 7 and aged three days after leading.
+) The values refer to 50 cc of fuel.
The glass was added in the form of glass tubes in experiments 1 to 4; in experiments 6-8 rough glass shot was used which had previously been cleaned with a strongly alkaline solution and was then treated with a mixture of chromic and sulphuric acids.
The effect of the pressure of the oxygen in the bomb seems to be small. This may be seen from table 3.

Table 3
Relation between ageing and oxygen pressure.

No of exper.	Oxygen atm. excess	Temp. during ageing	Resin content mg/50	mg/100	Conventional method mg/50	Content in vol.% dec. T.E.L. Total	dissolved	sep. off	Time of Ind.
1	5	100.8	7.2	33.0	19.0	0.0580	0.0405	0.0175	195
2	8	100.8	5.8	19.6	20.6	0.0575	0.0400	0.0175	190
3	5	101	10.8	146.0	28.3	0.0790	0.0555	0.0235	170
4	7	101	11.5	100.5	30.4	0.0760	0.0515	0.0245	160

For experiments 1 and 2, the fuel 76/40 contained 0.1195% vol. T.E.L.; of these 0.0010% vol. were attacked; the ageing was carried out one day after the leading.

For experiments 3 and 4, the fuel 76/40 contained 0 .1175% vol. T.E.L. of these 0.0097% vol. were attacked; the ageing was carried out 29 days after the leading.

It is apparent that the sample treated at a lower pressure of oxygen shows a higher resin content when the DVL method is applied. This would point to the theory that the oxidation at lower pressures produces substances which have a greater power of condensation and polymerisation.

The greatest source of error lies in the alteration of the fuel with time; this is shown in fig. 2. We are here dealing with a leaded fuel which was kept corked in a brown bottle without any access of light. Portions of this fuel were subjected to the bomb test at various times. After an initial falling off of the resin numbers, a pronounced increase of resin formation is observed after 5 days, (the variations which may be seen here are partly due to the fact that the evaporation times could not be kept constant throughout on account of experimental difficulties)+.

Fig. 2 : The effect of ageing a leaded fuel on its behaviour in the bomb.

Fig. 3 shows the quantity of decomposed T.E.L. as a function of the age of the leaded fuel. The marked dependence of the aged fuel on the manner in which it is boiled down is apparent in fig. 2. This effect is much stronger in the samples treated according to the DVL method than in those treated in the conventional way. The strong dependence on the manner of the boiling down and of the working up indicate that the polymerisation and condensation proper for the greatest part only occur during the blowing off on the water-bath, particularly as far as the DVL method is concerned. For the aged fuels treated according to the DVL all the groups capable of reacting are free if they have not already led to condensations or polymerisations. This means that the resin numbers may be larger than they are in the conventional method although the decomposed T.E.L. has been removed and one has to consider the potential resins (which are formed during the decomposition of the lead slime which has separated out.) The p_H displacement is also an important factor; it occurs during the DVL treatment. According to out present experience the 0.5% solution of HNO_3 which is employed in the treatment according to the DVL does not have any effect on the results obtained with the samples. Resin formation is at any rate much inhibited if one quickly removes the substances capable of undergoing reaction (50 cc fuel and quick boiling down). One recognises how important it is to fix the conditions under which the evaporation takes place. The DVL treatment is more significant in relation to actual practice in as much as fuels which have aged naturally do not retain in solution more than about 0.005% vol. at the maximum (absolute proportion) of the decomposed T.E.L. (apart from triethyl-and lead (II) compounds the decomposed T.E.L. mainly comes down as diethyl-lead carbonate; during bomb ageing however 10 times and more than that amount may remain in solution. The quantity of resin bound to the lead seems to be very low; this at any rate was

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+Footnote: The working up of the fuel generally occurred on the same day as the bomb ageing, the evaporation on the following day. The values naturally depend on the amount of breaking of the glass bottles. Only 85 cc of the aged fuel 2 (21 days old) were available for evaporation. In this case the evaporation was carried out three days after the working up.

the result shown by an analysis of the lead slime. Table 4 gives an example of the dependence of the resin numbers on the time of evaporation (water bath boiling strongly and waterbath simmering)

Table 4

Influence of time of evaporation

No. of Expt.	Waterbath	Resin Content (conventional treatment mg/50)	Time of evaporation Actual t/Min.	Total t/Min.
1	boiling vigorously	40.0	ca.12	20
2	simmering	78.5	ca.30	40

The fuel 53/40 was altered 6.5 hours at 100°C in the bomb five days after it had been leaded.

Table 5

Relation of resin content to separation of lead.

No. of Expt.	Entry No. of fuel.	Resin content DVL mg/100.	Content by vol.% of decpd. lead tetraethyl.		
			Total	in soln.	Sepd. off.
1	76/40	20. 9	0.0635	0.0405	0.0230
2	108/41	16.0	0.0178	0.0166	0.0012
3	137/41	2.3	0.0175	0.0 155	0.0020
4	151/ 41	2.7	0.0085	0.0075	0.0010

Table 5 gives a comparison of the decomposition of lead and the formation of resins. It is apparent, that no simple relation exists between the formation of resins and the decomposition of lead for the bomb treatment of leaded fuels.

Some sources of error have been shown up for the bomb test with the aid of some examples. It would be necessary to estimate the magnitude of the various factors by a larger series of experiment; this would have to be done under consideration of the factors whose importance has been ascertained while all other conditions are kept strictly constant, then one would be able to obtain significant values for the several factors. From the experiments quoted above the following may be directly and safely inferred, under certain circumstances, a difference of a few days in the age of two otherwise completely identical leaded fuels may, play a large part. The effect of age may be considerably reinforced by transport, quite apart from the effect of the container walls. Furthermore it is apparent that the manner of evaporation is important; also there is the somewhat smaller effect of the temperature during ageing. The ratio of resin formation and lead decomposition varies strongly so that it is particularly the estimation of the total of the decomposed lead tetraethyl which should be adduced for the rating.

The following is therefore proposed to improve the reproducibility of bomb ageing as carried out so far:-

1) If possible one should ascertain and state the age of the leaded fuel which has to be tested. If necessary the bomb treatment should be repeated within fourteen days. For practical rating one should only employ fuels which had been leaded at least one month before.

2) The atmospheric pressure should be quoted with the resin and load values.

3) To increase the reproducibility the evaporation should be carried out with 50 cc of fuel. The question is yet undecided as to whether the DVL values obtained with evaporated fuels approximates more nearly to actual conditions when the volume of fuel is 100 cc or when it is 50 cc. At the present moment, at any rate, the values obtained with 100 cc are more significant.

4) Thewater bath must boil with bubbles both before and after the evaporation; the depth of immersion of the glass vessel should be ascertained accurately.

5) The quantity of air (litres/hour) employed for the evaporation should be constant and should always be blown on in the same manner. Furthermore the air should always be sufficiently pure.

6) The glass insets should all be made of the same material (Tena glass) and should not be cleansed with alkaline substances.

7) The DVL method should also be employed; at least not all cases which are ambiguous and for the investigation and rating of newly introduced synthetic substances.

Bomb tests carried out according to these directions should show a satisfactory degree of reproducibility. It may be expected that the reproducibility of the method will then be greater than corresponds to its usefulness, particularly in the range which concerns aviation fuels. It is necessary to collect yet further relations between the bomb test and practical conditions; the fuel containers employed for storing always have to be accurately specified.

What is evident now remains to be investigated. The mechanism of ageing will have to be explained; one will have to find out those substances which have an unfavorable effect on storage. For the time being it is necessary to obviate the existing difficulties by using inhibitors or, if necessary testing their effectiveness under conditions of natural storage.

Storage characteristics of fuels.

— By Dr. H. Velde, Ruhrbenzin A.-G., Oberhausen-Holten.

In what follows I should like to report on experiences which we have gained in the storage of the primary products and the cracked components of the synthetic process. Although we are not here dealing with aviation fuels or components of aviation fuels, I do believe that some of these experiences will prove to be of interest.

There are two properties the changes in which have to be specially watched in the storage of fuels.

1. Octane number

2. Resin Content.

There are various factors which directly cause a diminution of the octane numbers; of these I shall diregard those which are purely physical i.e. those depending on the gassification or vaporizations of the easily volatile components; I shall only deal with the chemical factors.

If all the hydrocarbons contained in fuels, those containing olefinic double bonds are the ones mainly reponsible for chemical changes. This is due to the fact that these double bonds are particularly reactive and above all easily combine with oxygen. This refers to both aliphatic and cyclic olefines. Hydrocarbons with two double bonds have a particularly unfavourable effect, particularly those hydrocarbons which have conjugated double bonds e.g. cyclopentadiene. It is thus understandable that fuels which have a preponderance of cracked gasoline are particularly sensitive to storage. The primary products of the gasoline synthesis also contain a considerable proportion of straight-chain olefines, as, these are almost pure mono-olefines the conditions are quite special so that the primary synthetic products are fundamentally different from cracked gasolines.

The properties of olefines are known from experience obtained with cracked gasolines; it was to be expected that the primary products of the synthesis would have the same general properties, we therefore started early on investigations into the effect of storage time on fuels mainly composed of primary products of the synthesis. After a number of preliminary experiments we started a whole series of experiments in order to elucidate the storage stability of the primary products, the storage stability of the cracked gasolines obtained from the high boiling primary products, the stability of mixtures of the two both by themselves and with the addition of inhibitors, fuel spirit and lead. In this way we have stored gasolines in 200 litre-flasks. The following additions were made:-

1. Cresol as inhibitor 0.2 gm/litre

2. Fuel spirit 11.5% vol.

3. TEL 0.5 cc/litre

The samples 4 to 7 consisted of mixtures 1,2; 1,3; 2,3; and 1,2,3. In order to find out the extent to which the material of the vessel affects the alterations during storage, containers were chosen of galvanized iron as well as pure iron.

The gasolines were again examined in 1940 , after having been in storage for two years. Some very interesting observations were made, the most important of which shall be reported here.

1. Change in the octane number

The octane numbers of the original samples had fallen strongly. For primary gasoline for instance O.N. fell from 58 to ∼40 and for cracked gasoline from 66 to ∼43. This diminution of the octane number was almost completely prevented when an inhibitor was added. Under these conditions the alteration in the octane number is about 3 or 4 units; this may partly be explained by an evaporation of a small quantity. Fuel spirit has also had an inhibiting effect on primary gasoline, the octane number thus remaining constant, for cracked gasoline, however, there was a decrease of from 4 to 6 octane number units. The addition of TEL, astonishingly has so strong an inhibiting effect on both primary gasoline and on cracked gasoline that the octane number stayed constant, at 72 in the case of primary gasoline and at 80 to 81 in the case of cracked gasolines. There is one restriction however:- the inhibiting effect of the TEL was only observed in galvanised iron containers. When the container was made of pure iron the primary gasoline fell by 7 units and the cracked gasoline by 12 units. As the single components have essentially inhibiting properties, it may be understood that the mixtures also kept the octane numbers at their original levels.

In some cases, particularly in the original products, the octane number has been observed to fall off. This is due to a quick new formation of peroxides. It is known from the literature that pero xides may have a very considerable effect on the octane number. Let me refer here to the work of Schildwächter in combustion chemistry 19 38. In this work he represents the dependence of the octane number on the content of peroxide for one of the gasolines under investigation. He finds that the octane number is lowered by 11 units when the peroxide content is 700. The increase in the peroxide content is partly quite considerable in our samples, in the original primary gasoline for instance it is 600 to 700 mg and in the original cracked gasoline 1000-1400 mg of active oxygen /litre. Further formation of peroxide is however strongly inhibited by the above mentioned additions. After two years' storage the formatio n is below 10 mg/litre for almost all samples of primary gasoline to which the above mentioned additions had been made. A larger increase was observed only in the sample with lead addition amounting to 160 mg in the galvanized iron container and 460 mg in the iron container, all the same it is still considerably below that of the original product. The difference between pure and galvanised iron is again remarkable here, the sample in the pure iron container showing a larger increase of peroxide. As was to be expected it emerged that the inhibiting effect of additions is less for craked than for primary gasoline. For all samples with cresol additions it is of the order of magnitude of from 30 to 60 mg/litre. When cresol and fuel spirit are added it is reduced to 10 to 20 mg. The effects of fuel spirit and TEL singly and in combination is not as good as it is in the case of primary gasoline; in these cases the increases in the content of peroxide exceed 100 mg. With an addition of pure TEL the increase mounts to 1000 mg in the iron vessel, in the vessel of galvanised iron the increase was again less.

2. Resin content

The following tests were carried out for the resin determination; the evaporation test as well as the bomb test with 7 atm. excess pressure of oxygen, the latter test it should be mentioned, was carried out according to the form as modified by the BV i.e. at 70°.

The primary gasoline had in all cases remained stable after two years' storage. The maximum value of all the evaporation tests is at 6 mg/100 cc and for the bomb tests it is 7 mg at 70°. Obviousl the periods of induction are more than 4 hours in every case; that means that the increase of peroxide content to more than 700 mg O_2/litre due to oxidation, though its affect on the octane numbers doesn produce any separation of resin. The gasoline has also remained perfectly clear. For all the cracked gasoline samples provided with inhibitors the results obtained were equally favorable whereas the originals showed evaporation tests up to 385 mg and times of induction from 100 to 120 mins. Of the samples with TEL addition it was again those in the galvanized vessel which remained stable; in the vessel of pure iron the time of induction fell strongly. The samples with additions of fuel spirit also have evaporation tests above 10 mg; in the bomb test the time of induction is still more than 4 hours, the evaporation tests however give 20 mg.

3. Other analytical data

Of the other analytical data it is in particular worth noticing that there has been some increase of the neutralisation number only in the few cases which there had been a rise in the peroxide content; even then it did not occur in all cases; when there was no increase in the peroxide content one could not observe an unambiguous change in the neutralisation number.

In the course of two years' storage only a very small quantity of low volatile components had evaporated. The vapour pressure, for example, and fallen by about 0.05 kg/cm² in the mean, according to Reid's measurements. Similarly the boiling number has risen by two units, corresponding to the mean boiling behaviour.

Summary

The storage characteristics of primary and cracked gasolines may be summarised thus: Primary gasoline, which mainly consists of mono-olefins, has considerably more peroxide after storage; this has caused a diminution of the octane number but has had no effect on resin formation. The formation of peroxide and with it the diminution of the octane number were largely suppressed by addition of inhibitor, fuel spirit and to some extent also TEL .

Original samples of refined cracked gasolines gave both a diminution of the octane number and an increase in the resin content; due to the increase in the content of peroxide. In this case the lowering of the octane number and the increase of resin were also lessened by adding inhibitor, fuel spirit, and to some extent also TEL.

If the primary gasoline is employed as a component in the mixture no effect may be expected even after long periods of storage since the velocity of oxidation is strongly reduced by the dilution.

It is worth mentioning in this connection that all gasolines which contain olefins are extremely sensitive to light. This is partly known from the literature. I carried out some experiments in this connection: primary gasoline was exposed to day light in a tightly closed flask; one observed an extremely rapid increase of the content of peroxide. This amounted to ~ 350 mg in 30 days. The addition of inhibitors again almost completely suppressed the oxidation effect; this was seen from the fact that parallel samples to which an inhibitor had been added only gave an increase of 40 mg O_2/litre after having been exposed to daylight for 30 days. In these experiments the increase in peroxide was again accompanied by a lowering of the octane number, whereas the resin content remained unchanged.

Storage Stability of Fuels

By Dipl. Ing. Wallner, Test-station Travemünde.

A number of leaded and unleaded fuels were stored in the test station of the air force at Travemünde. The purpose was, on the one hand to check the practical storing stability of these fuels, and on the other to find out the relation between the practical storage stability and the behaviour in the ageing bomb.

The following gasoline groups were employed in the experiments:

1. Aviation fuels
2. Catalytic cracked gasoline pure and in mixture with aviation benzol.
3. Czech aviation gasoline pure and in mixture with aviation benzol.

4. Leuna automotive gasoline in mixture with automotive benzol, lead tetraethyl and iron carbonyl.

The standard 30 litre containers which had been used several times previously were employed for the storage at the test-station. These containers consist of sheet iron without an interior protective paint and are provided with an attachment-pipe for ventilation. At the end of this pipe there is a pot filled with silicic acid gel. This is inserted for the purpose of drying the air which is drawn into the container when the temperature oscillates.

The storage time extended over a period of two years. The gasolines were completely analysed at the start of the storage after one and after two years' storage. In the intermediate periods, short determinations were made to check those most important properties which are decisive for their later use; these include the octane number, the lead content and evaporation residue. Only these properties were included in the rating of the storage stability. We did not consider any changes involving the specific gravity, the refraction, the boiling characteristics etc. for the purpose of rating the storage stability: changes in these quantities are solely due to the evaporation of low boiling components.

The results of the storage may be stated thus: Favorable storage characteristics are shown by all unleaded fuels and leaded fuels with low content of aromatics. Highly aromatic leaded fuels must be considered to be unstable; one could not however observe any definite relation between the proportion of aromatic substances and the ageing tendency. There is no doubt that the lead tetraethyl content has a deciding influence on the stablility. It appears that fuels with a high content of lead tetraethyl have a lower storage stability than those with little lead tetraethyl.

Before storing, the fuels were subjected to a stability test in the bomb in order to ascertain the relation between the behaviour in the bomb and practical storage stability.

The following picture resulted when the practical storage stability was compared with the ageing in the bomb: Of 16 fuels under consideration a clear correspondence between bomb test and practical storing could be observed in only 3 cases. In the other cases, the rating according to the stability test was considerably less favorable than it turned out to be under practical storage conditions. In one case the fuel was stable in the bomb test whereas actually there was a considerable increase of the resin content and turbidity due to precipitation of lead. Judging on the basis of the available investigational material it would not seem to be expedient to rate the storage stability of fuels according to the present ageing test.

We intend to undertake the present ageing test also for further storage samples so as to be able to arrive at more definite conclusions with the aid of extended experimental data

Inhibitors

By Dr. Ing. I. Morghen DVL, Berlin Adlershof

In general the oxidation of fuels by air is accelerated in the presence of T.E.L., the T.E.L. decomposing at the same time. This acceleration of the oxidation is strongly dependent on the type of fuel; this forces one to the conclusion that the oxidation is reciprocal.

The mechanism of the oxidation is not understood in its details. It was however possible to elucidate it in part. On the basis of the investigations some fuels or groups of fuels were proposed by the DVL in the winter of 1940 as being specially suitable as inhibitors for leaded fuels. The leaded fuels to which these substances had been added give very good results for the stability test in the bomb; this may be seen with the aid of the table.

Table

Effect of inhibitors

Content of T.E.L. by vol.%	Age of leaded fuel days	Appearance of leaded fuel	Addition vol. %	Resin content mg/100 DVL	conven. treatment	Content of total decomposed T.E.L. vol.%
				after ageing in the bomb		
0.1190	0	clear	-	19.2	47.4	0.0630
0.1170	9	slight turbidity of decomd. T.E.L. solution 0.0040 Vol.%	0.0040 sub.1	2.3	8.3	0.0145
0.1170	9	"	0.0055 sub.2	2.7	7.2	0.0137

It should be mentioned in this connection that carbon dioxide is also suitable for inhibiting the ageing of leaded fuel; from this point of view then the lead decomposition is really more vigorous in the bomb. Not much can be said about the corrosion behaviour of the inhibitors in question. A laboratory experiment with ~~the~~ inhibitor most liable to corrosion gave the following result: A fuel was mixed with 0.0075 vol. % of inhibitor and left in a bomb under pure nitrogen for four hours in the presence of strip s of iron, zinc, aluminium and electron metal. All the metals remained unchanged with the exception of zinc which showed a decrease of weight of 4.5 mg. The other inhibitors which had been preposed by the DVL should behave much more favorably. The quantity to be added depends on several factors (for fuels which have just been produced the quantity averages 0.001 to 0.005%). Since two test stations have carried out experiments with some of these substances we may perhaps hear reports about them from the stations.

Experience in the Determination of Aromatics and the iodine number.

By Dr. H. Veldé, Ruhrbenzin A.-G., Oberhausen-Holten.

I should like to mention some of our experiences in the determination of aromatics and the iodine number as a contribution to the discussion of the test methods. We are here dealing with a field which has been tackled by an extraordinarily large number of investigators; one has not however, been able to reach a final conclusion as to the absolute reliability of one or the other method. I should therefore like to confine my remarks to those methods which we have used or tested.

The determination of aromatics has no significance for our primary products since these do not contain any aromatic compounds. We have however come to grips with the estimation of aromatics when we analysed our cracked gasolines and some other products. Here one can differentiate between fuels composed of a number of single hydrocarbons and some narrowly cut fractions. If the fractions are very narrowly cut then one can make statements about the proportion of aromatics on the basis of physical data alone including density, refraction etc. For fuels these methods of course fail and other methods have to be used. The sulphuric acid method has not proved itself. With sulphuric acid method I mean that method in which the olefin content is estimated with the aid of 90% sulphuric acid and the olefinic and aromatics content is determined by means of the Kattwinkel reagent. The Kattwinkel reagent in particular is ill suited for estimating the true proportion of aromatics plus olefins; the presence in the fractions of larger amounts of substances containing oxygen makes further difficulties. Consequently we have come to speak, only internally so far, not at all about olefines and aromatics; we now term the volume diminution as SPL, "soluble in sulphuric acid, phosphoric acid."

I should however like to point out that in specially stored cases the Kattwinkel reagent has proved itself very well. Above all, well reproducible results are obtained for all gasolines which contain only aliphatic olefines; it is also possible to obtain fairly good absolute values if instead of taking the ratio of acid to product as 3: 1 one takes it to be 4:1; otherwise the analysis turns out to be definitely too low if the products contain a high proportion of olefines. If one is dealing with narrowly cut fractions of the gasolines mentioned one reaches good agreement with the olefine content estimated from the iodine number and the molecular weight. According to our experiences I should propose to undertake the joint estimation of aromatics and olefines only when one is dealing with narrowly cut fractions; because in these cases one can apply confirmatory physical methods.

Similar conditions are found in connection with the iodine number; it is generally known that the main difficulty in determining the iodine number lies in the fact that there is no sharp end-point, the assimilation of iodine continuing by substitution. Branched chain olefines are particularly prone to allow this process. I refer here to the work of Grosse-O etringhaus, Kaufmann, Richter and Koch who, besides many others, have discussed and criticised these iodine number methods.

It should be stated that the principles according to which one should select an iodine number method are as follows:-

1. The accuracy required
2. The experimental difficulty
3. The availability of reagents.

When stating the required accuracy one should always take into account the type of olefines that is expected to be present. If, for instance, one investigates a polymer gasoline, one cannot apply a method which is known to lead to substitutions. If, on the other hand one is dealing with a gasoline in which there are few branched chain olefins, as for instance the primary gasoline from the synthesis it is quite permissible to employ a method which would under different circumstances lead to substitutions.

As to point 2. it should be said that in many cases one is dependent on obtaining results relatively rapidly; one cannot in consequence apply any method which presupposes that the iodine number reagent should be in contact for several hours.

A general comment on point 3 is that, particularly to-day, during the war one should think of the supply position of reagents. One should if possible make use of methods which do not consume too much iodine and iodine compounds especially if it is a question of series investigations involving large quantities of material.

Having regard to the above considerations we have had very good experience with the following methods: For primary products we work according to Rosenmund and Kuhnhenn; this method has now also been adopted by the ZB. For gasolines with chains which are not too much branched this method gives a sharp end-point; it has the additional advantage that the reaction time is 2 minutes. The experimental side is also very simple, for the addition one uses a solution of bromine in pyridine sulphate and one back-titrates with arsenious acid. Iodine is not used at all in this method.

We have not yet adopted one final method for analysing gasolines with olefines having more highly branched chains; all the known methods of determining the iodine number have some defects. We have had rather good experiences with Kaufmann's method. The iodine thiocyanogen number and the iodine number according to Wigs may only be applied to a limited extent since the addition is frequently still incomplete after the time of reaction normally indicated. The Hanus iodine number has not proved itself either; one reason being the tendency to substitution; the other reason is that the Hanus reagent is extremely sensitive to external influences e.g. traces of water, this, it is true, is a property which it has in common with iodine thiocyanogen.

One of our laboratories is therefore occupied at the present time in working out yet another iodine number method which should also be suitable for more highly branched chain gasolines.

We have so far also applied the Rosenmund and Kuhnhenn or Kaufmann method to lubricants. We are not however quite certain yet whether the values obtained are quite accurate.

So far my remarks have only dealt with gasolines with mean or high iodine numbers. If one has to determine the olefinic content of aviation oils i.e. products which have an iodine number in the neighbourhood of 5, it is in my opinion advisable to select one's method according to considerations different from those mentioned above. The accuracy need not be greater than about ½ iodine number units in most cases. Substitution therefore no longer plays as important a part as before and the experimental difficulties now become the main consideration. In view of the present knowledge gained from our investigations I propose in this case also to use the method of Rosenmund and Kuhnhenn which has already been prescribed by the ZB. This method has the advantage of involving only easy experimentation and of requiring a reaction time of only a few minutes. In order to obtain a final clarification one might carry out an experiment in which a small number of fuels would be tested at various test station.

On the Determination of aromatics according to the design regulations for aero-engines BVM 1940.

By
Dr. Mayer-Bugström (DVL, Berlin Aldershof)

Following a suggestion of the DVL directions for the determinations of aromatics and unsaturated compounds were included in the design regulations.

Former method of the DVL (Riesenfeld and Bandte):

Shaking vessel : Eggertz-tubes 50 cc capacity
Acid : ca. 38 cc monohydrate
Fuel : " 12 "
Limit . Vol.%

Present method BVM

Shaking vessel : P henolanalyser according to Kattwinkel
Acid : 50 cc Kattwinkel acid
Fuel : 15 cc
Limit : per cent by weight

The present method was introduced in analogy to the Dutch standard method of analysis of Shell. This prescribes:
Shaking vessel : graduated separating funnel
Acid : 75cc 98% sulphuric acid
Fuel : 25cc
Limit " Per cent by weight

The reasons for altering the methods used so far were these:

1. Insufficient reproducibility which is due to the variable composition of the monohydrate. The various deliveries of the monohydrate already vary by several tenths of a per cent on delivery; during use the H_2SO_4 content still further decreases on account of water being taken up; in practice it is working with an acid whose proportion of H_2SO_4 varies between 99 and 100%. The results therefore become significant only when the H_2SO_4 content of the acid has been stated. Variations of tenths of a per cent already play a large part for the proportion of aromatics. The agreement with the results of other test-stands was bad, also on account of the low reproducibility.

2. It was desirable to state the value of aromatics plus unsaturated compounds in per cent by weight, in analogy to statements on naphthenes. Thus one was left with a larger residue of fuel for the determination of the specific gravity; this residue is often very small (in the case of highly aromatic substances) and also has to be used for the determination of the aniline point.

3. One used to make but one extraction. For highly aromatic substances it is necessary to make two extractions. This is more easily carried out in the phenol analyser since there is always some loss when one makes transferences from or to Eggertz tubes.

4. A larger excess of acid may be employed in the phenol analyser; this also seems advantageous for the analysis of highly aromatic fuel.

Table 1 gives a comparison of the two methods for 5 gasolines, at first without transforming into per cent by weight. It is apparent that the values obtained after both the first and the second extraction are higher in the case of the second method.

When one carries out the transformation into per cent by weight one finds a further increase for the new as compared to the old method. (Table2) The reproducibility is good as is also shown by table 2.

Table 1.

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Extraction of fuel with monohydrate (1) and Kattwinkel-acid(2)

1) Employed were: ca. 38cc monohydrate 99.5% and ca. 12 cc fuel.
   Shaking vessel: Eggertz-tube of capacity 50 cc.
2) Employed were: 50 cc Kattwinkel acid (30 gm P_2O_5+ 100cc conc. H_2SO_4) and 15 cc fuel
   Shaking vessel: Phenol analyser of Kattwinkel.

Fuel method	265/40		268/40		267/40		272/40		270/40	
	1	2	1	2	1	2	1	2	1	2
cc of fuel before the 1st extraction	12.5	15.0	12.5	15.1	12.2	15.1	12.5	15.0	12.3	15.0
" " fuel after the 1st extraction	11.7	14.0	11.1	13.0	11.1	13.2	10.3	12.1	8.7	9.9
Loss per cent by vol.	6.4	6.7	11.2	13.9	9.0	12.6	17.6	19.3	29.3	34.0
cc. fuel before 2nd extraction	11.5	14.0	11.0	13.0	11.1	13.2	10.3	12.1	8.6	9.9
" fuel after 2nd extraction	11.2	13.7	10.7	12.2	10.4	12.3	9.8	11.2	7.8	8.6
Loss(% by vol. of initial volume)	2.4	2.0	2.4	5.3	5.7	6.0	4.0	6.0	6.5	8.7
Total loss(% by vol. of initial vol.)	6.8	8.7	13.6	19.2	14.7	18.6	21.6	25.0	35.8	42.7

Reproducibility of the joint determination of aromatics + unsaturated compounds according to the BVM method.

Fuel analysis	10/40		11/41		16/40		17/41		18/41	
	1	2	1	2	1	2	1	2	1	2
cc. of fuel before the 1st extraction	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0
" of fuel after the 1st extraction	5.1	5.2	6.5	6.4	14.1	14.1	8.5	8.4	13.8	13.8
Loss (Vol. %)	66.0	65.3	56.7	57.3	6.0	6.0	43.3	44.0	8.0	8.0
cc. of fuel before the 2nd extraction	5.1	5.2	6.5	6.4	-	-	8.5	8.4	-	-
" " fuel after the end extraction	4.5	4.6	6.0	5.9	-	-	7.8	7.8	-	-
Loss (% of vol. of the initial volume)	4.0	4.0	3.3	3.3	-	-	4.7	4.0	-	-
Total loss (% of vol. of the initial vol.)	70.0	69.3	60.0	60.6	6.0	6.0	48.0	48.0	8.0	8.0
% by wt. of aromatics plus unsaturated compounds.	74.0	73.4	65.2	65.8	5.9	5.9	53.0	53.1	8.6	8.5

On the Determination of aromatics and olefins in gasolines according to the design regulations 1940.

By

Dr. W. Hirschberger, I.G. Farbenindustrie
A.-G, Ludwigshafen Rhine.,

High Pressure experiments.

The official method prescribed in the design regulations 1940 is that of Kattwinkel. This consists of measuring the decrease in volume of the initial gasoline; the sum of aromatics and unsaturated hydrocarbons is then found after extraction with Kattwinkel acid (conc. H_2SO_4 with phosphorus pentoxide). One can calculate the propo rtion of the aromatics by themselves by first estimating the unsaturated compounds by extraction with 90% H_2SO_4 and then sub trating that part from the total sum.

The result obtained from a large number of investigations has shown that the olefin values as determined by the prescribed working method lie far above what is possible and far above the values as determined by other methods (e.g. the iodine method;) they also vary to a large extent.

Example 1. The following values were found for the sample in one ring experiments at six different test stations: 3.5; 5.0; 11.8; 3.4; 19.3; 16 per cent olefin.

Example 2. According to this method the following olefin values were found in olefin free (refined) model samples:-

Mixture	80 %	aromatics	+ 20%	normal	gasoline	14.5	Vol.%	Olefin
	50%	"	+ 50%	"	"	8.9	"	"
	20%	"	+ 80%	"	"	4	"	"

i.e. almost 20% of these aromatics were estimated as olefins. These examples should suffice to demonstrate that this working method is quite inadequate for the estimation of olefins. In consequence the value of aromatics, calculated by a difference is also affected by these erroneous results. One can thus only consider the sum of aromatics and olefins in the assessment of the Kattwinkel-method. At this stage it should be pointed out that in the design instructions several factors whose large effect is well known have not been fixed in detail. Thus only very general indiciations are given for example, for the temperature regulation during the process and the time and intensity of shaking. Furthermore the following sentence:- "If the diminution in v olume is more than 10 in 100 one has to run off the acid, add fresh acid and shake again" may be interpreted in various ways depending on whether diminution in volume denotes the contraction or the shaking up of the aromatics by the acid. Another defect of the method is due to the small quantity of gasoline that is involved: small errors in the readings and the adhesion of drops to the walls of the vessel may cause quite considerable errors.

Under these circumstances one cannot expect satisfactory agreement among the analyses carried out at the various experimental stations. As a matter of fact the following values of aromatics plus olefines were obtained with 3 samples of gasoline at 6 different experimental stations:-

		max. Difference
Sample 1 :	17; 12.5; 21.6; 15.5; 18; 13;	9
" 2 :	61; 60; 65.6; 66; 65; 61;	6
" 3 :	39; 37; 44; 43; 43; 36;	8

Deviations are higher for lower concentrations of aromatics than for higher concentrations.

It seems quite plausible that if one sets out very detailed working directions one should be able to obtain a considerably better agreement among the results.

Even then it is still questionable whether and in how far the reproducible values found in this way correspond to the actual proportion of aromatics.

In the basis of the available data one can say that the values given by the Kattwinkel method are too high.

3 mixtures of olefin free aromatics and normal gasoline were analysed; the results were as follows:

When 80% aromatics were used 81% were found
" 50% " " " 52.2% " "
" 20% " " " 23.5% " "

Even larger differences were found for other samples with a known content of aromatics and other residual gasolines:

For 35% aromatics + unsat.-compounds 47% were found
" 45% " " " 50 % " "
" 64% " " " 67% " "

Further evidence which indicates that the Kattwinkel reaction cannot be an exact separation method is given by the fact that continually new quantities of gasoline are dissolved by the sulphuric acid after repeated extractions.

Thus in the case of one gasoline a first treatment with Kattwinkel acid dissolved 51%, a second treatment dissolved 5% and another 3% were dissolved the third time.

Summarising one may say:

1) That form of the Kattwinkel method which is laid down in the design instructions does not satisfy the requirements which a technical method of analysis should satisfy.

2) It remains to be ascertained whether by laying down a detailed working process one can reach results which both agree among themselves and are reproducible

3) Further it remains to be seen whether the deviations from the theoretical value are within permissible limits.

The Determination of the aromatic content of gasolines according to the aniline-point method.

By

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Ludwigshafen/Rhine.

High Pressure Experiments

The method of calculating the aromatic content from the depression of the aniline point has been known for a long time but not very widely. This method is particularly suitable for application to technical purposes; it has therefore been used by us for several years. We have investigated it and worked it out first with regard to applying it to those types of gasoline which are to-day accrueing from our large scale hydrogenation works i.e. gasolines boiling between the limits of about 40 -165°C and containing 30-50% of components boiling up to 100°C. It has yet to be investigated how for the relations found between the depression of the aniline point and the content of aromatics may be applied to gasolines boiling in a different range and to fractions.

For our experiments we employed mixtures of pure single aromatics in proportions similar to those met with in large scale production (CV_2b, VT 706b, DHD); e.g. 20% pure benzene 41% Toluene 27% Xylene 3% ethyl benzene and 9% of higher aromatics. Increasing proportions of these aromatic mixtures were added to various residual gasolines; the latter had in each case been freed of aromatics and olefins by sharp refining with sulphuric acid. The aniline points of these mixtures were measured. Subsequently the aniline point II was measured for all the mixtures (i.e. the aniline point after the aromatics and unsaturated compounds had been removed). If one now plots the differences of A.P.I. and A.P. II against the known content of aromatics one obtains a slightly bent curve. (compare curve-sheet I). Expressed differently that means that one has to assume a variable and not a constant factor in the relation between the depression of the aniline point and the content of aromatics. For depression of 10° the factor is about 1.2, for 50° it is about 1.0 and for 70° it is about 0.9. Thus each depression of the A.P. corresponds to a definite content of aromatics; this is independent of the absolute position of the aniline point i.e. independent of the chemical composition of the residual gasoline.

When gasolines with a high proportion of aromatics were investigated (50% and more) it became necessary to determine the aniline point in mixture with normal gasoline. This is necessary because the normal aniline points lie below 0°C(melting point of aniline = - 6°C). In the course of this it appeared that the aniline point calculated from the mixture with Kahlbaum gasoline was several degrees higher (up to about 7) than the point measured directly e.g.:

		A.P.I direct	calc. from mixt.
1. 50% by wt. of aromatics	A.P.11=61.5°:	+ 11.6	+14.2
2. 50% " " "	A.P.11=57.5:	+ 7.7	+11.7
3. 50% " " "	A.P.11*52.5	+ 3.0	+ 7.9
4. 50% " " "	A.P.11=47.5	- 2.3	+ 2.4

This is due to the fact that the aniline point of mixtures does not follow the law of mixtures.

If one has to calculate the A.P.I from the mixture with Kahlbaum gasoline then it is not possible to express uniformly the relation between the depression of the aniline point and the aromatic content by means of a curve; the aniline point I calculated from the mixture with Kahlbaum-gasoline differs from the actual value (does not obey the law of mixtures); the extent of this deviation furthermore depends on the composition of the residual gasoline. We used one and the same mixture of aromatics for four different residual gasolines. With the aid of these we empirically determined the relation between the calculated aniline points and the theoretical aromatic content; this relation was expressed by means of a curve (see curve sheet 2).

For this purpose it would however also be possible to use a working method which would make it possible to apply the generally valid relation (found above) between the depression of the aniline point and the content of aromatics; this could be done if one uses a mixture with gasoline free from aromatics (e.g. normal gasoline) in the ratio by wt. of 1:1 both for the determination of the A.P.I and of the A.P.II. The aromatic content of the gasoline under investigation is then given by multiplying by two the aromatic content determined from the depression of the aniline point.

The following may be presented as an example of the agreement among the results of the three different methods. A mixture consisting of 60 .5% pure aromatic mixture and 39.5% by wt. of a residual gasoline of A.P. 62.2° was analysed according to the three methods; the results were as follows:

a) according to first working method

A.P. I measured directly =-2.7°
A.P.II =+ 62.2°
Depression of A.P. = 64.9 which
corresponds <u>60.5% by wt.</u> of aromatics as read off from curveI.

b) According to second working method
A.P. calculated from mixture 1:1 vols. with
normal gasoline = + 2.4°
A .P.11 = + 62.2°
According to curve sheet 11 a calculated A.P.1. = 2.4°
with an A.P. 11 = 62.2° corresponds to an aromatic content
of 60 .7% by wt.

c) According to third working method.
Samp le + normal gasoline (1: 1 by wt.) gives A.P.I = + 32.7°
" " " " " A.P.11= + 59.9
Depression of A.P. = 27.2

When read off on curve sheet I this corresponds to an aromatic content of 30.2% by wt. multiplied by 2 = 60.4% by wt.

Apart from mixtures of synthetic aromatics which have an essentially different composition, mixtures of aromatics which had been extracted from CV_2b were used with good success.

Exemple:

Composition of mixture	Aromatics			
	15% Benzene+ 31% Toluene +20% Xylene + 8.5% ethyl benzene + 25.5% higher ones		aromatics extracted from CV_2b	
	found according to A.P. method.	Deviations from theoret. value	found according to A.P. method.	Devtns from theoret. value.
5% Aromatics + 95% res.gas.	5	0	-	-
10% " + 90% " "	9.8	-0.2	-	-
15% " + 85% " "	14.5	-0.5	-	-
20% " + 80% " "	19.4	-0.6	-	-
25% " + 75% " "	24.2	-0.8	-	-
30% " + 70% " "	29.1	-0.9	29.5	-0.5
40% " + 60% " "	39.2	-0.8	39.5	-0.5
50% " + 50% " "	49.3	-0.7	49.2	-0.8
60% " + 40% " "	59.0	-1.0	59.5	-0.5

From our extractions of aromatics we know that the specific gravity of the mixture of pure aromatics extracted from high power gasolines is 0.872 at 15° with only very small deviations.

One can thus transform the aromatic contents obtained in per cent by wt. according to the A.P. method into per cent by vol. by the use of the following formula:

$$\text{per cent of aromatics by vol.} = \frac{\text{per cent by wt x sp. gr. of gasln.}}{0.872}$$

Effect of olefins on the determination of aromatics according to the aniline point method.

One had to find out first of all and quite generally whether, in the case of aromatic gasolines containing unsat. comp . the aromatic content determined by the depression of the aniline point includes unsaturated compounds, and if so, to what extent. Representatives of the two main types, aliphatic and naphthenic unsaturated compounds, were investigated viz. octylene and cyclohexane.

An aromatic gasoline has an A.P. = +4.4°
The same gas. + 5% cyclohexane has A.P. = +3.0° difference -1.4
" " " + 5% octylene " " = +6.0° " +1.6
" " " + 5% decylene " " = +7.5° " +3.1
" " " + 5% (cyclohexane + octylene + decylene 2: 1:1) = +4.8° " +0.4

(A.P . of cyclohexane = ca. -19°; octylene = + 34.8°; decylene = + 49.9).

In order to estimate the aromatic content of olefinic gasolines according to the the aniline point method one has to eliminate the olefins.. It appears that 80% sulphuric acid accomplishes this satisfactorily if one is dealing with low concentrations of olefins (up to about 5%). One measures the aniline point (called A.P.Ia) of this pre-treated gasoline. This aniline point serves as the basis from which one determines the aromatic content according to curve sheet I or II. The aromatic content found in this way refers to the olefin-free gasoline and has therefore to be corrected for the original gasoline. The above table shows that one cannot draw any conclusions about the olefinic content of the gasoline from the difference between A.P.I. and A.P.Ia. The olefinic content has to be estimated separately.

The following table which refers to synthetic mixtures shows the effect of the presence of unsaturated compounds on the estimation of aromatics by comparing results obtained with A.P.I. and A.P.Ia:

Example:

Composition by wt.%			AP.I	AP.Ia	AP.II	% aromatics from AP.II - AP.I		% aromatics from(AP.II-AP.Ia)(100 olefin)	
Aromatics	res. gas.	olefin				observed	Devts from theoret. value	observed	Devts. from theoret. value
50	47	3 cyclohexene.	-2.4	2.8	56.4	52.9	+ 2.9	49.9	- 0.1
50	45	5 "	0.6	2.2	56.0	54.0	+ 4.0	49.9	-0.1
50	40	10 "	3.7	2.7	55.6	56.5	+ 6.5	50.4	-0.4
40	45	5 Octylene	6.7	5.7	58.8	51.5	+ 1.5	49.7	-0.3
50	45	5(cyclehexane +Octylene +Decylene 2:III)	5.2	4.1	58.5	52.4	+ 2.4	50.3	+0.3

In this way we believe to have shown that if one adopts the working of the aniline method as described above one can obtain practically useful results in the analysis of technical gasolines, subject only to the reservations mentioned above.

Curve Sheet I

Relation between the depression of the aniline point and the aromatic content of gasolines when the A.P.I. is measured directly (not in mixture with normal gasoline)

Ordinate: Percentage by wt. of aromatics
Abscissa: Depression of the aniline point

Curve Sheet II

Relation between aniline point I and aromatic content of gasolines as a function of the aniline point II when the A.P.I of the gasoline is calculated from the A.P. of the mixture of the gasoline with normal gasoline (1:1 by vol.).

Ordinate: Percentage by wt. of a romatics
Abscissa: Aniline point calc. from the mixture with normal gasoline 1:1 by vol.

FKFS - Rapid Method for the Determination of the lead content of Aero-Engine fuels.

By
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There are a number of well-known methods for determining the lead content in fuels e.g. the chromate method of Calingaert - precipitation with bromine as $PbBr_2$ and determination as $P\ bCrO_4$; the $PbSO_4$ method of W.Ulrich, the HCl method of Calingaert and Cambrill and others. All these methos have either the disadvantage of giving values which are not well reproducible or they require much time.

The FKFS which had been developed some time ago is based on iodometric analysis; lead tetraethyl being transformed into lead tri-ethyl iodide and ethyl iodide.

$$Pb(C_2H_5)_4 + 2\ I = Pb\ (C_2H_5)_3\ I + C_2H_5\ I.$$

Other lead compounds require no or very little iodine. The hexaethyldiplumbane of which there are several tenths of a per cent needs only half the iodine for each lead atom. The following reaction occurs:-

$$Pb_2(C_2H_5)_6 + 2\ I = 2Pb\ (C_2H_5)_3\ I$$

Therefore the lead tetraethyl content found in the gravimetric method is 0.2 to 0.5% higher than that found in the iodometric method if the basic gasoline does not combine with iodine.

We startedby using an aqueous solution. Here we encountered two difficulties:

1. The aqueous iodine solution attacked the unsaturated compounds.

2. The reaction is light - sensitive.

We therefore tried to separate the unsaturated compounds or to saturate them with additions such as acetic acid, oxalic acid and trichloro acetic acid. These hydrocarbons could be separated with dimethyl sulfate. The use of dimethyl sulfate was however discontinued because of the poisonous nature of the substance. Up to a certain equilibrium state one can carry out the saturation with trichloroacetic acid; this reaction, however, is not quantitative. The lead tetraethyl is also attacked if the reaction is continued for a longer time. When the directions for the analysis were strictly adhered to one could carry out the lead determination with an accuracy of 5 to 10%.

We carried out thorough experiments with organic solvents. These have shown that in the first instance a solution of iodine is ethyl alcohol reacts with the lead tetraethyl; only in the presence of larger quantities of unsaturated compounds is some iodine added to the basic gasoline. The possibility of this is practically non-existent in the case of aviation fuels. The maximum error amounts to 3 to 4%, this is not significant for a rapid method such as the FKFS .

The FKFS rapid method has been tested for several fuels, the following among others:-

1) VT 702)
2) VT 707)
3) VT 802) A viation fuels
4) VHT 302)
5) 80 Vol.% VT 810+20 VHT 302)
6) Leuna-Benzin)
7) Fischer-Tropsch-Benzin) motor-car fuels

In the case of fuels No. 1 to 5we are exclusively dealing with aviation fuels; fuels 6 and 7 are motor-car fuels.

The fuels mentioned above were first treated with an alcoholic solution of iodine. This was done in order to ascertain the quantity of iodine taken up simultaneously with the error range present from the start. Various amounts of lead tetraethyl were then added to the fuels. On the basis of experience the following directions were worked out for the determination of lead in aero-engine fuels:-

25 cc of the fuel to be investiagted are shaken with 5 cc of an n/10 solution of iodine in ethyl alcohol in a 100 cc iodine number.. flask; the shaking is carried on for from 5 to 10 mins/ 5 mins. for fuels with low lead content, 10 mins for fuels with high lead content). The excess iodine is back titrated with an n/10 solution of sodium thiosulfate. The iodine solution is prepared by shaking 12.7 gm of iodine "pro analysi" with 1 litre of 98% ethyl alcohol for about half an hour; the potassium iodide which has not gone into solution is left as a deposit on the bottom.

The quantity of n/10 alcoholic iodine solution that has been used up is multiplied by 0.0391 to give the content of lead tetraethyl in per cent by volume.

The basic fuels were treated according to the given directions for lead determinations in order to test their sensitivity to iodine.

Table 1

Assimilation of iodine in basic fuels and the value of the lead tetraethyl content calculated therefrom.

Shaking time:	5 min	10 min	5 min	10 min
Fuel	Consumption of $^n/10$ alcoholic solution of iodine (cc)		Content of lead tetraethyl (volume per cent).	
VT 702	0	0	0	0
VT 707	0.02	0.025	0.0008	0.001
VT 810	0.02	0.02	0.0008	0.0008
VHT 302	0	0	0	0
80 vH VT 810 + 20 vH VHT 302	0.03	0.04	0.0012	0.0016
Leuna-Benzin	0	0	0	0
Fischer-Tropsch Benzin	0.026	0.04	0.001	0.0016

It may be seen from table 1 that the consumption of iodine corresponding to the various fuels lies between 0 and 0.04 cc; 0.04 cc of an n/10 solution of iodine here corresponds to 0.0016% by vol. Thus the assimilation of iodine is relatively low and consequently gives rise only to a small error.

Table 2

Lead values found when the theoretical value was 0.0326 per cent by volume.

Shaking time:	5 min	10 min	5 min	10 min
Fuel	Consumption of $^n/10$ alcoholic solution of iodine (cc)		Content of lead tetraethyl (volume per cent).	
VT 702	0.835	0.835	0.0326	0.0326
VT 707	0.83	0.83	0.0325	0.0325
VT 810	0.84	0.85	0.0328	0.0332
VHT 302	0.83	0.835	0.0325	0.0326
80 vH VT 810 + 20 vH VHT 302	0.80	0.81	0.0313	0.0317
Leuna-Benzin	0.83	0.83	0.0325	0.0325
Fischer-Tropsch-Benzin	0.835	0.84	0.0326	0.0328

Table 2 contains the lead values of fuels, obtained by the FKFS method, the theoretical value being 0.0326 per cent by volume of lead tetraethyl. The lowest observed value was 0.0313 per cent by vol., the highest was 0.0332 per cent by volume.

Lead was added to the seven basic fuels to give a total of 0.1306% by vol. The observed lead numbers may be seen from table 3. The lowest lead value found was 0.1275 and the highest was 0.1302% by vol.

The FKFS method is very simple it may be carried out rapidly and if possesses all the advantages of a volumetric analysis . There is no filtration, glowing, weighing and one obviates working with bromine, nitric acid and sulphuric acid. The following equipment is needed:

1 Miscroburette, 1 pipette
3 flasks, 1 measuring cylinder
1 iodine number flask

Observed lead values when the theoretical content was 0.1306 per cent by volume.

Shaking time:	5 min	10min	5min	10 min
Fuel	Consumption of $^{n}/10$ alcoholic iodine solution.		Content of lead tetraethyl (volume per cent)	
VT 702	3.26	3.33	0.1275	0.1302
VT 707	3.28	3.30	0.1282	0.1290
VT 810	3.285	3.32	0.1284	0.1298
VHT 302	3.32	3.33	0.1298	0.1302
80 vH VT 810 + 20 vH VHT 302	3.3	3.32	0.1290	0.1298
Leuna-Benzin	3.29	3.32	0.1287	0.1298
Fischer-Tropsch-Benzin	2.28	3.33	0.1282	0.1302

The time required is 15 mins. at the maximum. This time may be shortened considerably if one has a suitable shaking machine and if there is a large number of fuels for which lead determinations have to be made. Working with the FKFS method one can easily carry out a lead estimation for 6 fuels in the course of ½ hour.

The iodine rapid method leads to difficulties if the fuels to be analysed contain large quantities of unsaturated compounds and peroxides.

This led to the development of another method by means of which the lead content of all fuels could be determined with the highest accuracy.

Trichloroacetic acid, which had already been used for the saturation of the gasoline hydrocarbons, is, under certain conditions, capable of quantitatively eliminating the lead tetraethyl from the gasoline in the course of 2 minutes. Depending on the temperature 2, 3, or 4 ethyl groups are probably displaced by the trichloracetic acid. Probably we are dealing with lead trichloracetate (tetravalent lead) when we are making the lead determination. Further investigations are on foot, into the composition of the several lead compounds. The lead contained in the lead trichloracetate is precipitated as lead chromate by an n/10 solution of potassium dichromate; the excess of potassium dichromate is back titrated with sodium thiosulfate.

On the basis of the experience gained so far the following directions were laid down for the quantitative estimation of lead in fuels.

In a boiling flask provided with a separating funnel (fig. 1) 10 cc of fuel were boiled for 3 minutes under reflux with 5 cc of 50% trichloracetic acid.

The solution of trichloracetic acid is separated with the aid of the separating funnel which is provided on the boiling flask. The fuel is then twice washed with 50 cc of 50% Trichloracetic acid. The total washing liquid is strongly heated for 5 mins. in a second boiling flask with filter arrangement (fig.1) and boiled down until white fumes of trichloracetic acid escape. After adding 5 cc n/10 potassium dichromate one neutralizes with an ammonia solution. The precipitate of $PbCrO_4$ is then filtered by means of the 1 G 4-Filter joined to the boiling flask. The potassium dichromate which had been collected in a suction flask was back titrated with an n/20 solution of sodium thiosulfate. The quantity used up, in terms of an n/20 solution of potassium dichromate gives the lead tetraethyl content in volume per cent when multiplied by 0.0324.

The lead determination takes 30 mins; for the gasolines analysed so far the error has been 1 - 2%. In the matter of equipment we used the experiences gained in the DVL method.

Apart from the usual aviation fuels mainly olefin rich gasolines and gasolines containing peroxides were analysed by means of this rapid method. The two rapid methods mentioned for the determination of lead thus supplement each other very well.

Whereas the first method is particularly suitable for mobile laboratories - its usefulness during the war has already been proved - the second method may be employed for exact laboratory analyses.

In conclusion I should like to point out that Dipl. Ing. gross has found a rapid analysis method at the Institute Kamm. In this method the Pb- content of fuels may be determined very rapidly and exactly by means of the absorption of x-rays.

The DVL has received the following late alteration from the author:

The paper is to be altered as follows from the penultimate paragraph p.5:

Another method was therefore developed which allowed of an accurate determination of the lead-content of all fuels.

Trichloracetic acid, which has already been used for the saturation of the gasoline hydrocarbons is capable of transforming the lead tetraethyl quantitatively in the course of two minutes; this has been confirmed by experiments of Owens Hand, Brown and E. Emmet - Reid.
A similar decomposition of the lead tetraethyl by sulphur monochloride had already been observed by B. Carli, lead (II) - chloride being produced as the reaction product.

The DVL achieves a quantitative transformation of lead tetraethyl into diethyl lead chloride by the use of sulfuryl chloride. The lead is, in this case determined volumetrically by dithiozones.

A similar process occurs with the trichloacetic acid; ethyl lead chloride compounds are again formed initially; lead II chloride is formed eventually; the lead may then be estimated as lead chromate.

On the basis of the experiences gathered so far the following directions have been worked out for making quantitative lead determinations with trichloracetic acid:

A 30 cc boiling flask was used to reflux 10 cc of fuel with 5 cc of 20 % trichloracetic acid. (fig 1a)

Fig. 1a: Boiling flask for the decomposition of lead tetraethyl.

The boiling flask is then inserted into the ground in a separating funnel (fig. 2), a short admission of air being allowed through the top of the separating funnel. After a short shaking the boiling flask is taken off carefully; the solution of lead in trichloracetic acid is run off and poured into a wide-necked 100 cc Erlenmeyer or into a beaker.

The boiling flask is washed twice; each time with 3 cc of 20% trichloacetic acid; the whole of the washing liquid is collected in the wide-necked 100 cc Erlenmeyer or in the beaker.

Fig. 2a. Separating funnel for the separation of the aqueous lead solution.

The liquid is evaporated to dryness; white fumes of trichloracetic acid escape in the end; these have to be completely removed. In order to avoid splashing the Erlenmeyer is held by a clamp and kept rotating all the time. The trichloracetic acid vapours are removed by slight blowing; the temperature must not be too high on account of the decomposition of trichloacetic acid and the formation of lead oxide. In order to eliminate any traces of trichloracetic acid a few drops of NH_3 are added to the residue obtained; this is then boiled for a short time with no more than 3 cc 5% acetic acid and some sodium acetate. The lead is then precipitated from the solution with 5 cc of an n/20 solution of potassium dichromate. The mixture is boiled up again after the precipitation.

The liquid containing the precipitate of lead chromate should be cooled quickly; it should then be filtered through a sinter glass filter 1 G 4 into a 250 cc pressure flask. Excess potassium dichromate is then back titrated against n/20 sodium thiosulfate after the addition in the pressure flask of about 0.2g potassium iodide and 5 cc of analytically pure hydrochloric acid.

The volume used up in cc of the n/20 solution of potassium dichromate gives the content of lead tetraethyl in volume per cent after multiplication with 0.0324.

The accuracy of the FKFS trichloacetic acid method may be seen from table 4.

The remainder of the paper is unchanged.

Discussion of the Papers on the 17th June 1941.

Storage and chemical characteristics.

To I: Fundamental and
II: Chemical characteristics of the storage properties.

It may be that the low reproducibility of the bomb test may already be due to the storage of the samples before the test. Thus two samples of leaded gasoline which were filled from one container into two different flasks gave quite different bomb tests. Probably the "breathing" of the two samples is different in spite of the apparently identical treatment; and this may cause the observed differences. The greatest care must therefore be paid to the selection and storage of the samples.

There are also some more favourable experiences with reproducibility. The I.G. (Dr. Ester) obtains reproducible values even for leaded fuels, the maximum time for the evaporation being 15 mins. (usually 10-15 mins). CV 2b which had not been aged gave the following quantities of resin: unleaded 5 to 6 mg, leaded (with 0.12% TEL) 9 mg; aged and leaded 59-63 mg according to the conventional treatment, 13to 14 mg according to the DVL treatment. Wifo (Dr. Kiemstedt) find that the bomb test is useful as a relative measure but cannot be employed to predict the storage time of a fuel. It is still an open question whether one can use the decomposition of the lead compound as a criterion. It is impractical to store the fuel for one month before carrying out the test.

As regards the conditions of the experiments, it is requested that these be laid down accurately in the BVM. The ageing temperature and - time (100°C, 4 hours) generally give too severe a rating for fuels with 1 to 2 years storage time, the opposite has also occurred. When cracked fuels were aged the experimental conditions were still too wild for tropical conditions entailing high storage temperatures and - times. This point has a practical significance since one has to consider the possibility of using cracked gasolines in tropical regions.

In order to keep to the one time of evoporation for higher boiling fuels too, the I.G. (Dr. Ester) uses an evaporation temperature of 150°C. At other stations it has been found that the temperature of the boiling water bath is satisfactory. The quantity to be evaporated has been proposed as 50 cc in order to be able to keep to one time of evaporation. It is also recommended to use a higher drying temperature viz. 110°C.

One has to consider the state of the residue. One has to indicate whether one is dealing with a resinous residue or a residue with oily constituents. If one can establish the condition of the residue quite unambiguously one could permit a larger amount of residue than is prescribed by the supply specifications. The RLM (Dr. Dehmlow) point out that fuels with a high residue of an oily nature may be diluted with a fuel of low residue in such a manner that the residue of the mixture satisfies the conditions of supply. This is, however, not permissible if the residue is a resin. Even among the resins themselves one has to make distinctions between more or less noxious ones. Newly formed resins are less noxious than older ones.

The supply specifications should be as severe as possible. Therefore the RLM cannot permit mitigation of the supply specifications. This had been proposed by one station on the basis of the ambiguity of the results of bomb tests. It is pointed out that polysulphides were very important in the practical storage of cracked gasolines, the former were formed by the treatment with a solution of sodium plumbite. During the storage of olefinic fuels it became apparent that lead tetraethyl may also act as an inhibitor. This is quite comprehensible from a theoritical point of view since even oxygen may have an inhibiting action on some substances (e.g. at higher pressures). Carbon disulphide decomposes lead compounds even in the dark. The method of Yule and Wilson can give no more than an indication in the control of peroxide determinations; the values obtained from this method are not accurate. When fuels are stored in smaller vessels the results are less favorable than in larger vessels because of the relative increase in the surface. Small vessels are therefore to be preferred when the storage characteristics are judged. If the storage vessels are opened frequently one has to expect an increased formation of resin. For samples with the same resin content there is a linear relation between the logarithm of the time of resin formation and the reciprocal of the temperature.

There is some variation in the composition of the ethyl fluid. Newly opened containers with ethyl fluid should therefore always be subjected to a lead determination. The question is still open, whether one can infer anything as to the TEL content of the ethyl fluid from the varying behaviour of leaded gasolines.

An empirical datum was reported from Travemünde (Dr. Wallner): Practical difficulties were already experienced in the Me 109 engine with a fuel which had 20 mg resinous residue. In Rechlin 60 mg of resin were added without any operational trouble occurring after a 50 hours run. In USA gasolines with 120 mg of newly formed resin could be used without difficulty.

The practical evaluation of the resin determinations is based on empirical data which have been taken from the carburettor engine and from unleaded gasolines. In this connection one still has to consider that the unfavorable effect in the inlet system is noticeable only when the temperature there is above the dew point. Otherwise resinous components will be dissolved in the gasoline and thus come into the combustion chamber and burn. One has to expect troubles with resins in the case of injection operation:-

1) At the injection nozzle (one would have to find out whether the formation of residues is a physical or chemical effect

2) At the piston rings through coking and piston ring sticking.

It is generally agreed that the quantity of permissible resin should be restricted to 10 mg. It is recommended however to carry out experiments in order to fix accurately the limit beyond which the resin content must not go in injection operation.

To 111 Practical storage

The judgment on the bomb test by the I.G. (Dr. Ester) is not as condemning as the judgment of the lecturer. If an unleaded gasoline gives a bad bomb test one can infer that the storage characteristics will be bad; but this inference cannot be made for highly aromatic fuels. Thus three different leaded highly aromatic fuels showed no change at all after two years' storage. The fuels were however stored in completely full barrels which were not opened during the storage time. The conditions may well be less favorable in the case of the fuels used in practice since there is much contact with the air; above all one has to assume that the fuel is trasferred about ten times from vessel to vessel in its course from the manufacturer to the consumer.

In Rechlin practical experiments on injection engines were carried out with fuels with resin additions up to 40 mg. (Rechlin) No bad effects or deposits have ever been observed. The resins that were added, however, were probably not identical with those formed in the fuel. The solubility of resins in the fuel is important for the practical effect of large quantities of resin.

To IV :Inhibitors

The significance of natural inhibitors is pointed out. Thus one frequently finds 0.01 to 0.02% of phenols or even other inhibitors which are definitely advantageous. All the same it is not envisaged to alter ~~the~~ supply specifications so as to admit these inhibitors. It might occur that the chemical groups in question include some accelerators as well as inhibitors It is therefore advantageous to use inhibitors of known compos- ition (Wifo, Dr. Kiemstedt). One could also assume the point of view that one should permit a competition between natural and added inhibitors in such a way that consumers receive both types of fuel and then judge for themselves (Rechlin, Dr.Werner).

The water solubility of inhibitors must not be too large because the fuels come into contact with large quantities of water in practice. A sufficient number of inhibitors is available however which are insoluble in water (particularly those inhibitors containing nitrogen) and which also do not impart a strong colour to the fuel. A coloration could be permitted by the supply specifications if it can be proved that the coloration is due to the inhibitor.

One should not carry out corrosion experiments with inhibited fuels on too small a scale: experiments with small sheet iron strips give a bad picture; preferably one should cut the storage cans open after a certain storage period and then investigate the cans. In the case of mixtures of inhibited fuels one should examine the extent to which the inhibitors influence one another.

Resolution:

It is proposed to carry out storage experiments with inhibited fuels for the following purpose:

1) To obtain by the addition of inhibitors fuels which are

stable on storage.

2) To find out the effect of the inhibited fuels on the tank.

3) To find out the relative effect of inhibitors on one another.

Travemünde and Rechlin are the research stations. The highly aromatic fuels under investigation are provided with inhibitors by the manufacturers themselves. The amount added should not exceed 0.01% (the cup test must not exceed 10 mg/100cc) The addition is made 1 to 2 days after the fuel has been manufactured: 200 litres each of inhibited and uninhibited fuel are sent to the research station simultaneously with 200 litres of uninhibited fuel which are sent to the DVL. All the fuel has to be sent away without having been leaded. Information on the quantity and kind of the inhibitors have to be available to the-RLM (Dr. Beyer, GL 5 11) early enough for the RLM to cause the inhibitor to be changed, should different manufacturers have intended to use the same inhibitor. The latest date for the dispatch is the 5th July 1941.

The material for the experimental vessel is: Iron, galvanized iron, case hardened steel and one material which has yet to be announced by the RLM.

The fuels are rated by means of the normal laboratory methods of analysis.

To V Other test-methods

Uniform application of methods is the purpose of the design regulations. It is not possible to carry out proposals for alteration very easily; as a rule one will have to make ring experiments before making alterations. RLM stations may take part in the ring experiments of industry only if the RLM has been informed about it. The lack of staff prevents one carrying out a large number of experiments.

Laboratory methods may be divided into those which are intended for manufacture control and those which are intended for use in testing for suitability in practice.

Since a relevant DIN-sheet is not yet available, RLM directions shall be issued for the selection and drawing of samples.

Dr. Velde reports that H_2SO_4 methods have not proved themselves for making separate determinations of olefins and aromatics. The Kattwinkel reagent failed in particular in the presence of larger amounts of compounds which contain oxygen. Anything extracted by this reagent is not denoted as "aromatics" but as "soluble in sulphuric acid-phophoric acid" (SPL). The ratio of acid: fuel is 4:1.

The method of Rosenmund and Kuhnhenn is recommended for determining the iodine number of primary products. Pure xylene gave an iodine number of about 7 according to the method of Hanus . The consequences following from a knowledge of the iodine number are of practical importance (e.g. unsuitable gasolines may have to be hydrogenated once more). With respect to it is proposed to use for the present the form of the Hanus method contained in the BVM 1938. The second proposal is that until clarity has been obtained the upper limit for the iodine number should be eliminated from the supply specifications thus getting rid of the practical difficulties of supply. The RLM accept the first proposal but not the second. The I.G. is to publish its test directions for the determination of the iodine number; they pointed out however that their directions are not yet ripe for publication. The method of the central bureau shall also be taken for comparison.

One of the two methods of determining lead (by means of trichloro-acetic acid), by the one by Dr. Widmaier, has a form similar to that of Dr. Morghen, proposed at the DVL. The apparatus employed is also the same as that of the DVL (DVL-FB 1292). It will probably be left to later judgments to decide whether the one or the other method is the more suitable.

Resolution:

The directions for the determination of aromatics and for bomb ageing are to be altered by the DVL. The directions of 1938 shall be used for the determination of the iodine number.

Ring experiments are envisaged for the determination of aromatics and of the iodine number as well as for bomb ageing. The RLM shall inform the DVL as to which stations should participate in this work.

The DVL proposes the methods to be tested to the various stations and then undertakes the dispatch of the samples.

FD2877,46113 NID/PG/25409

Industrial Group :- Car Industry,
Berlin.

30th May, 1942.

re :- Improvement of low temperature starting capacity

In addition to and in accordance with our letter of May 19th 1942, please find enclosed the detailed account of the meetings of May 14th and 15th,

etc., etc.,

Signature.

RECORD

of the meetings on May 14th and 15th, 1942, at 10 a.m., in the House of the Industrial Group :- Car Industry, 8 Hardenbergstrasse, Berlin-Charlottenburg 2.
re :- Improvement of low temperature starting capacity

Present :-

Authorities :-

The "Führer's" Inspector General for motor-cars (GBK)		Werlin (2nd day)
		Zanke (" ")
		Slevogt (1st and 2nd day)
Deputy-General for motor-cars		Lt. Junkers (1st and 2nd day)
Commander-in-Chief/Army Agk		Col. Gothsche (1st day)
	Wa Prüf 6	Col. Rothardt (1st and 2nd day)
	Training Dept. for Army engines	Col. König (1st day)
		Lt.Col. Holzheuer (1st day)
	Ag K/M	Major Ing. Kozinowski (1st day)
	Wa Prüf 6	Hausmann (1st and 2nd day)
	Wa Prüf 6	Dr.K.O.Müller (1st and 2nd day)
		Dr.Weber (1st day)
		Dr. Schildwächter (1st day)
	Wa Prüf 6	Strunz (1st and 2nd day)
	Wa Prüf 6	Cremer (1st and 2nd day)

Accessories - industry :-

Akkumulatorenfabrik System Pfalzgraf	Pfalzgraf	(1st day)
Bartel	Rotho	(" ")
Robert Bosch G.m.b.H.	Dr. Rassbach	(1st and 2nd day)
	Dr. Callsen	(" " " ")
	Dr. Heinrich	(1st day)
	Dr. Buck	(" ")
Deutsche Vergaser	Gruber	(" ")
	Dalchow	(" ")
Deutsche Waffen und Munition	Wiethüchter	(" ")
	Schmucker	(" ")
Garbe, Lahmeyer & Co.	Zeuchen	(" ")
E. Hähnel	Breitling	(" ")
A. Kärcher	Kärcher	(" ")
Sächsische Lötkolben-Fabrik	Hähnel	(" ")
VDO-Tachometer	Dr. Lertes	(" ")

Oil - industry :-

Deutsche Gasolin	Dr. Brunck	(1st and 2nd day)
	Lüth	(1st day)
Deutsche Vacuum Öl A.G.	Richter	(1st and 2nd day)
	Thurn	(" ")
Nerag	Dr. Gönningen	(" ")
Jul. Pintsch	Erichsen	(1st day)
Rhenania-Ossag	Rössig	(1st and 2nd day)
	Dr. Lütkemeyer	(2nd day)
Zentralbüro für Mineralöl	Dr. Charpentier	(1st and 2nd day)

Car - industry :-

Auto-Union	Mader	(1st and 2nd day)
	Dr. Enders	(1st day)
	Bareiss	(1st and 2nd day)
	Neumann	(1st day)
B.M.W.	Strobel	(" ")
Büssing NAG	Dr. Bäse	(" ")
Daimler-Benz	Oberbaurat Schmidt	(1st and 2nd day)
	Bokemüller	(" ")
	Winkelmann	(" ")
Hanomag	Pollich	(1st day)
	Dr. Franck	(" ")
Klöckner-Humboldt-Deutz	Hasselgruber	(" ")
	Prettenhofer	(" ")

MAN	Huss	(1st and 2nd day)
	Hofmann	(" ")
Opel	Boehner	(" ")
	Medick	(" ")
Phänomen	Hennig	(1st day)
Dr. Porsche KG	Vogelsang	(" ")
Wirtschaftsgruppe Fahrzeugindustrie	Vorwig	(1st and 2nd day)
	Klümpers	(" ")

Chief Government's Surveyor Schmidt is President of the Conference where the Chairmen of the Committees make their report on the work done and their proposals on improvement of low temperature starting capacity, which are now discussed in detail :-

I

Adaption of the electrical plant to low temperature starting conditions. (Chairman of the working committee, Dr. Callsen (Bosch)).

1) Measures taken concerning the battery.

a) Refinement of test procedure

The makers of the lead storage batteries have taken up this suggestion already made in the conference of April 9th, and Mr. Pfalzgraf submits a draft - here enclosed - which will be published as section 5 to DIN 72311 (Deutsche Industrie Norm - German Industrial standard). This standard draft provides for a tightening up of the test regulations for determining the starting capacity, by 20%. In this case it is, however, necessary to increase the maximum lead content by 8% for the battery built according to DIN 72311, page 2, but the maximum nickel content hitherto permissible for the battery built in accordance with page 3 is still sufficient to improve the starting capacity by 20%. The Government department has already given oral agreement in principle. In the first instance this agreement is given for two years. A written confirmation will arrive shortly. (In the meantime the Government department for metals has given written permission dated 19th May, 1942). Furthermore a better separation between the plates must be achieved in order to improve the starting capacity of the battery. The use of "Decelith"-separators with greater permeability seems to have good prospects of success. These perforated and corrugated separators are principally made by the firms : "Conti, Hannover" and "Deutsche Celluloid Fabrik, Eilenburg (German Celluloid Factory, Eilenburg). The intended improvement will probably necessitate an alteration of existing plant of those two makers. A priority permit covering delivery of the necessary tools might be obtained by the "Führer's" Inspector General for motor-cars, or by the "Deputy-General for motor-car affairs".

These stricter test regulations can be put into force on August 15th 1942. Generally this period for the change over is considered too long. Mr. Pfalzgraf, however, emphasises that this is the earliest date possible.

b) Uniform directions for the supervision of lighting and starter-batteries at the front.

For this Mr. Pfalzgraf submits a draft as per enclosure No.2. It appears that its final wording must still be discussed with Dr. Callsen and approved by the relevent Army authorities.

c) Warming up the battery

At -30° the capacity of the battery is practically nil. After thorough experiments the working committee suggests therefore warming the battery up or keeping it warm by means of a wick-lamp as having the best prospects of improving the low temperature starting capacity of the battery. It was found for instance that the efficiency of the starter could be raised by approximately 40% and the capacity of the battery by approximately 400% when it was warmed up from -20 to +10°.

As warming-up the battery or keeping it warm takes a long time (up to 18 hours) and as no attendance at all can be given during this time, it is imperative to use the right lamp for this purpose. Two lamps have been found to be useful. One is a lamp made by Messrs. Nier but burns with kerosene only, and another one is a burner made by Messrs. Thiel and Bardenheuer, Ruhla, Thuringia, working with all Diesel fuels, and also with ordinary gas oil. The letter has been tested in particular by Messrs. MAN.

The first lamp would permit a comparatively simple solution of the capacity problem, but the supply of kerosene is hardly possible. For the second lamp, though, Messrs. Thiel and Bardenheuer could supply wick-burners in sufficient quantities but the lamp itself would have to be made by a larger firm (e.g. by Messrs. Nier).

After thorough discussion agreement is reached in the latter sense. Units operating exclusively on gasoline need to be supplied with Diesel oil. As, however, the lamp uses very little, no difficulties will be met and the army also agrees to it.

Dr. Callsen, Mr. Mader (Auto-Union), and Mr. Huss (MAN) will work out a suitable container for the wick-burner and examine with the relevant firms the best means of producing it. In order to simplify the production of this container, it is agreed to use one burner lamp only and if possible to choose a pot already on hand. One, two or three such lamps can then be used according to the size of the battery.

Messrs. Bosch found out that for sufficient heating we need :-

1 lamp for a 6 volt/50 to 90 amp/hours battery
2 lamps " " 12 " " " " " " "
3 lamps " " 12 " 90 to 150 " " "

These data will however be examined again by Messrs. Bosch before a final decision is made. The firms must have the dimensions of the "mono-lamp" (single-burner lamp) by May 25th 1942. In the meantime Messrs. Thiel and Bardenheuer can supply the burner and with a pot specially made for the purpose heating experiments may be undertaken at once.

The army authorities (Col. Gothsche) believe they will require about 1.2 million. Needless to say the burner of which the sample still contains substitute-metals will be made of sheet steel or plate steel or something similar. Messrs. MAN inform us that relevant experiments have been made and that probably a change over will not be difficult.

The urgent need for this lamp is again emphasised. The aim for the future is to make a heating lamp which can be fed with any fuel and which will warm up a battery without any attendance. We shall also try to make a lamp which will burn with loaded gasoline and which will be ready for the winter. Dr. Callsen reports that experiments have been begun but that one cannot say if such a lamp can be got ready for the coming winter.

A further task for the future is to use cooling-water or hot air from the exhaust whilst driving for the heating of the battery. Here the problem to be examined is whether the battery can be kept sufficiently warm during the normal waiting period (about 10 hours) when it had been warmed up whilst driving, by providing good heat insulation.

According to the High Command it is desirable that this heating up of the battery could - if possible - be combined with heating of the driver's cabin also.

d) Heat-insulation of the battery

Heat insulation is essential in order to warm the battery up and to keep it warm for as long as possible. It should consist of a plywood or kapok box with air as insulating layer. As a minimum insulation, 10-15 mm. air is suggested, and the thickness of the wood should be 15-20 mm.

Dr. Callsen has already sent drawings about this to the firms. We await their final decisions. We may say now that such insulation-boxes can

can be fitted to vehicles already in use at the front: with lorries this is always possible, with passenger-vehicles it will be possible in most cases. Though it will not be possible to make the same pattern of insulation-boxes for the various battery-sizes because there are so many different places where the battery is mounted in a car, a large variety of makes must not be allowed as it would impede easy handling of them necessary at the front. This means that we must aim at obtaining a few selected patterns. As soon as we have the answers Dr. Callsen will submit suggestions how best to combine all the types. But the firms must consider this problem at once and - as soon as Dr. Callsen's final proposals are at hand - they must together with the army tackle the production and supply of these boxes, as far as their particular types are concerned. For future new production the mass-produced fitting of a heat-insulation sufficient for the battery must be taken into account.

e). Best position for the battery in the car

In the first place, underneath the front seat is thought to be the best position to fit the battery in future because at this point there is the largest space for a satisfactory heat-insulation and mounting of the heat-lamp and because the battery does not receive any additional heat from the engine in summer.

The next best place is underneath the bonnet. In this case special attention must be paid in summer to sufficient fresh air cooling of the heat-insulated battery. In this connection is must be emphasised that the insulation box must not be taken away in summer but care must be taken to provide enough cooling.

Fitting of the battery on the running-board is rejected for many reasons. This place would be most unfavourable as regards low temperature starting capacity as the battery is there subject to cold more readily than anywhere else.

The "Opel" factory takes over the work of studying the future battery-mounting underneath the bonnet as regards heat-insulation and fresh air supply.

f) Easily broken cable-connection

In order to make it easier to take batteries away we suggest according to an idea of the Gebekraftfahr a battery terminal with a screw which can be loosened easily. In this way by means of a thumb nut the cable may be loosened or tightened easily and simply without breaking the connection of the pole-terminal. Samples of this new terminal are shown and approved by all. This terminal meets the essential requirement, viz., to use the terminal of the pole already there, and protects above all the head of the pole which will not now be destroyed even when the battery is removed frequently.

This battery terminal could be supplied by Messrs. Eifeler Metallwerke in sufficient quantities.

It is decided to fit the terminal to all batteries which for reasons of space have no heat insulation and therefore cannot be heated in the car, in order to avoid destruction of the pole-head terminal. Of course this top terminal cannot be used with all batteries because of lack of space, but if possible this new terminal should also be fitted to the batteries with heat-insulation so that when removing the battery for charging, its advantages may be used.

g) Terminal for an external source of current

At the same time we suggest, as a task for the future, providing the vehicle with a pair of terminals to make it possible to charge the battery in the vehicle and to start it with an external source of current. The best place for fitting these terminals in accordance with the wiring is again the insulation box. For this device Messrs. Bosch have made a suggestion to the firms. When deciding upon the insulation box, the place for fitting the external current terminals should be considered

2) Alteration of the regulator features.

At the meeting of April 9th 1942, a proposal was made to alter the features of the regulator in order to improve the low temperature starting capacity. Messrs. Bosch have thoroughly worked on this problem. They found, together with Messrs. Garbe, Lahmeyer & Co., that the present known temperature-compensated regulators - including the type produced in the U.S.A. by Ford - do not allow a quicker charging of the battery when there is a very low temperature. In order to achieve an efficient improvement when charging a battery cooled down to approximately -30°, the voltage of the regulator must be increased to 18 volts. Such voltage increase can however not be permitted, having regard to an overloading of the electrical equipment. Furthermore the regulator must be controlled by a temperature controller on the battery and not as hitherto by the temperature compensator on the regulator itself. In this latter case the temperature compensation is to a large extent rendered ineffective because the regulator itself is warming up. When the battery is kept warm, the problem of the regulator may be disregarded for the time being, as Dr. Callsen pointed out.

This, however, does not imply by any means that research on this question should not be continued, but this technical and production problem will take a long time to solve and so can have no practical consequences during this winter. Therefore this question, which is likely to influence greatly the electrical system (protection against overloading), must be left to future experiments to be pursued with energy.

3) <u>Ignition-spark control.</u>

The question was also discussed at the meeting of April 9th 1942, of regulating the resistance in the ignition-coil in order to obtain a good ignition-spark at the moment of starting. Dr. Callsen reports that in the view of Messrs. Bosch and Messrs. Gerbe, Lahmeyer & Co., we need not increase the ignition-effect during the starting process when the battery is warmed up. Apart from that, he reported that the ignition coils for 12-volts made nowadays by Messrs. Bosch correspond already in their ignition effect to those with the rheostatic resistance formerly used during the starting process.

II

Warming-up device for engines, gears and back-axles (Chairman of the Committee, Mr. Winkelmann (Daimler-Benz)).

The Army has ventilated this question for some time, according to Colonel Rothardt. They considered providing heat from the cooling-water, or by means of a blower. As there was not other instrument available, the cooling-water heating apparatus by Riedel only was used as a make-shift last winter. Now it will be replaced by a new heating device called a "heat-exchanger". This instrument is made and supplied by Messrs. Deutsche Waffen & Munitionswerke, Berlin-Borsigwalde (German Arms and Munition works, Berlin-Borsigwalde). The source of heat for the heat exchanger is a blow lamp. It is however essential that it burns for 30 minutes without going out. The warming up of a battery is a slow process taking a long time and keeping it warm is considered preferable. An engine, however, must be heated up in such a way that it gets warmed up from -30 to 40° within 20 to 30 minutes at the latest and is ready to be started. The exact heating up times for Diesel and carburettor engines fixed by the Army will be made known shortly. The development of heat-retaining equipment for the engine was postponed intentionally.

Apart from that, various hot-air heating devices especially for air-cooled engines, were worked out. Here again air was heated by blow lamps and then supplied to the engine or again to the cooling-water by blowers or by air pumps.

The working committee-Chairman Mr. Winkelmann, made experiments in the meantime and in this case suggests and agrees in principle to the use of the heating device (heat-exchanger) as developed by the Army. Two experiments by Daimler-Benz showed that engines heated up more quickly by water than by oil. The reason is that water allows a more favourable transfer of heat and it has a greater specific heat than oil. Besides, water gets at those parts of the engine which offer the greatest resistance when cold. Therefore it appears that heating up of engines by oil should be postponed in favour of the cooling-water process. But if oil is not warmed up it must be diluted to a certain degree during periods of low temperatures. How much dilution is required depends probably upon the various car types, and should be examined for every one of them. According to experiments hitherto made, Mr. Winkelmann believes that a dilution of oil of about 30% will be required without damaging the engine. Dilution of oil with Diesel fuel should be avoided on principle in engines because of its strong dispersion with regard to the setting-point. Dilution with light spirit already supplied for experimental purposes proved advantageous. The working committee does not think it necessary to warm up the gear box and the back-axle. It should suffice to dilute the oil in the gear-box or in the back-axle with 20% gasoline or gas-oil. It remains to be seen which is better for this purpose. The experiments at Daimler-Benz show that motor-oil cannot be used in the back-axle because here the film strength of motor-oil is not sufficient.

In order to get a car started in extremely low temperatures, experience in the East has shown that it is sufficient to add at very low temperatures 15% gasoline in the case of standard engine and rear-axle oils, and 10% gasoline in the case of standard gear oils.

The state of oil in the back axle can be found out by putting one driving-wheel on a jack or block and then cranking the engine. As for the gear, the driver of the car will be able to feel the thickening of the oil when changing gears.

Dr. K.O. Müller is reluctant to let the men at the front dilute the oil when this is necessary. He believes that this cannot be done correctly by them. He would like to start with a thin oil. His opinion is shared to a large extent by the car- and oil industry. Therefore the proposal of the Army High Command of using low viscosity oil with the same film strength for both summer and winter is agreed. There is hardly any difficulty in preventing leakage. Dr. Müller will put the results of experiments made in Wünsdorf at Mr. Winkelmann's disposal.

This results again in a supply- and a filling problem which, however, can easily be solved. As far as difficulties crop up in this direction we may use the old gear- and rear-axle oil with gasoline or gas-oil dilution as before.

So we only need the heating device mentioned before to heat the engine up. Only the one draft apparatus will be needed for smaller engines. For larger engines with a 5-litre stroke-space we need two one-draft apparatuses connected in parallel. They should be fixed permanently on the car in the branch connection of the cooling-water. In summer, when the "heat-exchanger" is not needed, it should be left on the car all the same. A blend flange can put it out of action and protect it against corrosion. It works on the thermosyphon principle. One or two blow lamps which are fed by gasoline or light spirit serve as the heatingsource.

Both devices, the "heat-exchanger" as well as the blow lamp, need further technical development still.

If leaded gasoline is used, choking occurs not only in the nozzle but also in the angl- plate of the blow lamp after some burning. The sediments are so hard that they can scarcely be removed in a practical manner.

Up to now brass was used very much in blow lamps. But in the meantime there has been a great change over so that bronze is needed for the burner only. In future we must try to change them also into steel-burners. Experiments in this direction were made by Messrs. Hähnel, and promise some success.

The greatest bottle-neck at present is the production and supply of the necessary quantity of blow-lamps. The Army has already placed an order in France for 100,000. In spite of this, special action is needed in any case to help the manufacturing firms.

It has now been definitely decided to use as a rule light spirit only as fuel for the soldering lamps. This light spirit is anyhow at our disposal both with Otto-engines and Diesel-engines for the purpose of diluting oil. Should supplies fail at times, normal gasoline may be used. This however will cause a smaller working capacity of the lamp.

The way in which the "heat-exchanger" works and also the experiments with it will be found in Mr. Winkelmann's notes of May 1st 1942. These were sent to all members of the committee and to the car firms, together with drawings. These notes were very elaborate so that we here simply refer to them. As the industry, together with the Army, shall be responsible for the manufacturing of this device, Mr. Winkelmann is requested to speed up its technical development in collaboration with the Army. There are suggestions for improvement of this device from many quarters which will have to be taken into account: e.g., standardised flanges should be used for the mounting and the formation of water traps must be prevented because of the danger of freezing. Furthermore, it would be good to try and make this device in such a way as to be able to mount it both horizontally and vertically. In future it will be best to get the collaboration of a capable radiator-factory or a plate-making firm to help in working out a good "heat-exchanger" (we think, e.g., of Messrs. Längerer & Reich, or Süddeutsche Kühlerfabrik Behr & Ambi-Budd).

Further satisfactory experiments with the "heat-exchanger" have been made by Messrs. Hanomag, Büssing-NAG, Klöckner-Humboldt-Deutz, as well as by Messrs. Daimler-Benz. Büssing-NAG keeps an engine going already for 80 hours with an oil-dilution of 30% without having any difficulties. Klöckner have not completely answered the question of diluting lubricating-oil.

Finally we find it necessary that this "heat-exchanger" goes to each firm as quickly as possible. It will be mass-produced later. At present the experiments mentioned above are made by make-shift instruments made by each firm on its own. When all the firms have a mass-produced apparatus each firm must examine how best to instal it in their various types of cars which are now used at the front or still on the war production.programme. The installation itself should if possible be done by the servicing and maintenance staff of the firms as there is a danger that it is not done correctly by others.

The Army has already ordered 140,000 "heat-exchangers" with Messrs. Deutsche Waffen- und Munitionswerke (German arms- and ammunition works), and the first 5,000 are said to be ready in approximately four weeks. Mr. Strunz and Mr. Wiethüchter fear a delay in this supply if single specially made "heat-exchangers" must still be sent to the firms before this time. After some discussion it is agreed that 14 one draft and 9 double draft "heat-exchangers" will be sent to committee members by May 25th 1942.

Mr. Wiethüchter is given an exact distribution list during the conference. (During the meeting in the afternoon it was decided that 30 one draft "heat-exchangers" should be provided).

Mr. Winkelmann will see if Daimler-Benz, Marienfelde can send some welders and other workmen for this purpose and will then communicate with Mr. Wiethüchter.

All members are clear about one thing. The most important thing is to supply the "heat-exchangers". All other wishes, e.g., as regards profitable manufacture or further technical development are of a secondary nature. The committee is furthermore convinced that the suggestions mentioned above are for the time being the only possible ones for heating up engines.in order to overcome the difficulties of starting engines during the coming winter.

In order to fit all this into the priority programme Colonel Rothardt will communicate with the GBK (Lt. Junkers) if the Army High Command should be unable to go ahead with the organisation hitherto in force.

Future tasks are :-

1) The mounting of a "heat-exchanger" in a standardized form. If possible the exhaust-gases of the "heat-exchanger" should be used for warming up the carburettor and the suction-tube.

2) The development of an instrument which not only heats up the engine but keeps it warm.

3) With regard to air-cooled engines, the experiments with the oil heaters already tried by the Army should be continued. The bottleneck of making blowers is emphasised. For the rest the makers of air-cooled engines are requested to investigate the possibilities suitable for their engines.

4) Air-heating by blowers will also be examined. If these generally larger devices cannot be supplied in larger quantities Army units can at least use them as aggregates.

6) In order to avoid any unnecessary duplication emphasis is laid upon the necessity for manufacturers to work in closest collaboration.

Messrs. Auto-Union and Messrs. Bayerische Motorenwerke were elected new members of the committee.

III

Measures regarding mixtures and fuel (Chairman of the committee 8 Mr. Boohner (Opel)).

The working committee has examined the problem thoroughly and found differences concerning the fuel and the winter-oil. These differences, however, are treated separately later in the report.

The experiments at Opel's refer to the 3.6-litre engine with a 12 volt/50 amps/hrs battery, starter 1 h.p., throttle-valve carburettor Opel down draft. At the first cranking resistance was found without gasoline and without ignition and then starting trials were made with gravity feed gasoline and ignition switched on. The number of revolutions of the starter was nil when oil was diluted with 15% light spirit and at a cooling-chamber and battery temperature of -45°. Under the same conditions the number of starting revolutions was 8 r.p.m. when oil was diluted up to 40%. The result was :- The warmer the battery and the greater the oil-dilution, the higher the starting revolutions. The larger electrical equipment as formerly used in the "Opel-Blitz" 3 ton lorry, viz., 1.2 h.p. starter and a 75 amps/hr. battery, gave approximately double the revolution figure with a corresponding improvement of the starting time.

The starting tests with oil dilution of 15%, cooling-chamber -45°, and battery temperature +20° showed that only when about 150 ccs of warm light spirit were poured into the air-inlet and at the same time the starter was operated, ignition took place at once and the engine ran.

With an oil dilution of 30%, cooling-chamber temperature -40°, battery temperature +7° (car) gasoline of -40° was used as starting fuel. The engine was started by pulling and closing the choke and fully opening the throttle in addition to closing temporarily the carburettor air-inlet completely with the gloved hand. The revolution figure of the starter was

30 r.p.m. in the beginning. The first ignition took place after 17 seconds at about 70 r.p.m., and after 110 seconds the engine ran.

The other firms represented in the committee also made experiments, but they could not reach temperatures of -40° in their cooling-chambers and therefore they made their experiments at temperatures of -28° and -30°. Besides, time was too short to make thorough tests.

Comparative tests made by Auto-Union and Daimler-Benz showed already that the new winter oil as compared to the old standard oil really improved starting by 7 to 8 degrees.

Experiments with the Horch 3.8-litre, 8-cylinder engine, with a battery of 75 amps/hrs., plus 10° heat and 1.8 h.p. starter showed without oil dilution a starting revolution figure of 40 r.p.m. at -28°. Through injection of 12 ccs light spirit this figure rose at once to 60 r.p.m. and after 34 seconds the engine ran. This showed again that the use of light spirit when starting plays a very important part.

The Daimler-Benz tests proved also that starting requires more fuel. According to Mr. Winkelmann this depends upon the type of engine. Side-valve engines used more fuel than overhead-valve engines. It was also found that the starting carburettor by "Solex", regulated correspondingly, can feed the engine with the required amount of fuel. No difficulties were met with a 3-litre overhead-valve engine fitted with a gravity feed carburettor with a mass-produced standard nozzle 160/5 and 50 r.p.m.

Experiments with a 170 V bucket-seat car showed - as already found at Opel's - that under certain conditions a "heat-exchanger" is not needed. But Daimler-Benz insists upon having the device also with this type as conditions are usually less favourable in practice than during experiments (e.g., the sparking plug is in bad condition, etc., etc.) If, at the front, supply of light spirit does not arrive, in time, and so all other means fail, the warming up of the engine will still be possible.

Messrs. Phaenomen and Porsche K.G. report on the question of what measures should be taken in the case of air-cooled engines. According to what has been said before a "heat-exchanger" cannot be used to warm the cooling-water. As time was too short and above all because there was no cooling-chamber for temperatures down to -40°, experiments could not yet be completed.

Messrs. Phaenomen first tried oil-heating by means of a soldering-lamp. This, however, is not advisable, because it is too dangerous and can result in tension-cracks in the cylinder.

Furthermore, the following special starting means were used in experiments with the new type "Granit 1500" during last winter :-

Injection of about 2 ccs. of mineral oil or fuel per cylinder into the priming-cocks of the cylinder-heads at the beginning of the cooling-times.

Injection of the same quantity of fuel before starting.

Pre-heating of the lower part of the carburettor by a heating flange of 30 amps. current strength built in between carburettor and suction-tube.

The oil in "KdF" cars was also warmed up with a soldering lamp at first and an increase of temperature was obtained up to 66° within 8 minutes. This action of the soldering lamp which should burn with a large flame will be improved still further in order to reduce the heating-up time of the oil. When oil was diluted with 30% light spirit and the battery was warmed up by 20° the engine started running after only 30 seconds with a starting speed of 87 r.p.m. The temperature, however, in this case was not below -28°.

It is believed by Phaenomen and others that by using light spirit and the other expedients mentioned already, a heating device (the heat-exchanger) is not needed. Final results will be gained by the end of this month and will be submitted to a meeting of the working committee on June 2nd 1942. If it should prove impossible to obtain temperatures of -40° in the cooling-chambers, the experiments must be done at temperatures of -30°, and conclusions may eventually be drawn for conditions at -40°C by using given correlations.

It is stated that injector-nozzles and the alteration pieces required can under no circumstances be supplied in time for the coming winter. Furthermore the injector-nozzles can only be used for the new production and cannot afterwards be built into those cars already made. Apart from that, a certain skill is needed to operate these injector-nozzles. We cannot expect to have skilled men at the front at all times. It is therefore considered better not to use this means.

The other firms of the committee report in a similer way. Final judgement may be passed only when all the experiments are made and most important of all when they have been made at extreme temperatures of -40 to -45°. Immediate action cannot therefore be taken with regard to this point. The firms of the working committee will conclude their findings by June 1st 1942 and submit their proposals.

The following matters should be considered for further experiments :-

1) Pre-heating of the battery up to at least +10° or sufficient insulation of the same, guaranteeing this temperature with certainty during a waiting time of 10 to 12 hours. For starting, ignition by

battery has been found better than magneto ignition.

2) Oil-dilution sufficient to allow the required starting revolutions - it has not finally been established whether 30% dilution is the right one. The experiments so far made did probably not take into account the fact that the admixture of light spirit must under no circumstances be made when the oil is warm as the low boiling light spirit will evaporate too quickly.

3) The engine should be fed with a sufficient amount of fuel. It is necessary to examine in particular the delivery pump in relation to low temperature. The flowing and delivery characteristics of the fuel at -45° must at all costs be examined exactly. We may find that the parts and devices we use now fail altogether. It would be advisable to fix a gravity feed tank of about 2 litres capacity with a special tube of sufficient diameter leading to the carburettor. It should be possible to turn the tube off by a tap or cock from the driver's cabin. The filling should consist of light spirit, starting-fuel or gasoline. We must find out if the head is sufficient. If not a membrane pump which may be operated by hand or by foot must be inter-connected.

4) A special investigation of a carburettor particularly suitable for feeding the engine with sufficient fuel for starting in all circumstances - in this connection the following fact must be noted :- The "Opel throttle-valve carburettor" is very much better than the starting carburettor by "Solex". Furthermore, considerations emerge in regard to low temperature starting which could not be followed up at a time when Army vehicles were forbidden to use the "Opel carburettor". So this whole matter must now be taken up again with the Deputy GBK General for cars and the Army High Command. Messrs. Opel therefore will apply for a new decision in this matter.

5) In the light of what has been said above, Mr. Bochner, acting for Messrs. Opel thinks that a heating-device like the "heat-exchanger" will not be needed. In spite of this opinion it is decided that all firms are to examine this problem in detail again.

Messrs. BMW were afterwards elected new members of this committee.

IV

Starting aids for Diesel engines (Chairman of the working committee, Mr. Bokemüller (Daimler-Benz)).

As Mr. Bochner's committee dealt only with starting aids for carburettor-type engines, a special committee for Diesel engines was needed. This committee for Diesel engines was formed under the Chairmanship of Mr. Bokemüller and confirmed at this meeting. Apart from Daimler-Benz, Messrs. Klöckner-Humboldt-Deutz, Messrs. MAN, and Messrs. Bosch are member of this committee.

In addition to the aids which increase the starting capacity at low temperatures for both carburettor-type and Diesel engines, there are some other various simple starting-aids for Diesel engines which can be applied with good success, viz. :-

1) An adjustable link for the control rod of the injection-pump to feed an increased quantity for starting.

2) Filling cocks for starter fuel at the suction tubes, and at the inlet pipes, or previous pumping of fuel by hand operation of the pump tappets.

3) Spraying nozzles at the inlet pipes together with a small auxiliary tank and hand-pumps (System Sum or Solex).

4) Electrically heated glow plugs or heating flanges in the combustion chamber or in the suction tube.

5) Hot air generator, operated by soldering-lamp, or burner for solid fuels.

Mr. Bokemüller made the following comments on the above :-

re 1) The adjustable fuel-valve fulcrum for the governor-rod may be used both for the cars to be mass-produced and for the cars already in service. The simplest way is to alter the adjustment of the governor-cams on the injection-pump. This can be done quickly with the aid of short working instructions. Therefore the committee recommends this to all Diesel firms.

re 2) Previous hand-pumping has approximately the same effect for the softening of the lubricating oil film of the piston-guide as filling a few ccs of Diesel fuel through the priming-cocks or filling-valves at the cylinder head cups or suction-tubes. As regards suitability for mass-produced installations or later installations, the remarks under 1) apply.

re 3) The use of spraying nozzles is much more difficult than the measures recommended in Nos. 1) and 2) (compare also what has been said before about spraying nozzles for gasoline engines). This device can probably not be used for cars already in service, at least not as an immediate priority measure.

re 4) Diesel engines with combustion chambers (anti-chambers), turbulence chambers and air cells and also mass-produced glow-plugs possess very excellent means for making starting easier. Heating flanges, however, have only a very limited effect at very low temperatures and their load on the storage batteries is 10 times greater than that of the glow plugs.

re 5) The "I.G. starting-charcoal" as proposed by Professor Wilke has a mixed reception. Some think it advantageous, some point out - as was already seen in the conference of April 9th 1942 - that we obtain the same effect with a rag soaked in fuel and with an open flame. In addition it should be emphasised that this "starting-charcoal" will not be available yet in the coming winter in sufficient quantities and its further supply will also be difficult. Col. Rothardt pointed this out when he spoke about the heating up device.

With reference to the proposals made above we can see that Diesel engines need not be heated up at temperatures down to -30°. The Diesel manufacturers will continue to test warming up devices for the cooling-water in order to reach a high safety-margin for low temperature starting.

This ended the conference as it was late (8 p.m.). Further discussion of problems still to be dealt with was adjourned to Friday, May 15th 1942, 8 a.m. This conference was attended by the gentlemen specially named in the list.

V

<u>Cranking devices to start the engine. (Chairman of the working committee, State-Engineer Heusmann (Army High Command).</u>

At first a crankshaft gasoline starter with a "Fichtel & Sachs" engine of 250 ccs. was developed for armoured cars and tractors. This method will be examined further for large engines; it is not of much interest here. Our problem is how to start the gasoline- and Diesel engines normally used for motor cars by means of an external power source.

The experience of last winter gained by the Army has shown that the "Orgassa" device is best. This starts the engine by a motor-cycle, the rear wheel of which drives a belt. Hitherto only a special motor-cycle could be used. Mr. Winkelmann developed this idea further and succeeded in connecting the motor-cycle by rollers. This made it possible to use any type of motor-cycle. If necessary, for larger engines, two motor-cycles or even a motor-car could be used as a power source.

There are generally no difficulties in starting a motor-cycle. There are always ways and means to park a motor cycle in such a way as to protect it against frost or to warm it up quickly. Besides, a motor cycle ready to start can start another one which will not start.

With regard to the cranking device for gasoline engines up to 4-litres capacity, Messrs. Bosch and the Army laid down the standards both for the cranking-dog and the shaft end of the hand-starter or the external starter. The Standard-Sheet DIN 73050 Fl has been sent to the firms concerned on May 6th by the industrial group so that they may introduce these patterns forthwith. Measures to introduce these new patterns later into the cars which are already used by the Army have to be taken by the firms when they have got in touch with the Army authorities.

Dr. Callsen reports that recently difficulties arose in fixing the cranking-dog to the crankshaft. Whilst everything is all right with the cranking-dog of the starting device so far as gasoline engines are concerned, a linear expansion of the thread was found when used with the Opel engine, with a torque of 45 metres/kilogram and an engine temperature cooled to -30°. The cranking-dog is shown and Opel will examine the matter. (In the meantime this has been done). It was found that Opel cannot use steel St C 16.61 but only tempered steel St C 45.61. This fact and Dr. Callsen's report will result in an alteration of the relevent notes on the DIN Fl-sheet. The firms will be informed.

Furthermore it should be noted that the external starter need servicing. It must not be pulled out of the cranking-dog before the engine is stopped as this would destroy the parts at the front of the engine. Simple working instructions will ensure correct handling.

Difficulties about fixing the cranking-dog to the crankshaft already met and mentioned above with regard to gasoline engines increase considerably with Diesel engines. Messrs. Bosch's experiments with a slipping or slide coupling were not successful. Therefore this was entirely abandoned. A solution is being sought by means of a direct or positive coupling. A diagram will be sent to the firms concerned.

The committee which is joined by Mr. Reitz of Messrs. Triumf will continue to examine the question of an external starter for Diesel engines under special consideration of the coupling problem. If it is found that an external starter cannot be operated by every soldier: regulations must be issued, according to which only "Schierrmeistern" (Senior skilled equipment N.C.O.'s) or personnel specially trained for operating the device will be allowed to handle it.

It is decided that each firm examines the fixing of the cranking-dog in the crankshaft of their own cars at the front and that they make the relevant tests. The first mass-produced starter devices will come out soon at Messrs. Daimler-Benz. Perhaps each firm may then have one in order to make their experiments. No difficulties will be met in getting motor-cycles from the home front. If, this however, should not be possible, two Army motor-cyclists could go from firm to firm with an external starter to test its cranking-dog with the crankshaft.

GBK decides that that is outside his sphere, but this should not prevent the Army High Command from finishing the work in collaboratorion with the industry.

Finally, questions are discussed which were already roughly dealt with above, viz. those relating to lubricating oil and fuel. They are examined in the light of the experiments so far made. As to the oil question raised by Opel, the oil industry make the following statement :- In order to clear up right away a certain prejudice of some motor car firms against paraffin base winter oils, it is necessary to point out various well-known trade-mark winter oils produced in peace-time which were also made fromaparaffin base. Some of them set already at -8°C or -20°C. Nevertheless they permitted good starting even at considerably lower temperatures, e.g., the oil mentioned first"Valvoline" always made starting possible at temperatures even below -20°C. This was a very good result in those times. On the other hand some oils which were still completely bright, clear and liquid at -35°C showed certain difficulties for starting already within the range of these temperatures, i.e. below -20°C. But also the "Arctic" oil of "Vacuum" which may be considered one of the best winter oils produced in Germany showed similar results with regard to starting capacity also below the real setting point. It is, however, true that this oil set only at approximately -20°C. Today's winter oil of "Vacuum" uses the same raw materials and the same process as the old "Arctic" oil, but its behaviour at low temperatures with regard to the practical starting of an engine is even better still. The same may be said of the other oils with a paraffin base, disregarding the fact that their analysis data may show them to set at approximately -16 to -20°C.

The only oil that we may call low-setting because it has a Voltol base is Shell's. We may, however, expect that the paraffin-based winter oils show similarly good results at the same "pole height" and testing conditions. Dr. Brunck believes the differences which these winter oils will show by virtue of their different significant methods of manufacture will not be large enough to be in comparison with the other uncertainties met in their practice, with low temperature starting at -40°C.

The prejudice against paraffin-base winter oils which at low temperatures assume the form of paraffin/oil paste and which is first recognised by the cloud point of the oil arose mainly from attempts to draw conclusions from viscosity measurements below their setting points as to their real flowing and low temperature behaviour in practice when starting an engine. With the exception of the "Schwaiger" viscometer which today permits us to draw reasonable conclusions as to the behaviour of a paraffin-base oil at low temperatures up to a maximum of -20°C there are no reasonable measuring methods for oil or oil-paste viscosities at low temperatures below the setting point of an oil. We give as counter evidence to the erroneous opinion outlined above the example of the old winter-oils mentioned previously and the partial results so far obtained from starting tests with the new winter oils which were made far below the setting-points of the oils in question. E.g., an 8-cylinder Horch engine was started without difficulty with a new winter oil not diluted at -28°C, having a setting-point of -16° to -18°C. The engine had a cold start standard