described in Engler-degrees of probably something like 750 to 3400°E, and the oil gave viscosities already above 4000°E at -20°C. Therefore these viscosity measurements are misleading. Other rotation tests at low temperatures had the same result. These facts destroy the prejudice against paraffin-base oils and in addition the claims of the oil industry have been clearly proved by several experiments, viz., that for low temperatures the new winter oils are an improvement on the old standard oil. However, quite apart from the mentality of the troops, two other points must be considered which make the production of paraffin base oils with lower setting-points desirable. Firstly it should be possible to handle the oil more easily at low temperatures (e.g., changing the oil from drums into smaller containers or re-filling the engine itself). Secondly it is necessary that oil continues to flow freely to the oil-pump of the lubrication circuit. In most cases this oil pump must still be protected against foreign substances by filters.

In this connection we must consider the question at which temperatures we should start to dilute winter oil with light spirit, a question which was already dealt with further above. We should like to emphasise again that oil should be diluted only when the temperature of the engine is such that evaporation of the dilution spirit from the oil film between piston- and cylinder-wall is hardly to be expected. Otherwise the dilution will not have its full effect on the engine when we want to start it.

The degree of dilution with light spirit of the lubricating oil still needs - as mentioned above - further thorough investigation. The oil industry says that, if and when the cold start standard of the various engine types are correctly found (until now anything between 750 and 3400° Engler), at temperatures of e.g. -40°C, we need not go lower to make efficient starting possible as far as the oil question is concerned. Of course particular circumstances may be met at such extremely low temperatures. These can only be found and examined by exact experiments. In any case, and as we use dilution, it is unnecessary to require more, if and when viscosities of oil diluted with light spirit can be ascertained beyond doubt. Perhaps a safety-margin should be allowed to provide against the possibility of evaporation. a 30% dilution of the new winter oil with light spirit will result in a viscosity of approximately 48°Engler only at -40°C. This must be regarded excessive compared to the utmost demands for low temperature standards of an engine at 750°E.

Dr. Weber says that it is intended to produce light spirit with a boiling point of 30:100 instead of the old ratio of 50:100. Dr. K.O. Müller thinks this change unnecessary for oil dilution. As regards fuel only difficulties arise at -40°C. Therefore a boiling point of 30:100 had been suggested. No decision has been made up to now.

Mr. Hossig is against this as not only does the danger of explosion increase, but also shipping then becomes extremely difficult. The Army, however, points out that light spirit with a boiling point of 30:100 can be easily transported in jerry-cans but the industry follows Mr. Rössig's opinion. Therefore exact investigations are to be made whether the boiling point at 30°C of light spirit is absolutely necessary for fuel purposes. A decision will be postponed till all low temperature starting experiments have been completed.

Dr. K.O. Müller submits the data for the four kinds of oil supplied for the low temperature starting experiments. These data were found by the chemico-technical State Institute (Chemisch-Technischen Reichsanstalt). It appears that contrary to what was hitherto believed - there are great differences between these oils. With the approval of the oil industry it is therefore decided that Messrs. Opel (Mr. Bochner) and Messrs. Daimler-Benz (Mr. Winkelmann) together with Mr. Rössig, will make thorough comparative tests to examine low temperature starting. Mr. Rössig points out the importance of the rotation tests. Dr. Brunck suggests making these experiments with paraffin-base oils of the same inspection characteristics but with improved setting-points, and with Shell oil which has already a favourable setting point. Mr. Rössig is then asked to come to an agreement with Mr. Bochner and Mr. Winkelmann as to how these tests are best carried out. Mr. Rössig undertakes to supply the oils necessary.

Here Mr. Winkelmann points out that the fuels and light spirit quantities supplied up to now are not sufficient for the tests. The Diesel firms represented in the sub-committees also need light spirit. Agreement on that point is reached after the conference with the Chairmen of the sub-committees and accordingly measures have been taken to approach the Army High Command and the central office for mineral oils.

Messrs. Opel report marked clouding and signs of incipient crystallisation of the gasoline when low temperature starting tests were made at -46° and later at -40°. One observed that the fuel no longer flowed efficiently at places where there was a marked narrowing of the diameter so that difficulties may be expected from this side in low temperature starting. Furthermore they complained about the rather high degree of benzol in the fuel.

Dr. Schildwaechter reports that both the gasoline and the Diesel fuel were supplied last winter and no other qualities will be obtainable in future. There is some clouding, hardly noticeable, at -18° which will not lead to a change of viscosity even at -43°C.

The reason for this small amount of clouding may be that the winter fuel is filled and supplied at approximately +15° outside temperature. Such abrupt drop in temperature causes the very small quantities of water to crystallise out. As for the high degree of benzol (20%), nothing will happen according to Dr. Schildwächter, as it did not give any trouble last winter even in the lowest temperatures.

Probably the real trouble with fuel not flowing sufficiently will be found in the delivery pump or fuel lines. As mentioned by the sub-committee concerned with mixtures and fuel this matter needs thorough investigation.

All measures concerning the improvement of low temperature starting have now been dealt with. As far as the proposals can be carried out under first priority the Chairman of the sub-committees will inform those firms not represented on the committees immediately. The carrying out of the disposals will necessitate a great supply and organisation programme, the latter, above all, for cars already in service,

This organisation programme needs special attention and has to be discussed with the Army High Command.

— It is very likely that the support of the Inspector General for cars and of the Deputy General for cars is needed to tackle the supply problem.

No war contract has been given so far for the development of low temperature starting. The Army has been asked to take the steps necessary for this purpose as it is feared that the firms might have difficulties in carrying out their experiments. Colonel Rothardt will examine the question. The Inspector General for cars (GBK) expressed his thanks for the elaborate work done and the tackling of the problems so far, but points out the urgency of the matter again. He wished theory now to make way for practice so that the means required for the coming winter will really be available.

Appendix I

DRAFT

German Standards. June 1942

Lead-storage batteries for motor cars
for starting, lighting, and igniting
testing regulations

DIN
72311
page 5

Article 1

General

Batteries not charged when supplied should be treated according to the directions of the suppliers: the same applies to the re-charging of the batteries.

Article 2

Gravity of acid

When fully charged the gravity of the acid should be: -1.28 ±0.01

Article 3

Determination of capacity

Current intensity (strength) of discharge in amperes during the discharge constant at :-

(a) 10 hours of uninterrupted discharge equivalent to one tenth ($\frac{1}{10}$) of the numerical value of the capacity in ampere/hours.

(b) 5 hours of uninterrupted discharge equivalent to one sixth ($\frac{1}{6}$) of the numerical value of the capacity in ampere/hours.
Permissible minimum value of the battery voltage at the end of discharge at a nominal voltage of 6 volts : 5.25 volts. - at a nominal voltage of 12 volts : 10.5 volts.
Temperature of acid at the start of the discharge 20±2°C.

Testing can be done either according to (a) or (b).

Article 4

Determination of starting capacity

Current intensity of the discharge in amperes during the short-circuit constant 30 times of the 10 hours' discharge-current.
Admissible minimum values of the battery-voltage at a nominal voltage of :-

(a) temperature of acid at the beginning of the discharge 20±2°C

	6v.	12v.
after ¼ minute uninterrupted short circuit	5.22	10.44
" 1 " " " "	5.1	10.2
" 3 " " " "	4.5	9.0

(b) temperature of acid at the beginning of the discharge 0±1°C

	6v.	12v.
after ¼ minute uninterrupted short circuit	4.86	9.72
" 1 " " " "	4.8	9.6
" 3½ " " " "	4.5	9.0

A test according to Article 4 should always be preceded by a discharge according to Article 3, followed by re-charging the battery according to Article 1.
Testing may be done either according to (a) or (b).

Article 5

Conduct of Tests.

(a) Tests according to Articles 3 and 4 must begin within 2 hours after the charging of the battery.
(b) The supplier may request two repeats of the test if the first test is not satisfactory.

Article 6

Exceptions.

(a) The gravity of the acid for charged batteries to be used in the tropics should be 1.23±0.01.
(b) Batteries according to page 1 may be tested according to Article 3 only.

The Chairman of the technical department 14
(Accumulator- and galvanic-batteries)
of the industrial group - Electro-Industry.

Appendix 2

Suggestion
for the care of lighting and starter batteries at the front

(1) The acid gravity of the battery fully charged is 1.28 (1.23 in the tropics) and decreases with continual discharge.
When the gravity has decreased to 1.20 (1.15 in the tropics) starting may no longer be expected for certain and the battery should be recharged.
Sulphuric acid must not be used under any circumstances to guarantee this testing possibility.
Distilled water only must replace any evaporated liquid.

(2) The gravity of the acid and the replacement of the liquid by distilled water must be done every 2 weeks. In the tropics every 8 days.

(3) The decrease of the gravity of the acid is caused :-

(a) by discharging
(b) by getting old
(c) by a fault in the electric plant

re (a) - after re-charging the battery outside the car the subsequent test of the 10 hours' capacity should at least be 80% of the standard capacity. If this value cannot be obtained, repeated charging and discharging must show if the battery can be made serviceable again or should be discarded.

Before fitting the battery in the car again after it is thought serviceable another test is required to see whether it is capable of starting the car. The fully charged battery must be loaded with thirty times the 10 hours' current at a constant load. The cell voltage must not fall below 1.5 volts during at least 4.5 minutes at a temperature of the acid at the beginning of the discharge of $20\pm2^{\circ}$C. To the acid temperature at the beginning of the discharge 0°C the battery must be put under the same constant current for at least 2.5 minutes.

re (b) - old batteries will generally not reach the full cell-voltage of 2.6 to 2.7 volts and also will not reach the minimum capacity of 80%.

re (c) - a fault in the electrical plant is in particular the fact that the batteries in the car discharge themselves within short intervals and without being used.

(4) If the car is not in use the battery must be discharged every 4 weeks.

Before every 3rd re-charge the battery must be discharged with a current of $\frac{1}{10}$ of its capacity up to a cell-voltage of 1.75 volts.

(5) In order to test the batteries properly, reserve-batteries must be supplied in sufficient numbers for each unit.

24th January, 1946.

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30/5.01

Doc. - 4 pt.

LABORATORY TEST METHOD FOR THE AGEING OF LUBRICANTS

By: Dr. Mayer - Bugström, DVL, Inst.BS.

Experimental conditions of known methods of oil ageing

Method	Quantity used		Experiment. Time h.	Temp. °C.	Oxidising agent	Metal	Constants Determined
	gm	cc					
Method of the British Air Ministry	-	40	2 x 6	200	15 ltrs. air/h.	-	Increase of sp. gr. vis. and coking
Method of French Air Ministry	-	200	120	140	Air jet over stirrdd oil	-	same, plus increase in asphalt content
Indiana method	-	300	to be det.	172	10 l.air/h.	-	Time to form 0.1 and 1% of asphalt and to increase vis. by 25%
Sligh test	10	-	2½	200	oxygen	-	Asphalt
Evers & Schmidt	15.5	-	1 hr./ 40 mins.	100	"	Heavy metal oxide on silica gel.	consumption of oxygen, increase in acid number, sap no. and content of asphalt.
DVL dish method	10	-	4	285 uncorr. 275	air	-	volatility, asphalt in residual oil.
WAE method (Wright Aeronautical Corp.)	10x35	-	5	288 uncorr.	"	Al dish	material insoluble in petr. ether, also asphalt material soluble in chloroform.

The experimental conditions to which the oils have been subjected in the course of the ageing methods have been collected in the table. If those conditions are compared with those to which oils are exposed in practice large differences are apparent. The aging temperatures are mostly much lower and there is never pure oxygen acting on oil under practical conditions. Also the action of air is not as in some ageing methods where bubbles of air are allowed to rise in the heated oil. Moreover, during testing the oil is in a glass vessel, whereas under practical conditions it comes into contact only with metal.

The time of oxidation and the temperature are very low in the method of Evers and Schmidt i.e. it has less effect than in the Sligh test. On the other hand this method is not only carried out in an atmosphere of oxygen but also the oils to be examined are spread out as a slim layer on a contact substance. The severity of seperate conditions of oxidation is thus amply equalised among the different methods mentioned above. It has been shown that even a small change in the experimental conditions may produce a considerable change in the oxidation stability. The test conditions are also important for the result i.e. the period of cooling and the time interval before the products of oxidation are determined. It is therefore necessary to lay down an exact method of test. The rating may become erroneous if the conditions are made more severe, e.g. by rising oxygen instead of air or by increasing the temperature.

One has to make a fundamental distinction between the total oil in circulation on the one hand and locally overstressed parts of it on the other hand. Hadmer states that in contra-distinction to oils which have been used under normal conditions mineral oils can no longer be regenerated after they have been artificially aged at temperatures over 125°. The latter appear to have under-gone an irreversible chemical change throughout their mass.

It would be desirable to make certain "tests" at various temperatures. It has not yet been possible to do this in practice on account of its intricacy.

Ring sticking, at least as far as aero-engines are concerned, is mainly due to changes in the oil and not in the fuel. Oxidation is an important factor here. That oxidation occurs predominantly in the combustion chamber may be deduced from the large quantities of oxygen which are found in the "oil-carbon" of the combustion chamber. In one analysis, for instance, one circulating oil contained 14-17% oxygen, whereas the content of a sample from the combustion chamber was 22-27% oxygen. Substances produced by incomplete combustion of the fuel also play a part because products such as formic acid, acetic acid, aldehydes and phenols tend to form resins. It is not enough to determine the total asphalt as the proportion insoluble in petroleum ether, and the proportion of asphalt soluble in chloroform also has to be determined. The oxidation tests do not include the humidity as a factor in the experimental conditions. This is a drawback because the penetration of water into the lubrication system is an important factor in the formation of sludge in the engine.

The determination of viscosity i.e. thickening is not essential. More stress should be laid on the direct determination of ageing products.

The temperature has a very large effect on the formation of these ageing products. Mineral oils take 24 hours before 1% of sludge is formed at 200°C; only a few hours are required at 225° and only a few minutes at 250°. Similarly 1 gm. of oil at 110° requires 300 hours to take up 1 mg. of oxygen 48 hours at 125° and only a few minutes at 200°. In the neighbourhood of 250° vigorous destruction of the oil sets in accompanied by the visible external signs of decomposition. The Indiana Test, in particular has proved valuable in giving comparative data; especially in that form of the method in which the oils are examined until they have reached the same ageing state. Synthetic oils do, however, behave peculiarly in the Indiana method in-as-much as they do not form Asphalts even after 400 hours. It is characteristic of synthetic oils that they thicken considerably during artificial ageing; also that there is a pronounced formation of acid and saponifiable products.

The limits placed on carbon formation may well be somewhat too rigorous in the British "Air Ministry" method (a maximum of 1 for the carbon value according to Ramsbottom, or a maximum of 0.70 for the increase in the carbon value). The limit for viscosity increase that is stipulated (a maximum of 100%) can be met by the usual aero-engine oils, except compounded and synthetic oils.

Mayer-Bugström summarises his paper thus:

The residue formation in the combustion chamber is an essential factor in the sticking of the piston rings and the tendency to form sludge. Methods which are meant to measure the latter properties must therefore not depart too far from the conditions obtaining in residue formation. An ageing method should therefore not concern itself with the average change in the whole of the oil but with the change undergone by the overstressed part of the oil. A large proportion of the ageing methods do however work under conditions which though they change the whole of the oil more than it is changed in the engine yet change the overstressed oil less than it is changed in the engine.

One should strive to simulate practical conditions as nearly as possible without going to the extreme of over-severity.

The oxidation test can imitate practical conditions particularly in the following points.

1) Temperature

The tendency is to fix the temperatures higher than has been done so far. To imitate the processes in the grooves it will be necessary to use a temperature of from 275° to 300°C. If the temperature is raised step by step practical conditions may be still further approached.

2) Air.

The usual coking methods do not correspond to practical conditions in as much as the conditions in the combustion chamber are imitated only by the very high temperature but not by the exclusion of oxygen. It is shown by the thermal treatment of oil that a false picture is obtained when oxygen is excluded completely; the use of oxygen in place of air also does not correspond to practical conditions.

3) Material of the Vessel.

Ageing in glass vessels does not correspond to practical conditions. Metal vessels or the introduction of strips of metal constitute an improvement.

4) State of Motion of the oil during the ageing process.

The various methods exhibit wide differences in this respect, depending on whether more stress is laid on the formation of thin, strongly heated layers or on a thorough admixture of the air.

It is desirable to combine the measurement of the volatility with the oxidation experiment proper. The other properties relevant for the changes undergone by the oil in the engine, such as the capacities for dissolving and forming suspensions of asphalt, the reactivity of the "oil-carbon" should be determined in separate experiments.

The principle of measuring the tendency to age by the time required before a given state of ageing is reached seems to offer good prospects. The Indiana test is the only method based on this principle that has so far found wide application.

If greater reproducibility is to be attained with methods which arbitrarily fix the time of oxidation the experimental conditions have to be laid down precisely, not only during the oxidation test itself but also during the working up. In particular one has to lay down the time interval between the end of oxidation and the beginning of working up.

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ON THE CHEMISTRY OF THE AGEING OF HYDROCARBON OILS

By: Dr. Ing. Morghen. from the report on the lubricant conference 2nd part - AGEING.

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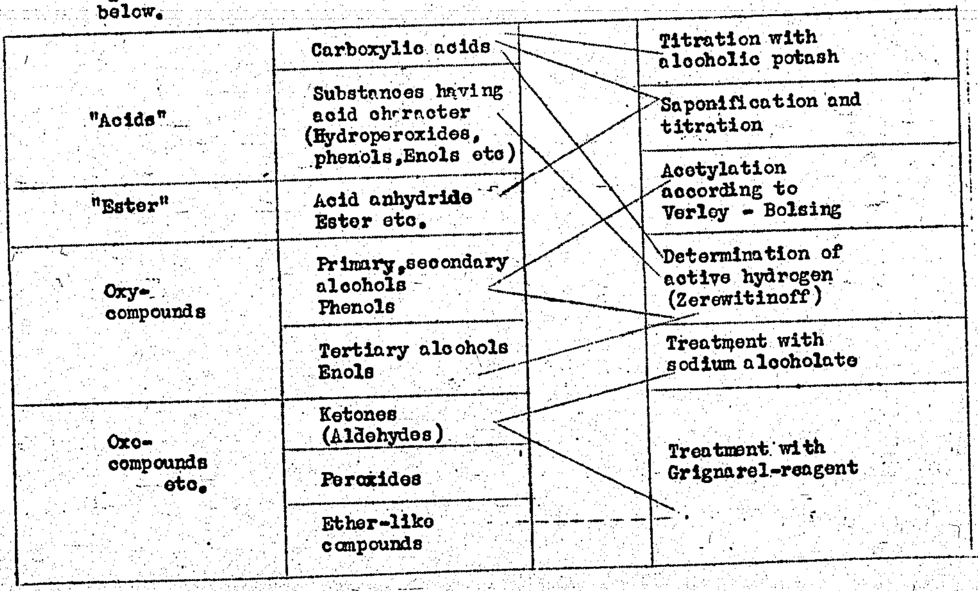
For years the DVL has been occupied with the task of elucidating the processes which occur in the ageing of oils. The war interrupted this work before it could be brought to a conclusion. The ageing of oils in the engine is largely dependent on the presence of molecular oxygen. To follow the mode of reaction is very difficult even in the case of well defined simple substances; so much more difficult is it in the case of lubricating oils which represent a scarely known mixture of hydrocarbons. It is difficult to separate the mechanism of oxidation proper from the side reactions. If we have stable oxidation products we are interested firstly in the stability at various temperatures and secondly, in the tendency directly or indirectly to enter into polymerisation and condensation reactions, thus forming higher molecular, sparsely soluble, substances of low volatility which manifest themselves as resins, asphaltic resins, asphalts, oil carbon or sludge. If one knows the functional groups one can take away the substances containing O2 and then make separate investigations of these substances and of the remaining pure hydrocarbons. Formerly one was satisfied with measuring the neutralisation number and the saponification number of an aged oil as a criterion of the oxidation change of the oil. The presence of small quantities of peroxides was demonstrated. Furthermore one determined the quantities of resin, asphaltic resin, asphalt, and "oil-carbon" either by fractional precipitation or by adsorption on earths. The terms mentioned above (resins etc) are of a somewhat arbitrary kind. The DVL carried out the ageing in special vessels at temperatures between 250° and 300°, with air, and for various lengths of time.

The saponification number was determined under such conditions that it represents only part of the real saponification number which for the residual oils tested amounted to about 1/3rd. of the total measurable forms of O_2 linkages. The method of the investigation is made clear by the diagram below.



"Acids"	Carboxylic acids	Titration with alcoholic potash
	Substances having acid character (Hydroperoxides, phenols, Enols etc)	Saponification and titration
"Ester"	Acid anhydride Ester etc.	Acetylation according to Verley - Bolsing
Oxy-compounds	Primary, secondary alcohols Phenols	Determination of active hydrogen (Zerewitinoff)
	Tertiary alcohols Enols	Treatment with sodium alcoholate
Oxo-compounds etc.	Ketones (Aldehydes)	Treatment with Grignarel-reagent
	Peroxides	
	Ether-like compounds	

Molecules containing-OH groups may be transformed into salts with excess of sodium alcoholate or with sodium amide in an atmosphere of pure nitrogen; they are then precipitated with very pure dioxane. In this way one can obtain an oil free from - OH. The DVL has various procedures for ageing.

1) Purely Thermal = 5 hours at 400° in a sealed off-tube in an atmosphere of nitrogen.

2) Oxidative = 23 hours at 275° in air

3) Thermo-oxidative = first 23 hours at 275° under N_2 then 23 hours at 275° in air.

4) Reducing = 5 hours at 155°

In saturated hydrocarbons the formation of residues is accompanied by dehydrogenation; this is substantially accelerated by oxygen which is a hydrogen acceptor. Metal filings can accelerate the dehydrogenation catalytically.

Large amounts of peroxides will not be detected in a lubricant which has been oxidised thermally; peroxides will occur as an intermediate stage, since, in general they are sensitive to temperature. Generally it is not the peroxides, as isolated, which are affected by inhibitors, but those addition compounds which are formed before the peroxides and are specially active or the activated but still oxygen free molecule itself, somehow so that either directly or by way of an intermediate chemical reaction, these unstable forms are "neutralised" and a chain reaction is prevented. It is still an open question whether in ageing phenomena we really have to do with chain reactions. It is known that in contradistinction to the inhibitors proper, compounds may retard an oxidation which themselves undergo a permanent change in the process.

In conclusion it should be said that our knowledge of the mechanism of oil ageing is still small, in particular when we are working at higher temperatures. A large amount of work will have to be done before the problem is satisfactorily solved.

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ON THE AGEING OF OIL AND ITS CHANGE IN USE

By: Dr. v. Philippovich

from the report on the lubrication conference 2nd part:

AGEING May, 1942.

The definition of "ageing of an oil" is unsatisfactory in as far as generally no strict dividing line is drawn between changes characteristic of a substance and its structure alone and those changes which are brought about by accidental impurities. Very different judgments have been pronounced on the attempts to establish a relation between the thermo-oxidative ageing of oils in the laboratory and the changes under gone by an oil in use. When one tries to find a thread running through this subject which seems so hopelessly entangled one can regard as such a thread only the fact that - apart from a few exceptions - it has not been possible to attain general agreement among laboratories, ageing and practical behaviour of an oil.

Philippovich arrives at the following definitions:

1) Ageing: is that change, characteristic for the oil, which occurs mainly when the oil is exposed to the effect of heat and/or oxygen (air). Thus it comprises all thermal and thermo-oxidation changes in the oil and may also comprise those changes which occur in the presence of catalysts.

2) Change of an oil in use: is the aggregate of all the partial changes undergone by an oil in use i.e. ageing + pollution, irrespective of whether one has to do with inactive impurities such as soot, dust, water, gasoline diluent, or with impurities which are chemically active (worn-off metal dust, lead oxide, corrosion products) and which can therefore affect the further oxidation of the oil.

3) The thermal decomposition of the oil hydrocarbons sets in at about 250° and is accompanied by a decrease in size of the molecule i.e. decomposition, on the one hand and by the formation of larger molecules i.e. coking on the other. Aliphatic compounds have a greater tendency to coke, since their C-chains break more easily. Thermal decomposition is not an equilibrium reaction but proceeds in one direction only. The purely thermal reaction without the effect of oxygen does not play a large part in the engine. The thermo-oxidative change in the oil is of greater importance. There is a critical temperature at about 120°, below this the reaction should be monomolecular, above it, it is assumed to be of higher order. In the case of synthetic lubricants the formation of asphalt is much less marked than the formation of acid. In the engine also synthetic oils produce very little asphalt but they exhibit higher acid numbers than do the mineral oils.

The velocity of the thermal decomposition increases with rising temperature; The residues become poorer in hydrogen, richer in carbon and less reactive. At high temperatures the tendency to form deposits opposes the combustion reaction; there is thus actually a temperature at which deposit formation is a maximum.

Oxidation similarly increases in intensity as the temperature rises; a change of a few degrees may under certain circumstances have observable consequences. If possible, oils should be tested at temperatures resembling the practical conditions. There is no doubt that the correct choice of temperature is a matter of considerable difficulty.

Every oxidation process may be favourably or unfavourably affected by catalysts. Fe, Pb, Cu are particularly effective. Water does not play an appreciable part in the laboratory ageing process even though it is of considerable importance in the engine.

Substances tending to prevent oxidation (inhibitors) act either by directly preventing the reaction between O_2 and hydrocarbons or by forming complexes with any metallic catalysts present in the oil. In thermal decomposition there are some substances which further the reaction but fewer substances which retard it.

The oxidation tendency of a mixture of oils of different types is greater than would be expected from the law of mixtures of the components.

The experiences gained with lubricating oils in engines have to be even more strictly applied to form a basis for the chemical processes used in the manufacture of lubricating oils. Apart from substances inhibiting the oxidation there are other addition agents which prevent the formation of coke and those which inhibit the deposition of sludge.

If a generally valid rating of the oil is to be attained one has to take into account a large number of properties: The thermal and the oxidative behaviour, the combustibility of the oil carbon, the suspensive capacity, the capacity to dissolve asphalt, the corroding tendency, all these decisively influence the behaviour under practical conditions. Each of these properties must be investigated as a function of the most important variable factors affecting the engine i.e. chiefly temperature and time. There is no all-round test to cover all practical circumstances. The sole effective evidence on which to base the grading has been and still is the full scale engine test; this method however is expensive in terms of time and money and it is difficult.

A laboratory test will tend to agree better with the behaviour in the engine as the part played by accidental changes in the oil becomes less. The engine experiment in its turn will tend to be more nearly reproducible when the accidental changes become more uniform.

Oberhausen-Holten
19.6.44.

CIOS Bag No. 2744
Target No, 30/5.01
Doc.No. 4 pt. Widmaier.

ARTIFICIAL AND ENGINE AGEING OF LUBRICANTS

from the report on the lubricant conference Part II.

In all the test methods it is important to age the lubricating oil as quickly as possible. This is attempted by increasing the temperature and by admitting oxygen over various periods of time. Aged oils are then graded according to formation of asphalt or viscosity, tendency to form carbon, formation of resins or neutralisation and saponification numbers. Up to now it has not yet been possible to obtain agreement between the ageing numbers and the values taken from the running of engines. The author has carried out several experiments in the laboratory and on the engine.

1) Indiana method

300 cc of oil were aged continuously for 45 hours at 172°C, air being introduced at the rate of 10 litres/hour. The proportion of asphalt was then determined. In all the oils that were investigated less impurities were found at 100-135° than at 172°, Significantly there were no large differences whether air was passed at the rate of 10,15 or 20 litres/hour.

2) Noak-Method

Here the ageing is carried out in the Noak apparatus, one hour at 250°, at a reduced pressure of 20 mm H_2O. The quantities of asphalt and mineral oil resin are then determined. The values obtained in this way cannot be compared with the Indiana numbers. If the quantity of air introduced is altered (20, 40, 60 mm.H_2O) the resin formation is only slightly affected.

3) Ageing of lubricating oils according to the DVL

The determination was carried out in hemispherical containers of glass, porcelain, aluminium and copper with the exclusion of air or oxygen. It is remarkable that the material of the container does not play an important part as long as, in accordance with the method, one excludes oxygen and air. If, however, concentrated or diluted oxygen is passed some of the results become very different. Resin content and the coking tendency are inter-related.

4) Effect of various gases

Widmaier heated 250 cc of oil in a closed round bottom flask to temperatures of 50, 100 and 250°C and introduced, nitrogen carbon dioxide or oxygen with continuous stirring: Volume of gas = 50 litres/hour; time of exp. = 3 hrs. The comparison shows that only oxygen effects a change in the viscosity but not N_2 or CO_2. The resin content is also considerably increased by oxygen. It is difficult to answer the question as to what products are formed from oil and oxygen at 250°. According to Suida very many chemical reactions occur in the oil, many new compounds being formed. It is very difficult to ascertain what the various products of oxidation are, the best method is still the saponification number.

When analoguous experiments are carried out in a single cylinder engine results are obtained which do not coincide with the values determined in thelaboratory. It appears to be questionable whether the resins formed in the engine have really a deteriorating effect on the oil. Especially at high temperatures these resins may even favour the formation of a lubricating film; resin formation is therefore open to objection as a measure of the oil ageing. Widmaier summarises as follows:

When lubricating oils are artificially aged the conditions selected, such as t time of ageing, temperature, concentration of O_2 and the working material are all very important because on them depends the mode of the ensueing reactions, including condensation, polymerisation, oxidation and cracking. The results are applicable to practical conditions only if the <u>same conditions</u> are kept to both in artificial ageing and in ageing in the engine.

The conditions obtaining in the engine, however, are subject to continual changes. The ageing resistance of engine oil lubricants therefore is a quantity very ill suited to be determined in the laboratory.

When the gases contained in the crank case were introduced into the oil, it was found that at an oil temperature of 250° only oxygen had any appreciable effect, whereas CO_2 and N_2 had no effect. Added metals such as Cu, Zu, and Al generally increase the content of asphalt, the viscosity and the deposit formation of the oils.

When the results of "naturally" and artificially aged oils are compared it is seen that in most cases the agreement is not good.

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Ruhrchemie Aktiengesellschaft
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Doc. No. 4 pt.

Report Schayen to Prof. Martin of 29.11.40

Re: Application of RB lubricating oils - report of 10.2.40

RB lubricating oil has been used in the "compressor house" since the beginning of this year as superheated-steam cylinder oil, compressor oil and to a small extent as machine oil. RB lubricating oil was introduced at the time because it became so difficult to procure the mineral oils which had been used up to that time. The supply of RB lubricating oil has now had to be discontinued suddenly according to a communication from Herr Niemann. In the future external oils will again have to be applied for and procured for the compressor house.

Operating results and experience with RB lubricating oils.

The oils supplied by the RB had the following characteristics.

Superheated-steam cylinder oil No. 3017.		Compressor Oil No. 3018.
Density $_{20^\circ}$	0.869	0.864
Viscosity$_{50^\circ}$ E	51.3	29.5
Vis.pol. height	1.76	1.78
neutr. no.	0.06	0.06
sapon. no.	0.14	0.13
Flash point	331°C	229°C
Setting Point	-29°C	-37°C
Volatile	1.24%	1.45%
Conrad. test	0.701%	0.440%
Ash	0.037	0.02
Resin/asph.	5.64%	4.22%
" acc. Noack test	8.35	6.28
Iodine number	24.0	-

Oxygen Test = 1.7° in 180 min. = 2.35° in 180 Min.

Initially the superheated steam cylinder oil received a special after-treatment according to directions by Dr. Goethel; later it became impossible to continue this in the interest of production. Both oils have therefore been used and they have shown essential difference in their performances. The oils have proved themselves very well at normal steam temperatures of about 350 to 375°. The lubricating film could everywhere be called sufficient; no formation of deposits could be observed. When the temperature of the steam was high, however, in particular when it was above 400°, lubrication was unsatisfactory. At these temperatures the piston rods ran rather dry so that parts very easily became overheated and the oil film disappeared completely. Under these circumstances the piston rod appeared covered with fine dark grey powder-dust. When parts become overheated one has to deal with much higher temperatures, of course. No troubles were observed in the steam cylinder itself at these high steam-temperatures; the piston rings still worked smoothly. Much less pollution and deposition was found in comparison with the mineral oils so far.

The compressor oil was quite successfully used in the nitrogen, coke gas and mixture compressors. Lubrication was smooth, no troubles occurred.

On a suggestion of Dr. S. Tramm and Goethel mixture of RB oil with Koff's high pressure - air - compressor oil (mixture ratio 1:1) was used for air compressors. This has however given rise to some difficulties. Deposits ("Oil carbon" and coke) were found in the second-stage cooler. From this one may infer that at higher temperatures (estimated to be above 200°) the oil has formed deposits which have eventually led to the complete blocking of the cooler. These very hard deposits could only be removed from the various cooler tubes by drilling them with a drilling machine. A cooler of this type may contain 125 tubes of an internal diameter 15 mm and a length of 3500 mm. Similar deposits have also been observed after the third stage. Under the high pressures of from 30-50 atm. and in the probable presence of easily ignitable "oil carbon," even oil explosions have several times taken place at this point. There was irrefutable evidence of combustion in the spaces of the pressure valves of the third stage and in oil separators connected in series. The temperatures rise so high in parts that the connecting tubes are brought to a red heat. The tin of the soldered tubes was of course melted and considerable leaks were caused in this way. The extent of the damage is unprecedented. I assume that under the influence of compressed oxygen the decomposition of the oil starts at temperatures as low as 190°; this would explain the continual disturbances in the air separators by a shift of the bottom of the rectification columns. No disturbances have so far come to my notice, however, at temperatures below 190°.

As not sufficient high pressure-air-compressor oil of the old quality is available at the present time we are forced to continue to employ the mixed oil for some time to come. Attention is of course paid to keeping the compression temperatures as low as possible.

Machine oil was only used in admixture with other oils viz. as circulating oil in the drive lubrication of all compressors and steam engines. Only a small percentage was used as an admixture. Nothing can therefore be said about the behaviour of the oil, the ageing in particular.

Refrigerator oil has not so far been supplied by the RB.

Communication Prof. Martin to Dr. Hagemann, D. Dr. Tramm
Re:- Application of Ruhrbenzin lubricating oils in our works.

16.12.40.

In view of the relatively favourable report by Herr Schayen of 29.11.40 on the behaviour of our lubricating oils one should really continue their use whereever no objections exist to the present method. Moreoever one should run a number of charges in our lubricating oil plant with addition to synthetic oils of those inhibitors which have particularly proved themselves according to the communication from Clar and Tramm. According to the reports of these gentlemen it is possible to produce particularly stable oils without any after treatment if one adds certain inhibitors. Such oils would therefore be well suited for use in our air compressors in charge of Herr Schayen. No other characteristics of the oils are supposed to be affected by the addition of an inhibitor. Thus the process of lubricating oil manufacture is to be carried out in the same way as before with the sole difference that certain inhibitors are added during the synthesis. I should be grateful to you if the necessary setps were taken for the production of larger quantities of inhibited oil and for its application.

C.I.O.S. Bag No. 2744
Target No. 2744
Doc. No. 4 pt.

Holten, 27.1.40.

Extract from " Intorim report No. 3"
Dipl. Ing. Schaub, 19.1.40.

The engine test is better capable of rating an oil, than are the laboratory methods.

The following factors are of importance:

a) Wear
b) Consumption of oil
c) Ageing of oil
d) Tendency to cause piston ring sticking
e) Consumption of fuel
f) Durability of bearings
g) Behaviour at low temperatures.

Points a) - d) were rated separately. For motor cars a) and b) are important; for aero-engines d).

An engine experiment takes 30 hours at present, including the running-in time. The temperatures of the oil well were varied as well as the temperature of the cooling water.

The following engines were used

1) 1.3 litres Opel 17.6 H.P. 2200 r.p.m.
2) 1.5 litres Opel 27 H.P. 2700 r.p.n.
3) 1.7 litres mercedes M. 136 27 H.P. 2700 r.p.m.

To a) Wear

Important places are the cylinder walls, the piston, piston rings, the crank shaft pinion and the bearing. The quantity measured is the decrease in the weight of the piston ring or the increase in the diameter of the cylinder. It becomes clear that the piston rings bear the main responsibility for the wear of the cylinder. Under the chosen conditions the wear was greatest not at the top dead centre but at the points where the piston ring velocity was particularly high.

The ash-content is taken as a third experimental quantity measuring the wear. The comparison does however assume equal initial quantities of oil and equal oil consumption.

Here the following play a part.

1. Construction of the engine
2. Running play between sliding surfaces
3. Metallurgical properties of the surfaces
4. Condition of the engine
5. Temperature of cooling water
6. Temperature of oil sump.
7. Consumption of oil in as far as it depends on mechanical factors.

8. Fuel
9. Speed and load
10. Nature of the suction air

Particular attention was paid to 1, 5, 6 and 7.

To 4) Condition of the engine

A new engine gives the greatest amount of wear when it is being run in because at that stage non-uniformities in the sliding surfaces due to the machining are being worn down. Afterwards the wear is much less and is a linear function of the time. In most experiments therefore, the wear in the running-in stage is considerably higher than it is during the main run. There were 3 exceptions in the course of 13 runs.

To 5). Temperature of the cooling water

According to the experiments the most favourable temperature for the cooling water should be between 60 and 70°. The wear at temperatures below 70° was greater than at 70°; this is due to the formation of a condensate on the walls of the cylinder. At higher temperatures there is an increase in the wear, the extent of the increase depending on the type of oil. The ash content of the lubricating oil rises steeply during the first two hours and then increases much more slowly when the engine has been warmed throughout (drawback of cold starting).

To 6) Temperature of oil sump

An increase in the temperature of the oil sump has a more detrimental effect than an increase in the temp. of the cooling water.

To 8) Fuel

If the mixture is too rich a fuel-condensate is formed on the cylinder walls which has the effect of washing off or diluting the oil film.

When wear is high as a result of a rich mixture the ash content does not, as is usual, rise with the wear of the piston ring and cylinder.

To 7) Oil Consumption

When the consumption of oil rises there is an abnormal increase in wear if the rise in the consumption has been caused by an increased supply of oil to the sliding surfaces of the cylinder. The dependence of wear on consumption of oil varies quantitatively for the various types of oil and their decomposition products. The basis of the relation between wear and oil consumption has not yet been elucidated, the main problem being whether it is consequence of chemical corrosion or of mechanical influences.

To b) Oil Consumption

Apart from the viscosity of the oil the decisive factor is given by the state of the engine. Neglecting losses due to leakage the consumption depends on how much oil is burnt in the combustion chamber and how much escapes unchanged through the exhaust. When the viscosity of the oil coming from the bearings is low, the amount of oil squirted away rises. When the fit of the bearing is very accurate the loss of oil is, surprisingly, lower than it is when there is more running play. When the play in the bearing is altered from 0.02 to 0.04mm the consumption rise to a multiple of its value. The consumption falls with oil pressure and thereby the wall of the cylinder.

To c) Ageing of the oil

The total change in the oil, here called ageing, is measured in terms of :

Density 20°

Viscosity 50°

Neutralisation number

saponification number

Ash

Naphtha and benzine in solubles, and hard asphalt.

Conradon test

Iodine number

It is still not known which of these quantities is significant for the use in the engine. No drawback due to thickening could be observed. The tendency to piston ring sticking similarly did not seem to be increased at greater viscosities. It appears doubtful whether the wear is increased by an aged oil. The connections between the hard asphalt or Conradson test and the ring sticking have not been elucidated. When the Conradson test was low the tendency to ring sticking has not always fallen. The ageing of oils is assisted by newly machined cylinder walls, by the oil consumption and similarly by high oil temperatures.

Summary

The experiments have shown that the behaviour of an oil in the engine is a function of numerous mechanical, thermal and other conditions. It is therefore absolutely essential for a valid rating to carry out several long duration tests in order to avoid faulty conclusions.

Further experiments on the parts played by the fuel the temperatures of the cooling water and of the oil, are to follow.

C.I.O.S. Bag No. 2744
Target No. 30/5.01
Doc. no. 4 pt

Memorandum from Dr. Schaub on the conference with Obering. Dr. Vogelpohl and Herr Föttinger of the Technische Hochschule, Berlin, on 19.2.42.

Re: Oil test apparatus

Dr. K.O. Müller has offered to pass on to the RB the Thoma-oil test apparatus belonging to the HWA and at present at the disposal of Dr. Vogelpohl, for the purpose of developing synthetic gear oils at the Ruhrbenzin. The conference with Dr. Vogelpohl was arranged for the purpose of hearing about his experience with the apparatus. Vogelpohl takes the view that none of the oil test apparatus in use at present permitted conclusions to be drawn as to the behaviour of oils under practical conditions. The Thoma apparatus is no exception to this general rule. Furthermore Dr. Vogelpohl reports that the apparatus is very sensitive as regards manipulation and that it shows constructional defects which lead to frequent damage. He believes that one year of thorough preliminary investigation is required before valid and reproducible results can be obtained with a test apparatus. Vogelpohl has now occupied himself with the apparatus for one year and he intends now to start a series of experiments with different oils. At the present time it would therefore be inconvenient to him if the apparatus were to be passed on the RB. On the other hand he would like to carry out tests for the RB; in general he is very interested in having a connection with practical application in this way. Schaub points out as a matter of experience that in the development of materials it is essential that the various experimental products are tested at one and the same place and that development work may be much held back if tests have to be made outside.

From a view of the apparatus I gained the impression that it will only be suitable for our purpose under certain conditions. Taking full flow measurements as we have planned it, in any case seems difficult with the present construction. If other oil test machines of the test station could be made available to us and we thus had the possibility of comparing the results of the various machines we should of course be interested in having the machine in question. It was settled that Schaub should once more communicate with Dr. K.O. Müller and that a final decision would subsequently be taken as to whether or not the machine should be placed at the disposal of the Ruhrbenzin.

~~C.I.O.S. Bag No. 2744~~
Target No. 30/5.01
Doc. No. 4 pt.

From the report on the lubrication conference Dec. 41, 1st part.

Friction and Wear

Holder experiments with the four-ball machine, page 169.

The four-ball machine is used to test extreme pressure lubricants. The opinions as to its value however, differ very widely since the test is carried out at extremely high pressures and since the results exhibit a fairly wide variation. The H.W.A. has recently incorporated the four-ball-machine test into its delivery specificationsfor gear lubricants. The present paper reports on the constructional experiments carried out by the I.G. The four balls of this machine have diameters of ½" and are arranged so that their centres form a tetrahedron. The lower balls are set in a ball holder which is shaped like a cup and which serves to hold the oil. The upper ball is connected at its lower end to a vertical shaft which is turned by an electro-motor over a belt drive. The ball holder is wound with heating wire so that the test can be carried out at various temperatures. The holder is also movable in all directions so that it can always be adjusted to correspond to the position of the fourth ball. For the measurement of the turning moment transferred to the three lower balls the ball holder is supported against an indicator which registers the force transmitted at any instant.

The experiment can be carried out in two different ways. Either one works with a constant load and measures the time before seizing occurs or one works with a load rising from zero and determines that load for which seizing occurs. This seizing causes a sudden strong deflection on the indicator. One can either work at different loads or also at different temperatures.

The first method gives a wide variation in the results. The second course was therefore taken by the I.G. in order to find out whether this would yield better values. The machine was there started while the balls carried no load. At the instant at which the motor is switched on a water pipe is opened throught which is a egess of exactly 0.15 litres/sec. The water flows into a container which serves as the load. The time between starting up the motor and seizing is measured. No marked improvement of the scatter of the variational range could be obtained with the method.

From the coefficients of friction that have been determined it follows that what is measured is a state of so-called partial lubrication.

If the test is carried out for five oils of different viscosities at different temperatures one observes that in all cases seizure occurs earlier at higher temperatures. The more viscous the sample of oil the better was in general its behaviour i.e. very viscous oils show the best results. The machine gives particularly wide variations in the results for certain ranges of R.P.M. 2000 revs/min proved to be better than 1500 or 800 revs/min.

The report states that in some cases one did not work with running water but with a constant weight. Rotring was preferred as a test oil. Most of the fatty oils gave very wide variations; this contrastswith the oils which had extreme pressure additives made to them. The mineral oils varied amongst themselves. Among other the following were tested. Wehrmachtseinheit-oil Valvoline, a Hypoid-gear oil with extreme pressure additives, also additives such as $C\,Cl_4$ and a sulphur compound. The quantities amount to 5-9%.

Ruhrchemie Akt.
Oberhausen-Holten, 27th June, 1939

CIOS Bag. No. 2744
Target No. 30/5.01
Doc. No. 4

AGEING OF LUBRICATING OILS

from

Directions for the buying and testing of lubricating oils
Eighth Edition 1939.

The ageing which occurs when oils are used manifests itself in an increase in viscosity. This is partly due to the evaporation of low boiling constituents and partly to the formation of resinous, soluble ageing products. In bearing lubrication and particularly in circulation lubrication any excessive increase of the viscosity may have an adverse effect on the lubrication. The oil line may even be blocked if particularly viscous ageing products are formed. The viscosity of oils in combustion engines is reduced if any fuel is taken up; this may under certain conditions lead to a break down. It is therefore absolutely necessary to check periodically the viscosity of an oil in use.

Ageing tendency

If, over a long period of operation, an oil is exposed to the air, to intense heat and to contact with metals, the properties of the oil undergo a gradual, more or less extensive change i.e. the oil ages. This ageing manifests itself as a change in the chemical structure of the oil, ageing products being formed which are mainly made up of free and combined acids (characterized by acid and saponification number) and of resinous and asphaltic compounds. In the first stage of ageing these compounds are still dissolved in the oil. As their concentration increases, however, they may come down in the form of sludge or hard asphalt. This process is accelerated by foreign matter which appears during the run, viz, dust, worn off particles of the bearing metal, fabric fibres and water. One of the consequences of this ageing is an increase in the viscosity; to a certain extent, particularly in the case of bearing lubrication such an increase may be tolerated. If, however, the viscosity increases to beyond the limit set down in the specifications one has to replace the aged oil and return it for recovery.

Oils which are used in the lubrication of gasoline (carburettor) and Diesel engines age just like all lubricating oils. The ageing is however further accelerated by absorption from the cylinders of unburnt fuel. This causes a diminution of the voscosity and decreases the lubricating capacity. It is therefore necessary to replace oils regularly after a certain running time, 2000 to 3000 km for motor-cars. If longer continuous runs with motor-cars are undertaken, particularly on "Autobahnen" one has to avoid overheating the oil, because ageing is accelerated by this, as has already been mentioned. The maximum permissible temperature of the oil in the crank-case has been found by experience to be about 90°C.

Oils which are intended to have a long life, especially insulating oils for transformers and switches as well as steam turbine oils should in the interest of operational safety, be tested with respect to their ageing tendency when they arrive from the manufactures and they should then be graded accordingly. For this purpose a number of test methods are available which in a short period of time artificially imitate the ageing which occurs during operation. In these methods one measures the increase in the acid number, and the saponification number as well as the formation of sludge, resin acids, hard asphalt and "oil-carbon"; according to these data the oil is graded. Some test methods introduce into the process all the metals with which the oil comes into contact during operation whereas other methods take no account of this factor. The former category to which belongs Baader's ageing test, are to be preferred to the latter category to which belongs the determination of the "Tarring Number."

After-treatment of aviation oils for technical experiments produced in the technical App. H.L. (larger quantities).

Starting material: an untreated residual oil 10°E.

No. of exp. Cat. No.	Treatment	O_2 Test 140° " 150°	Iodine No.	Therm. Stabil. 3 hrs. 330°	Ageing Test 6 hrs. 160° O_2							
					O_2	Cooling Air	+ V_{50}	+ IK	N.N.	S.N.	H_2O	Oil
2854/2	1 x 0.75 % $AlCl_3$ 180° No cracking products formed.	not bleached 15.12.39.90' + 20.2 bleached 16.12.39.95' + 19.7 18.12.39.92' + 19.8 21.12.39 110' + 19.8	 50' 60' 60' 90'	-	-	-	-	-	-	-	-	-
2854/7 K 1709	1 x 1.5 % $AlCl_3$ 4 hrs. 200°, then bleached with 3% Tonsil	not bleached 8.1.40 126' + 20.1 8.1.40 148' + 20.2 bleached 9.1.40 170' + 21.1 15.1.40 139' + 19.6	 90' 120' 120' 110'	75% -98°	10%	1910 lts.	bleached 96%	0.64	14,-	36.3	6.5 cm³	1.3 cm
2854/7 K 1722	K 1709 + 0.3 % β-Thionaphthol	150° Lab. 0.2 % Juh. 16.1.40. 93' + 20,- 150° Techn.Ex.0.3% J. 17.1.40. 104' + 20,-	- < 10' 70'	1% -130°	4.2%	900 lts.	bleached 24%	0.23	4.1	12.5	3.3 "	0.6 "
2855 K 1711	untreated	14.3.40 130' + 20,-	100'	63 % -119	17.2%	2340 lts.	bleached 139%	0.70	17.8	39.4	8.3 "	2.1 "
2893	2855 (K 1711) + 0.3 % Phentiazin	150° 15.2.40 180' + 19.1	?		1.7%	890 lts.	7%	0.11	1.2	3.2	0.2"	0.4 "
2855/2	2 x 1 % $AlCl_3$ 4 hrs. 170° iod.no. = 31	18.12.39 180' + 5.2 19.12.39.148' + 19.7 20.12.39 162' + 19.7	170' 110' 120'	80% -68°	-	1170 lts.	90 %	0.64	16,-	33.1	6.8"	1.7"
2855/10 K 1710	2 x 1 % $AlCl_3$ 4 hrs. 200°	8.1.40 143' + 20.2 9.1.40 134' + 19.8 13.1.40 148' + 20.3	100' 100' 100'	87% -32°	11.9%	2210 lts	110%	0.66	17.4	36.1	6.6"	1.5 "

After-treatment of aviation oils for technical experiments produced in the technical App. H.L. (larger quantities).

Starting material an untreated residual oil 10°E.

(Continued)

No. of Experiment Cat. No.	Treatment	O_2 Test 140° 150°	Iodine No.	Therm. Stabil. 3 hrs. 350°	Ageing Test 6 hrs. 160° O_2 C_2	Cooling Air	+ V_{50}	+ DK	N.N.	S.N.	H_2O	Oil
2855/11 K 1723	2 x 1.5 % $AlCl_3$ 4 hrs. 200°	12.1.40 137' + 19.9	50'	78% -115	11.6%	2370 lts.	105%	0.67	15.1	38.8	9.5cm^3	2.4g

FD2877,46It12

Issued Spring 1940.
Checked February, 1941.

CIOS No.2744 - 30/6.05-12.
11th February, 1942.

SPECIFICATION FOR FUEL GASES

1). Composition:

Fuel gas is a mixture of C_4, C_3 and C_2 hydrocarbons, the lower calorific power of which should be 11000 k.cal ± 3%. It may contain up to 65% by weight of C_4 hydrocarbons. From April 1st to August 31st it may contain up to 75% by weight of C_4.

2) Vapour Pressure:

During the winter, viz. from September 1st to March 31st, the vapour pressure of the fuel gas should still be at least 1.5 atmospheres at -15°C. During the summer a vapour pressure of 0.7 atmosphers at 0°C is sufficient.

The filling plant is responsible for the pressures of the bottles which they fill being never at any time of the year above 16.7 atmospheres at 40°C.

3) Conditions of Purity:

The fuel gas should contain 97% hydrocarbon at least, the remainder being inert gases. H_2S content less than 0.2 mg/m^3 gas. Content of organically combined sulphur less than 250 mg/m^3 gas.

Elementary sulphur must not be present (mercury test). There must be no trace of carbon oxysulfide when testing with an alcoholic solution of lead. Mercaptans must not be found either, (Doctor Test), nor must any ammonia be present.

Water content: No ice or hydrocarbon hydrate should separate above -30°C. There must be no oil.

Resin and resin forming substances can only be tolerated in as much as they do not lead to break downs when driving.

APPENDIX

On future new controls will be built in accordance with the specifications given above. Old controls will be changed to meet the requirements. As regards these changes and the special measures necessary to overcome any further difficulties which might occur during the winter months, special arrangements will be made by the Zentral Büro and the manufacturers.

Works which at present can deliver oil containing fuel gas only, are allowed some time for this change, viz. up to January 1st, 1940. But they should endeavour to decrease the oil content immediately as far as possible by using other lubricants.

I. QUALITY

The fuel gas association of the "Ruhrworks" entrusted with the distribution and sale of the compressed and liquefied fuel gas products of its members, has laid down the following specifications and conditions for the quality of motor methane, Ruhr gas oil ("Ruhrgasol") and "B.V." fuel gas:

I. MOTOR METHANE

1) Calorific Value

The lower calorific value of motor methane must be 10900 K.cal/kg. Limits of error of ± 3% are permitted.

2) Bottle pressure

Unless other instructions are issued by the authorities the filling pressures of the bottles should not exceed 184 kg/cm^2 at + 15°C or 226 kg/cm^2 at 40° respectively.

3) Contaminants

There must be no oil or water in the bottles CO_2 content must not exceed 1 vol.% Sulphur content (total sulphur) must not exceed 0.4%. Corroding substances must be absent.

II "Ruhrgasol"

1) Calorific Value

The lower calorific value of "Ruhrgasol" must be 11000 k.cal/kg. Limits of error of ± 3% are permitted.

2) Boiling point.

The boiling point - as determined by the "B.V" apparatus - should show not more than 10% by weight of ingredients boiling above 20°-35°C, and none boiling above 35°C.

3) Bottle Pressure

The pressure of the "Ruhrgasol" at -20°C should not be less than 0.5 atmospheres (excess pressure). At +40°C a maximum pressure of 30 atmospheres should not be exceeded.

4) Accompanying substances

There should be no water separation from the "Ruhrgasol" at -20°C in the bottles. The inert content of "Ruhrgasol" should not exceed 3% in weight. The total sulphur content should not be higher than 0.4% in weight. Corroding substances should be absent.

5) Gum and Oil Content.

The gum content should not exceed 2mg/100 g gasol. The exact resin content of the "Ruhrgasol" is determined by the value found according to the "B.V" method. The lubricating oil content, if any, should not exceed 30 mg./100 g gas.

6) Gum forming catalysts

Oxygen from the air and available combined oxygen (e.g. peroxides) must not be present in the "Ruhrgasol" either in the gas compartment of the bottles or in the storage container respectively. No nitric oxides-not even traces of them - should be evident either in the "Ruhrgasol" itself or in the projecting gas compartment.

7) Inhibitor

All fuel gases which contain or might contain gum forming catalysts must be supplied with a suitable gum inhibitor.

III. "B.V" Fuel Gases

Physical Properties

1) Lower calorific value: 11000 calories/kg.
Tolerance ± 3%

2) Total density (air = 1): 1.7 - 1.8

This density must correspond to a composition of 35-50% in weight of C_3= hydrocarbon and 65-50% in weight C_4= hydrocarbon.

3) Bottle Pressure:

a) Temperatures below 0°C: At a temperature of -15°C the pressure of "B.V" fuel gas must under any circumstances be not less than 0.5 atmospheres (absolute or excess pressure)

(Manuscript Marginal Note: Winter above 1.5 @ 15°
Summer ~ 0.7 @ 0°)

b) Temperatures above 0°C: At the maximum working temperature of +40°C a maximum pressure of 16.7 atmospheres (absolute or excess pressure) must not be exceeded.

CHEMICAL PROPERTIES

1) Boiling Point. The boiling point is determined by the "B.V" apparatus.

Composition 35-50% in weight of C_3-hydrocarbons
65-50% in weight of C_4-hydrocarbons

"B.V" fuel gas must not leave any parts boiling at above 20°C when distilling in the "B.V" apparatus. The top limit of the inert content is 3% in weight.

2) Water content "B.V." fuel gas must not contain any water.

3) Conditions of purity.

a) Sulphur: The "B.V" gas fuel must not contain any hydrogen sulphide, elementary sulphur or mercaptans. At present a small content of elementary sulphur of not more than 0.1 mg./100g fuel gas is permitted.

b) Ammonia or other corroding nitrogen compounds must not be present.

4) Gum "B.V" fuel gas must be free from gum or gum forming substances.

5) Oil Content. Less than 10 mg/100g "B.V" fuel gas

Memorandum
Da/Bi

To: Dr. Grimme.

Re: Analytical methods.
Comparative investigations at the B.V.

On the 28.1.41 a conference was held with Dr. Hammerich on analytical methods and his work on the arithmetico-analytical determination of the Research-octane number of gasolines from the Fischer-synthesis. On the occasion of this conference investigations were carried out at the fuel laboratory there in collaboration with Mr. Vorreiter. Some samples had been taken there which had already been analysed by the sampling station of the B.V. for the Zentralbüro.

1.) Vapour Pressure.

Anal.No.		Sample dated	Rheinpreussen analysis 1.	Rheinpreussen analysis 2.	B.V.analysis 1	B.V.analysis 2.(together)	
GB	37	25.11.40	0.63	0.64	0.73	0.72	x)
A	1	3. 1.41	0.62	0.64	0.77	0.72	
GB	39	14.12.40	0.68	0.66	0.77	0.74	
GB	35	29.10.40	0.64	0.68	0.76	0.75	

x) Joint analyses in the Rheinpreussen Apparatus: 0.725.

The joint analyses were performed in the standard B.V. manner. The pressure chamber is heated directly by the flame up to 45°, with manometer fitted. The manometer and gasoline chamber are screwed on after the chamber has cooled down to 40°C. In this case there is no correction. We, however, screwed the apparatus together at normal room temperature and then corrected the observed values using correction tables. Earlier experiment had shown that starting at room temperature and then using the correction tables gives no appreciable deviation from the uncorrected values obtained by preheating the pressure chamber with screwed-on manometer to 40° in a drying cabinet. The small deviations might be due to the apparatus, which had been warmed to 40°C, cooling down by 1 or 2 degrees in being taken out of the drying cabinet and having the gasoline chamber screwed on.

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Anal. No.	Rheinpreussen	B.V.	Joint method with B.V.
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In general the results of the joint analysis agreed more closely with those previously obtained. The B.V. method is fundamentally the same as ours and the slow cooling has not been adhered to any more than is usually the case. This may well account for the excessive variation. I have therefore pointed out that the pour point of Diesel fuels should be measured with stirring; in judging the values one would then have to consider that they deviate from practical conditions by 3 to 4°. This point of view has been advanced in the letter to Dr. Hammerich of 31.1.41.

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Treibstoffwork, 3.1.41. Dr. Dannefelser.

Memorandum
Gr/Ba
12.11.39

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1. Carburettor fuels.

Octane number by the Research method in the I.G. engine or the CFR engine.

Appearance and colour.

Density at 15°C should be below 0.715 for finished gasoline.

Iodine number by Rosenmund and Kuhnhenn's method. The result of the comparisons with Kaufmann's method are be awaited before we decide on our method.

Reid vapour pressure at 40°C. The maximum permissible V.P. for finished gasoline is 0.78 in winter and 0.65 in summer.

Gum content, at 110°C in a glass dish in a current of air. The residue shall not exceed 10 mg. Whenever possible it should be stated whether the residue consists of oil or resins.

Oxidation Stability test, at 70°C. With addition of 10% alcohol no decrease should be observed after 4 hours.

ASTM Distillation. At 100° at least 35% of the finished gasoline should have come over, and at least 95% at 200°.

Lead content, expressed as cc Tel/litre.

Alcohol content, determined by extraction with calcium chloride solution.

Water content, in the case of fuel containing alcohol.

Benzene content, by a method which has not yet been agreed upon.

Neutralization value, after refluxing the sample to remove the carbonic acid.

Copper test. Results are purely qualitative and are only intended to distinguish between tarnishing and black colourations.

Volatility, by Dr. Hammerich's method. This should not exceed 22% in summer.

2. Diesel fuels.

Flash point in the Pensky-Martens-apparatus for differentiating the "danger classes" 3 and 2. Diesel fuels of the danger class 2 should be marked with a red label.

Appearance for the control of the content of impurities such as suspended matter or water.

Lower calorific value/kg should not be below 9700 cals.

Density at 15° for finished Diesel-fuels should not be below 0.81.

Pour point, still liquid at -10°C in summer, corresponding to a pour point of -12°C determined by the previously used method; still liquid at -18°C in winter.

Cloud point.

Filterability by Hagemann/Hammerich's method, 200 cc should take at most 60 secs. in the new apparatus, at -5°C in summer and -13°C in winter.

Neutralization value, according to the directions for lubricating oils.

Zinc test: 24 hours in the bomb at 50°C according to Hammerich's directions. The zinc used should be refined but not electrolytic. The limiting value of the weight decrease should not exceed 4 ± 1 mgm.

Ash content by DVM 3762 should not exceed 0.05%.

Coking tendency by Hagemann/Hammerich's method should not exceed 2%. Separation of hard asphalt and coke is not required.

Sulphur content, by combustion in the lamp or bomb, not more than 1% by wt.

Cetane number in the H.W.A. engine or cetane number by Heinze-Marder's method.

Viscosity at 20° in the Vogel-Ossag to be not less than 1.1° Engler and not more than 2° Engler.

Distillation by the ASTM method with uncorrected thermometer.

Aniline point for calculation of Diesel Index.

The analytical data obtained were communicated to the Zentralbüro Berlin and the works tests to the corresponding manufacturers. It has also been agreed to send a copy to the Benzolverband, Bochum.

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Memorandum
Da/Bi

To: Dr. Grimme.

Re: Analytical methods.
Comparative investigations at the B.V.

On the 28.1.41 a conference was held with Dr. Hammerich on analytical methods and his work on the arithmetico-analytical determination of the Research-octane number of gasolines from the Fischer-synthesis. On the occasion of this conference investigations were carried out at the fuel laboratory there in collaboration with Mr. Vorreiter. Some samples had been taken there which had already been analysed by the sampling station of the B.V. for the Zentralbüro.

1.) Vapour Pressure.

Anal.No.		Sample dated	Rheinpreussen analysis 1.	2.	B.V.analysis 1	2.(together)
GB	37	25.11.40	0.63	0.64	0.73	0.72
A	1	3. 1.41	0.62	0.64	0.77	0.72 x)
GB	39	14.12.40	0.68	0.66	0.77	0.74
GB	35	29.10.40	0.64	0.68	0.76	0.75

x) Joint analyses in the Rheinpreussen Apparatus: 0.725.

The joint analyses were performed in the standard B.V. manner. The pressure chamber is heated directly by the flame up to 45°, with manometer fitted. The manometer and gasoline chamber are screwed on after the chamber has cooled down to 40°C. In this case there is no correction. We, however, screwed the apparatus together at normal room temperature and then corrected the observed values using correction tables. Earlier experiment had shown that starting at room temperature and then using the correction tables gives no appreciable deviation from the uncorrected values obtained by preheating the pressure chamber with screwed-on manometer to 40° in a drying cabinet. The small deviations might be due to the apparatus, which had been warmed to 40°C, cooling down by 1 or 2 degrees in being taken out of the drying cabinet and having the gasoline chamber screwed on.

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B.I.O.S. Ref. 3441-30/5.01-76

Ruhrchemie Aktiengesellschaft Oberhausen-Holten
11 October, 1944
Précis of the discussions between Prof. Dr. Martin, Dir. Dr. Hagemann,
and Dr. Velde in Holten on 25. 9. 44.

Subject: Tar oil, and the use of tar oil and crude oil in gas turbines for the Luftwaffe

Prof. Martin reports on a discussion which he had at the instigation of Mr. Geilenberg with Prof. Hohlfelder, the head of the Institut für Motoren at the technische Akademie der Luftfahrtforschung in Berlin-Gatow. Prof. Hohlfelder is engaged on the development of the gas turbine for the Luftwaffe. The method of working is as follows: The fuel is sprayed out of a nozzle with the aid of air, is burned in a combustion chamber, and employed to drive the gas turbine. The fuel originally used was I_2, which boils between 100-300°, and should be produced by works making synthetic products, or by hydrogenation plants. After the hydrogenation plants ceased to be available, further tests were made, and it was established that crude oil and tar oil were basically suitable. Admittedly both products require to be preheated to 400°, as otherwise they will not burn in the combustion chamber without forming deposits. While this preheating is easily achieved with crude oil, coking occurs at the nozzle when tar oil is used.with prolonged running, so that it can only be used for 4-6 hours. We have therefore been asked whether we see any way of avoiding this coking at the nozzle. On his visit to Gatow, Prof. Martin found that the method of preheating used is extremely primitive; the tar oil or crude oil is passed through a pipe, which is very closely fitted, in a pipe which is heated from below by an open flame. A temperature of 400° was measured before the nozzle, but in spite of this considerable over-heating occurred, for according to Prof. Hohlfelder there is 20% decomposition on preheating. On the basis of this information, I am convinced that there must have been excessive preheating, since, because of its aromatic character, tar oil would not decompose at 400°. I actually established, in tests which I made with the Stinnes tar oil sample which Prof. Martin brought with him, that even at 500° only 1-2% of gas is formed. With regard to coking of the nozzle, it should be mentioned that it is not a question of hard deposits but of soft, pitch-like residues.

The main trouble with the crude oils available is the unsatisfactory setting point. In the type of which large quantities are available it is approximately 0°C, whereas the Luftwaffe demands -17°C for lubricating oils. To lower the setting point, I suggested the addition of paraflow, which reduces the setting point by 6-8° with an addition of 1%, or the use of mixtures of tar oil and crude oil, by which means the low setting point of the tar oil compensates for the crude oil, and the crude oil influences the combustion properties of the tar oil.

Dr. Hagemann referred to the fact that a similar problem arose some years ago when nozzles were being manufactured for Diesel engines, but that there was at that time no chemical means available to prevent the nozzles from coking, and they had to be content with structural alterations to the engine. I have seen this confirmed in the meantime in a dissertation by Dipl.-Ing. Wegemann of München, in 1939, on "Engine investigation of the tendency to coking of Diesel fuels at the injection nozzle".

As a further possibility of improving tar oil, the suggestion was made that synthetic Diesel fuels might be added. These sometimes precipitate certain components of the tar oil, which can then be removed by centrifuging or filtering. The method suggested by Prof. Hohlfelder, which consists in reducing the boiling point from 320° to 275°, does not appear to offer prospects of success as firstly this reduces the quantity and secondly at 275° there are still components present which could undoubtedly have a coking effect.

Prof. Hohlfelder mentioned further problems with which, as a machine constructor, he was not so directly concerned, and in the solution of which he would welcome our help. These were :-

1. Obtaining data on specific heat and heat of vaporisation of tar oil and crude oil at different temperatures and, 2. the investigation of the possibility of using tar oil as an additive to normal aero engine fuels in the gasoline engine. It is immaterial whether the mixture or the tar oil alone is used cold or preheated.

It was agreed that I should examine the samples which Prof. Martin brought with him, and make some decomposition tests, in order to ascertain how tar oil and crude oil behave at high temperatures; I was then to discuss the whole problem with Prof. Hohlfelder in Gatow, with preheating specially in view, as this has not been cleared up satisfactorily from the construction point of view, and is partly the cause of coking.

FD2877,46It30

C.I.O.S. Bag No.3445 Doc.No.58
Target No.30/5.01

Reich Institute for
Mineral Oil Research of the
Technical High School Hannover.

Hannover, 7.7.1944.

The Construction of an Apparatus for determining the critical temperature for vapour-lock of gasoline (abreisstemperatur), in aero-engines.

Summary

Researches which have already been made reveal that it is necessary to deduce the effective critical temperature for vapour-lock (abreisstemperatur) not only from the properties of the fuel, but also to take into account the engine conditions (construction of the supply system and working conditions). We therefore consider it important to classify the various types of engines and supply systems in terms of a critical ratio; this represents the volumetric ratio of vaporised to liquid fuel at which the delivery pump will still just supply the engine with sufficient fuel. This critical ratio is a function of engine speed and the construction of the engine, and therefore takes account of the causes of vapour-lock trouble attributable to the engines. The critical ratio is best found in practice by a single test with a reference fuel, but it can be found approximately by calculation from the delivery of the pump and the fuel consumption of the engine.

The causes of vapour-lock attributable to the fuel lie in the capacity of the fuel to develop an increasing volume of vapour as the temperature increases and the pressure falls in a closed system; at that temperature and pressure at which the volumetric ratio of vapourised to liquid fuel is critical for an engine, vapour-lock begins. The term "abreiss-temperatur" of gasoline appears thus to be clearly defined.

In classifying a fuel, therefore, account must be taken of its capacity to develop definite volumes of vapour; we therefore suggest that this capacity be represented by a diagram of "vapour or flash isochores"; these diagrams show at what combinations of pressure and temperature the fuel develops given volumes of vapour. If the volume of vapour is related to the initial volume of fuel, the result is the vapour isochore diagram; if this is related to the volume of fuel residue (after flash vaporisation), the result is the Flash isochore diagram.

A description is given of a simple apparatus for recording vapour isochores. The diagrams of 5 fuels (including 2 pure substances and an azeotropic mixture) are discussed.

It is shown that in principle the vapour or flash isochores represent vapour pressure curves.

A description is given of an apparatus, with mercury as a sealing liquid, which is not yet ready for practical use, after which an apparatus is described by which it is possible to obtain a Vapour and a Flash Isochore diagram by simple pressure measurements. Since there are as yet no extended series of measurements with this apparatus, discussion of the results is deferred to a later report.

(sgd) Dr. K.W. Schneider.
Director.

FD2877,46163/

C.I.O.S. 3445/58

AUTOMOTIVE INSTITUTE OF THE TECHNICAL HIGH SCHOOL DRESDEN

Archive Number B - 93 - I

Report by HAGER and EBERAN

Grading of fuels with respect to formation of vapour locks.

The pumps feeding gasoline to Automotive gasoline engines are generally far oversize; this is done in view of the possibility of the feed efficiency being affected by the formation of gasoline vapour. If vapours are evolved in the fuel-suction line the pump has to feed fuel of increased specific volume viz. liquid gasoline mixed with vapour bubbles. As long as the proportion of liquid fuel delivered is greater than the instantaneous fuel requirements the operation of the engine is not jeopardized. If, however, the volume of fuel being fed is enlarged still further by vapour bubbles, there will be a fuel shortage in the carburettor; this in turn will produce a diminution of the output, superheating, back firing and such like, and will finally lead to failure of the engine.

The factors determining the vapour-liquid condition of a fuel are temperature, pressure and the components of the fuel, volatile or non-volatile. The absolute pressure in the suction line is subjected to variations at each stroke according to the construction of the pump and depends on the cross-section of the fuel line, the resistance of the line, and the amount flowing through it per second. The factors determining the temperature of the fuel in the suction line are heat conduction and radiation. In considering the multiplicity of influences it will be understood that the "break-off" temperature (x) of a fuel feeding unit has not led to a definite grading of fuels with respect to their tendency to form vapour locks. It seems that physical properties (pressure, temperature, volume) are better suited for this purpose.

If the fuel pump is V per unit time and the fuel consumption of the corresponding engine V' one can calculate the safety factor of the pump or the volume ratio $K = V : V'$; the latter also indicates the extent to which the volume of the fuel-vapour mixture may increase beyond the volume of the liquid fuel before the vapour will lead to locking. For instance, if at normal temperatures the pump can deliver ten times the volume consumed by the engine, i.e. $K = 10$, then 90% of the volume may, if the fuel is heated and partially evaporates, be fed in the form of vapour (this part is ineffective in the carburettor). The remaining 10% of the fuel just suffices to supply the engine. If the specific volume of the fuel were increased further by vapour bubbles this would lead to a fuel shortage in the engine.

The safety factor of the pump determines (apart from the physical properties of the fuel) the particular point at which the presence of vapour bubbles takes effect. Therefore fuels can be compared and graded with respect to their tendency to form vapour on the basis of their physical properties alone if a constant safety factor of the pump is employed. The apparatus described below was developed on the basis of these considerations for the determination

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(x) See Bibliography.

of the properties of fuels for the purpose of judging their suitability.

The apparatus consists of a glass U-tube (see Fig. 1) the limbs of which are calibrated in millimetres. One of the limbs has a funnel shaped opening for pouring in mercury. At the bottom of the U tube there is a ground glass tap for running off mercury during the determination. At the top of the other limb is a calibrated pipette and glass isolation tap, for measuring the volume of gasoline under different temperatures and pressures. This limb is enclosed in a thermostatically controlled water jacket, fitted with two thermometers.

Before starting the measurements, the U-limb carrying the pipette is calibrated; the tube is then filled with mercury to beyond the stopcock of the pipette. Mercury is run off through the lower tap until the meniscus in the pipette is just below the tap; the pipette is then shut off by means of the tap and filled up to the calibration mark with the gasoline sample to be tested. When the tap is reopened, the gasoline meniscus falls somewhat below the calibration mark and the mercury in the other limb rises because of the extra pressure exerted by the column of gasoline. Mercury is run off the lower tap until the desired initial volume V_0 of gasoline has run into the U-tube. The tap on the pipette is now closed and a few drops of mercury poured into the pipette to seal off the U-tube completely. In the case of volatile gasolines, the sample must first be cooled considerably (Butane -30°) so that the low boiling components do not evaporate during filling. The pressure-volume measurement may then be carried out at a definite temperature.

If the measurement is to be carried out at a higher temperature, the filling has to be done at room temperature and the heating jacket then raised to the desired temperature, otherwise the gasoline sample may partially evaporate during filling. The initial volume is read when the desired temperature $t_E = t_A$ has been reached. The following quantities are measured:

1) Height of mercury in the left limb Hg_l (mm)
2) Height of mercury in the right limb Hg_r (mm)
3) Height of gasoline meniscus H (mm)

The mercury is now run off through the lower tap by stops of 50 mm., thus reducing pressure over the gasoline. The total volume of liquid and vaporised fuel at the pressure Hg_l is then read off the scale after waiting until equilibrium is attained. The results are reproducible if equal times are allowed before taking the readings. The absolute pressure is determined from the head of mercury,

$$\triangle Hg = Hg_l - Hg_r$$

and the barometric pressure B: $P_{abs} = B - \triangle Hg$

For an initial volume V_0 of liquid gasoline there is a column of gasoline H mm above the mercury in the pipette and this should be taken into account in the determination of the absolute pressure P_{abs}. In measurements at elevated temperatures, one side of the mercury column is heated in the jacket while the other side remains at room temperature. The difference in the specific gravity of the mercury in the two limbs should also be taken into account in the calculation. The two sources of error however have opposite signs and their correction may therefore be neglected. Also the equilibrium between the two mercury columns in the tube is unstable owing to the boiling and evaporation of the gasoline; even tapping the wall of the tube may upset it by causing new gas bubbles to emerge into the space above the liquid gasoline. Too great an accuracy must not be ascribed to the results, a measurement error of 1 - 2% being quite negligible. The total volume V of the fuel sample (liquid + vapour) is read off the scale. Figs. 2-4 show a plot of V against P_{abs} at constant temperature for the mixtures Tel, Tel + 10% Butane, and

Gembo Spirit "Tel" which is a mixture of high boiling components reaches a low pressure when it is expanded to several times its initial volume. Tel + 10% Butane shows a different behaviour since Butane has a very low boiling point. The pressure-volume curves of Tel were measured with increasing and decreasing pressures. Two curves are obtained as when the pressure increases less vapour re-condenses than was produced when the pressure was falling. The condensation delay is thus greater than the boiling delay which is quite noticeable when the pressure is falling. The interval between the two curves increases as the temperature rises, as the equilibrium of the two phases is then most unstable, and also with increasing distance of the point of pressure inversion from the initial volume V_o i.e. as $K = V : V_o$ increases. This volume ratio K is a measure for comparing different gasolines by their pressure or temperature characteristics. Fig. 5 shows the pressure-temperature curves of all three mixtures for K = constant, i.e. for a definite increase in volume. The characteristics of the three fuels are fundamentally different. It is remarkable that the characteristics of the fuels may be compared for any arbitrary value of K (K = 4 - 12) without producing any appreciable effect on the rating.

With an absolute pressure of $P_{abs} = 500$ mm.Hg. on the suction side of a fuel pump whose feeding capacity is 10 times the necessary capacity (K = 10) vapour locks are theoretically expected to occur at the following temperatures:

Mixture Tel + 10% Butane	35 °C
Gembo Spirit	46.5°C
Mixture Tel	66.5°C

Mixture Tel + 10% Butane will thus have the strongest tendency to form vapour locks. Tel mixture will be least sensitive to high external temperatures and any heating up of the fuel feeding unit. The results of these measurements are being checked in a heated fuel feeding unit.

Dresden, 30 March 1944.　　　　Dr. v. Eberan.

Literature.

Th. Hammerich: Die Bewertung von Leichtkraftstoffen hinsichtlich ihrer Neigung zur Dampfblasenbildung - Öl und Kohle 1939, Part 29 - ZVDI 1940, Part 17 (abstract)

Koch: Beitrag zur Frage der Dampfblasenbildung - Kraftstoff 1940, July No.

F.Schaub u.H. Velde: Zur Beurteilung von Kraftstoffen hinsichtlich der Dampfblasenstörungen am Motor - ATZ 1941, Part 22.

Fig. 1 - Pressure-volume measuring instrument for fuels.
1. Manometer U-tube
2. Mercury filling
3. Heating jacket
4. Measuring pipette

V_1 = volume of liquid part of the sample
$V - V_1$ = volume of gaseous part of the sample
V = total volume
B = barometric pressure
$\triangle Hg$ = difference of the mercury columns
$B - \triangle Hg$ = absolute pressure P_{abs}
$t_A = t_E$ = temperature in the heating jacket.

Fig. 2 - Pressure-volume curves for "Tel" mixture at constant temperatures.

Fig. 3 - Pressure-volume curves for "Tel" mixture + 10% Butane at constant temperatures.

Fig. 4 - Pressure-volume curves for "Gembo Spirit" at constant temperatures.

Fig. 5 - Pressure-Temperature curves of gasoline.

B - 93 - II

Intermediate Report.

Purpose of the investigation.

In the course of the cooperative experiments of the Zentralbüro für Mineralöl G.m.b.H., 9 fuels (a, b, c, e, f, g, h, i, k) were examined for tendency to vapour lock by the method described in the report B - 93 - I, using Prof. von Eberan's apparatus. The same test-substances were available elsewhere for examination by different methods. The other places were: Ruhr-Chemie A.G., Oberhausen-Holten, Reichskraftsprit G.m.b.H., Berlin, Olex, Deutsche Benzin -und Petroleum G.m.b.H., Berlin. The purpose of the cooperative experiments was to set up a simple uniform method of rating car gasolines according to their tendency to vapour lock.

Test Methods.

a) IfK - Test apparatus.

It was desired to shorten the test with this apparatus at the various temperatures, and avoid the careful cleaning of the apparatus which had to be done each time. To achieve this the pressure-volume curves of the test substances were measured for all temperatures with one fuel sample only. When the pressure in the U-tube manometer is increased a condensation delay occurs. This means that when the next measurement is started the initial volume of 2 cc is no longer reached because of a small gasoline vapour bubble which remains behind. This is shown in the pressure-volume diagram (see report B - 93 - I, figs. 2 and 4) by the fact that the curves for lower temperatures (20 - 50°) do not start at V = 2 cc. but at about 2.5 - 3.5 cc. At higher temperatures a larger part of the pressure-volume curve is lost. In the relevant region of pressure and temperature this does not come to the fore because those states correspond to low values of K.

The values of the PT curves at constant values of K of 4 and 12 were taken from the pressure-volume curves at constant temperature and then plotted. For comparison purposes, the values of the temperature for K = 4 and K = 12 at a pressure of 760 mm.Hg. have been entered into Table 1, giving an evaluation of the fuels. For K = 4 we get the following order: a - c - g - i - b - e - k - h - f
for K = 12 : a - c - g - i - e - k - b - h - f

where the vapour pressure increases towards the right. The order is the same in both cases with the exception of fuel b which in the lower series appears at a later stage.

Finally a 1 : 1 mixture of the non-volatile fuel a and the easily volatile fuel f was investigated in order to be able to predict the vapour locking tendency of mixed fuels from the characteristics of the components. The result is shown in diagram 11. The more easily volatile fuel f with higher vapour pressure is the decisive factor, as was to be expected. It is observed that the K of the mixture a + f does not by any means lie in the middle of the K curves of the substances a and f but that it is strongly displaced towards the more volatile fuel f. Thus for example at 760 mm.Hg. pressure and a fourfold volume increase (K = 4) the break-off temperatures are

Testfuel a 71.5°C

Testfuel f 50.0°C

and mixture a + f 56.0°C

A condition of the desired standard rating of fuels is that the permissible increase in volume K be laid down uniformly for all the possibilities of vapour lock troubles in running operation. A safety factor of K = 12 would probably not be attained by any fuel pump installation.

b) Safety factor of fuel pump installations.

The fuel pump equipment of motor cars now in general use consists of diaphragm pumps the stroke of which during suction is produced by a cam, and by a spring during compression. The delivery pressure of these diaphragm pumps is consequently limited to about 0.1 - 0.4 atm. excess. Fig. 1 shows a section of a Solex lever pump. Fig. 2 gives the pumping characteristics of this pump in the extreme cases of:

a) purely liquid-fuel pumping
b) purely gaseous pumping
and also for c) liquid-vapour mixtures of various compositions.

The mixed pumping was effected by injection of known quantities of air in the form of very fine bubbles by means of a porous plate. The installation shown in Fig. 3 corresponds to a fuel pumping system in the 3-to-Opel-L.K.W. The 100 per cent air pumping rate of the pump in litres/hour (case b) at the maximum number of revolutions (n = 1750 revs./min.) is about 3 times as large as the pumping rate of 100 per cent fuel (case a). An increase in the proportion of air fed to the pump decreases the quantity of fuel delivered.

Example:

n - 1750 revs/min.
Air throughput L - 100 litres/hour
Air/fuel throughput B + L - 115 litres/hour
Fuel throughput B - 15 litres/hour

The pump handled the full load consumption of the 3.6 litre Opel engine at all speeds with a safety factor of about 2. In the limiting case just before before the break-off the consumption is still covered when the pump has to convey 40 - 60 litres/hour of air or vapour bubbles. Theoretically the fuel to be pumped could take up 3 - 4 times its own volume by partial vaporisation without any fuel deficiency occurring in the engine. The K-curve of this vehicle installation in Fig. 2 shows that the critical break-off point of the fuel supply lies at n = 1550 and full load because at this point the increase in the volume of the fuel due to vapour bubbles must not exceed 2.75.

The mixture pumping characteristics of other vehicle installations are still being investigated. On the pump test apparatus shown in Fig. 3 particular investigations are carried out to see how far the formation of vapour bubbles on the suction or pressure side of the pump determines the critical fall in the throughput.

c) Road tests.

Trial runs were made with a 1500 cc. NSU Fiat on a flat stretch of the Dresden-Berlin Reichsautobahn to check under actual conditions the order of test fuel ratings obtained in the cooperative experiments of the Zentralbüro für Mineralöl - G.m.b.H.

The measuring arrangements and test points are shown diagrammatically in Fig. 4, and Figs. 5 and 6 show the instruments and modifications in the car itself.

The test fuel could be heated in a coil immersed in the engine cooling water until a break occurred in the fuel supply. Preliminary experiments had shown that vapour lock in the vehicle was reproducible only in a state of thermal equilibrium; the latter can be attained only if the temperature of the engine is raised gradually as well as the temperature of the cooling water and the fuel. In place of the radiator casing the experimental car was therefore provided with a radiator shutter which was continuously adjustable from the inside. The temperatures were measured by means of calibrated thermo couples and a millivoltmeter as well as by means of a distant reading capillary thermometer. The gradual temperature rise at all the measuring points was watched by continually reading and recording the temperatures at one minute intervals until the fuel supply locked. The following was the procedure of an experimental run. After the preceding experiment extending to the breaking of the fuel supply, the cooling water was run off and replaced by cold water. At a constant speed of 80 km/sec. the equilibrium temperature of the engine was then gradually raised by regulating the shutter in front of the radiator until the break-off point was reached. The failure of the fuel supply was immediately and unmistakeably noticeable first by virtue of the fall in output and secondly by virtue of the directly ensuing engine failure for lack of fuel. Diagrams 12 to 15 show the temperature course of some of the experimental runs with various fuels up to the breaking off of the fuel supply. From the results of the experimental runs it may be seen that the temperature of the fuel in the pump and pressure lines was raised by additional heat due to conduction and radiation from the engine. The temperature of the fuel in the pressure line was therefore always about 7° higher than in the suction line. Further heating occurred in the carburettor although the latter was screened from the exhaust-manifold by an asbestos screen. The temperature of the fuel in the carburettor was another 2 - 5° higher than in the pressure line. The temperature of the distance thermometer provided on the suction side was similarly affected by heat conduction. It agreed well with the temperature of the cooling water system. The temperatures, taken in the experimental runs at the moment of "break-off" of the test fuels a - k and OZ 60, are given in Table 1, page 16 (of the original).

When the break-off temperatures measured with the IfK-test instrument are compared with those measured in the road tests on the 1500 cc. Fiat, it is evident that:

1) Unlike the laboratory test, it is not possible to make a definite assessment of a fuel by measuring only one quantity in an experimental run, despite special precautions; this is due to the multiplicity of factors which determine the "break-off".

2) The break-off in a vehicle is not simply related to any of the following different temperatures:

t_{CW} = temperature of cooling water.
t_{SF} = fuel-pipe temperature suction side
t_{ST} = fuel temperature-suction side.
t_{PT} = fuel temperature-pressure side.
t_{CT} = temperature of carburettor.

3) The temperatures in the experimental run lie in the following order as a rule:

$$t_{ST} < t_{PT} < t_{CT} < t_{CW}$$

4) The temperatures t_{SF}, t_{CT}, being determined by conduction of heat, are nearly equal.

5) The value $\frac{t_{SF} + t_{CT}}{2}$ represents the mean temperature of the walls in contact with fuel, $\frac{t_{ST} + t_{PT}}{2}$ represents the mean temperature of the fuel itself.

6) The values of t_A measured with the IfK test apparatus at $P = 760$ mm.Hg and $K = 4$ lie between the mean wall and fuel temperatures leading to break-off in the experimental run.

$$\frac{t_{ST} + t_{PT}}{2} < t_A < \frac{t_{SF} + t_{CT}}{2}$$

The greatest deviation from this rule amounts to 2°.

Summary.

1) The rating of fuels according to the IfK test-method is, within wide limits, independent of the value of the factor K.

2) For the 3 t-Opel-L kw. the critical volume increase lies between $K = 3$ and $K = 4$.

3) The break-off temperature in the vehicle is not unequivocal as in the pumping system the fuel is exposed to temperatures differing by anything up to 25°.

4) The experimental run does however definitely confirm the low tendency to vapour lock of those fuels which attain high-temperature values in the IfK-test apparatus and vice versa.

5) The agreement between the break-off temperature given by the IfK laboratory test and the temperature which is to be regarded as decisive for break-off in the engine can be established to within 1-2°.

6) The IfK laboratory test may be taken to be sufficiently simple and accurate for the rating of fuels with respect to vapour locks.

Dresden 30.10.44.

Prof. v. Eberan.

Table of temperatures.

FUELS OF THE CO-OPERATIVE EXPERIMENT

Fuel	Test apparatus P = 760mm.Hg		1500cc. Fiat road test.							
	K = 4 t_A °C	K = 12 t_A °C	V Km/h	t_{KW} °C	t_{SF} °C	t_{ST} °C	t_{DT} °C	t_{VT} °C	$\frac{t_{ST}+t_{DT}}{2}$ °C	$\frac{t_{SF}+t_{VT}}{2}$ °C
a_1	71.4	75.6	90	81	74.3	61.4	70.0	74.7	65.7	74.5
a_2	72.3	76.4								
b	54.1	56.5	80	72	65.0	51.6	60.3	60.3	56.0	62.6
c	60.8	65.0	"	76	66.5	50.4	57.7	65.0	54.0	65.7
			"	74	65.0	51.6	56.3	62.4	54.0	63.7
			"	75	66.0	53.5	62.9	68.9	58.3	67.5
e	53.7	57.7	"	62	57.2	48.3	51.6	55.7	50.0	56.5
f_1	50.4	52.0	"	63	54.5	45.0	55.3	58.8	50.1	56.6
f_2	50.9	51.8	"	63	53.5	45.0	54.0	58.0	49.5	55.8
			"	58	50.4	44.2	53.3	54.0	48.8	52.2
			"	58	51.5	42.7	52.0	52.0	47.4	51.7
			"	63	53.5	47.4	51.0	52.0	49.2	52.8
			"	58	50.4	44.0	47.5	49.5	45.8	50.0
			"	57	50.4	42.6	48.0	49.5	45.0	50.0
g	60.5	63.8	"	68	63.0	52.0	60.3	63.5	56.2	63.2
			"	72	65.0	55.0	62.3	64.3	58.7	64.6
h_1	49.7	53.9	"	63	55.5	48.0	52.8	55.0	50.4	55.2
h_2	51.3	54.6	"	63	55.5	45.5	53.0	53.0	49.2	54.2
			"	60	53.5	45.2	49.6	53.0	47.4	53.2
			"	61	55.4	45.5	50.3	54.3	47.9	54.8
			"	61	53.5	44.2	48.7	49.8	46.4	51.6
i	56.3	60.7	"	73	64.0	54.3	61.8	63.8	58.1	63.9
k	53.5	57.5	"	69	60.9	49.0	59.1	60.5	54.0	60.7
			"	69	59.8	52.2	58.5	59.0	55.3	59.4
a+f	55.9	58.0								
OZ60	73.0	79.0	100	84	76.0	64.0	71.4	75.4	67.7	75.7
			"	88	74.3	65.4	68.0	72.0	66.8	73.1
			"	83	74.3	66.7	69.0	75.1	67.7	74.7
g	60.5	63.8	40	78	68.0	54.7	63.8	69.0	59.2	68.5
			60	76	66.5	54.0	63.0	68.4	58.5	67.4
			80	72	65.0	55.0	62.3	64.3	58.7	64.7
			100	69	60.5	46.2	54.3	58.6	50.2	59.6

t_{KW} = Cooling water exit, distance thermometer.
t_{SF} = Fuel suction side distance thermometer.
t_{ST} = Fuel suction side thermo-couple
t_{DT} = Fuel pressure side thermo-couple.
t_{VT} = Fuel carburettor thermo-couple
V = Velocity of car.

FD2877,46168

German Experimental Station for Aeronautics

Extract from "Report on more recent work of the Institute"
compiled by Dr.phil. A. v. Philippovich

Page 2

A. Laboratory

a) Research on fundamental relations and problems of the day

Combustion was of considerable interest in the case of fuels (3,4,5). The question was accordingly studied by Prof. W. Jost at present with the University of Marburg under contract with the D.V.L. He examined slow oxidation as well as adiabatic spontaneous ignition by compression (6). Under slow oxidation, results similar to those of Edgar and Estradere were obtained. The second line of work however led to the conclusion that a generally useful knock classification should be obtainable by means of adiabatic spontaneous ignition, fuels being characterized by their ignition delays. First the logarithm of the ignition delay was plotted against the reciprocal of the temperature of spontaneous ignition and a linear relation was found (fig. 1). Later Prof. F.A.F. Schmidt of the Institute for Thermodynamics of the D.V.L. and his co-workers showed that this linearity was valid only for relatively long ignition delays, appreciable curvatures occurring at higher temperatures and shorter ignition delays (7,8) (fig. 2). Jost originally assumed that the reaction of spontaneous ignition and with it the knock reaction are dependent on temperature only. As shown above this assumption turned out to be incorrect: there is an appreciable dependence on pressure which does not however become apparent at lower pressures. The endeavour to obtain a characterisation of fuels on a laboratory basis led the Institute to sponsor experiments elsewhere. M. Teichmann, a former co-worker of Jost did succeed in establishing a connection between the experiments of Schmidt and Jost by using the adiabatics for the characterisation of spontaneous ignition (9) (fig. 3). This enabled him to insert into the diagrams not only the conditions maintained in experimental apparatus but also those obtaining in engines under various modes of operation. It now became necessary to ascertain the pressures and temperatures and to compare them with the more easily ascertainable values of the experimental apparatus. There was thus some hope of continuing successfully along this line. Engine experiments of the Institute dealt with more fully below led to the following hypothesis, that knock in engines is the result not of the simple heat explosion but also of cold reactions with a negative coefficient of temperature in certain regions. In this way however the continuation of the absolute solution of the question of knock is even more doubtful: this is so at any rate on account of the numerous factors which are of practical importance. The experiments which should have been carried out for confirmation or otherwise of the assumption that measurement of adiabatic spontaneous ignition may be used for the investigation of knock characteristics of fuels in engines have therefore not been completed. It would seem interesting however to continue work in this direction. A final answer to the question of whether a simple laboratory method will be able to replace knock measurement in engines should thus be reached. The practical importance of this work depends on the further development of jet propulsion.

Page 5

Lubricants - The question of ageing or of oxidation of lubricating oils was dealt with. Besides its general importance there is also the question of its connection, interesting for aeronautics, with the tendency to form residues (18,19). The research was mainly meant to lead to a systematic study of all the oxidation products formed during the progress of ageing. The other main objective was to elucidate the mechanism of the reactions leading to the formation of asphalt (2). Analytical methods were evolved for this purpose which allow of the determination of practically all the modes of combination of oxygen. The method is essentially carried out as follows :

Carbonyl and Hydroxyl-groups are determined by means of Grignard reactions and by acetylation of the carbonyl groups; the results are used in combination with the acid number and saponficiation number of the substances (21) (fig. 5). The group separation of the oxidised products from the oil was also successful. Oxidation was then further studies with suitable model substances such as cetane which combine with oxygen in the same modes as does lubricating oil. Chromatographic adsoprtion analysis was successfully used to isolate, sometimes in a state of purity, the oxygen compounds formed during the oxidation of cetane. This research, requiring very much time has not yet been brought to a close.

Examination of lubricating qualities of oils showed wherein lay the difference in the usefulness of the aviation oils used. It is to be sought less in the difference in structure than in their content of sulphur and the latter's capacity to react with the metals of the bearing (22) (fig. 6). General experiences with high pressure lubricants and research at a different place (Prof. R. Glocker, Stuttgart) (23) shortly before the end of the war were combined with the above result. This led to the addition to the oils of organic phosphorus compounds. Fundamental experiments on the lubricating qualities of oils in the non-hydrodynamic region were carried out with the aid of a newly developed instrument. A new conception of the lubricating process resulted (24). Unfortunately this work too has had to be interrupted so that much that had been started on must remain without a solution. The following intermediate results of practical interest for the lubricating region under investigation may be reported here:

The existence of active groups is not an immediate pointer to good or bad lubrication. According to the lubricating substance, increase of temperature may have a favourable or unfavourable effect on lubrication. The life time of the thinnest lubricating films is exceedingly short. Each lubricating substance forms a characteristic sliding path, as may be expected from theoretical considerations (24). One can now determine the coefficients of friction of oils very accurately. This in conjunction with theoretical assumptions may lead to the synthesis of lubricants far more suitable for lubrication than any oil known so far. This work has only been begun (25).

Apart from this work of the Institution on lubricating qualities, researches of Prof. K.L. Wolf and co-workers, University of Halle, were encouraged. They aimed at determining accurately the interfacial tensions of substances relative to mercury by the drop-weight method in order to gain an indication as to the adhesive strength of these substances (26,27,28). Direct measurements on aero-engine oils with varied times and temperatures were being developed. A direct relationship between adhesive strength relative to mercury and practice could not so far be found. Dr. F. Seelich of the K.W.I. for physical chemistry Berlin, worked on the spatial arrangement of lubricant molecules at the oil-water interface, on behalf of the Institute (29). Prof. C. Erbecher of the K.W.I. for chemistry, also of Berlin, had the task of working on the surface characteristics of metals by means of radioactive elements (30).

<u>Page 7</u>

b) Development of test-methods and apparatus

Test methods

For the examination of fuels an exact and rapid semi-micro method for the determination of lead tetraethyl was worked out. This allows the percentage of lead to be found within 20 minutes by careful precipitation of lead tetraethyl with sulfuryl chloride as diethyl lead dichloride and titration of the latter by means of a dithiazone solution (31). With many different aviation fuels so far analysed, the accuracy was ± 0.001 vol. % T.E.L. The fuels must however be shaken with dilute sulphuric acid if the content of bases is high (addition of aniline). The quantity necessary for an analysis is only 2 cc.

The decomposition products of lead tetraethyl which may be partly dissolved in the fuel and which have less antiknock effect are also quantitatively determined in a very short time (12). For the control of ethylene bromide in the fuel, (of particular interest for fuels to which I-T-Fluid has been added on cold winter days), the bromine content of the fuel was ionized with zinc in presence of alcohol, water, acetic acid and pyridin and then determined volumetrically (according to Volhard) (32). This method requires 25 cc of fuel and takes 35 mins., the accuracy according to experience gained so far being about ± 010005 vol. % ethylene bromide. The usual bomb-test for fuels was also improved and extended (33). Films of collodion were adopted as an improvement on gelatine capsules in determinations of the calorific value.

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Apparatus

Studies of the lubricating qualities with different apparatus such as those of Almen, Wieland and Thoma and also those commissioned by the PTR had the following defects: a large variation in the grading of the oils (except in extreme cases such as fatty and purely mineral oil), inability to reproduce results and insufficient range of measurement (40,41). A new and handy apparatus was developed with a large resolving power and reproducible readings so that a suitable tool should be available especially for a fundamental investigation. The four-ball-air turbine apparatus that was constructed allows of the determination of the coefficient of friction of engine oils (coefficient of friction about 0.1) to within ± 0.001. It consists of three spheres fixed on a plane and touching one another which represent the guiding bearing. A fourth sphere serves as the sliding body and by way of an air turbine and two nozzles arranged in tangential symmetry, can be driven at a controlled speed (42). The conditions of lubrication are thus those chosen by Boerlage. The apparatus permits investigations with very small amounts at temperatures of from -20°C to +20°C in different atmospheres and with different materials (by electrolytic plating of the spheres with different metals).

For the chemical examinations an apparatus for the ageing of the oil was constructed. This enabled one to determine the ageing products of the oil quantitatively and secured the complete condensation of fogs and vapours by means of baffle walls and low temperature cooling (20). For the analysis of dragging substances containing tin which occur in synthetic oils an extremely accurate tin determination method was worked out (43). The research on the lubricating qualities of oils led to the determination of reactive sulphur by passing hydrogen over heated oil and determining the hydrogen sulphide formed. For the investigation of the anti-corrosive effect (adhesion) of oils a simple method was given (44). An accurate instrument was worked out for the determination of the different forms of combination of oxygen in aged oils and for the investigation as to composition of unkown lubricating oils and special oils; with this instrument quantitative Grignard reactions - determination of the methyl magnesium iodide added with or without evolution of methane - could be carried out (21).

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Engine Work

Fuels

The answer to the question of the practical use of 87 O.N. gasoline instead of 100 O.N. fuel was the following: The boost could be increased correspondingly by an addition of methyleniline and either aromatic compounds or isoparaffins in small amounts as well as by an increase of the lead content to 0.16 vol. %. The increase of lead content to 0.16% was hazardous because of greater danger of damaging the valves and plugs: it could not be avoided however if the preassigned task was to be accomplished at all (54). At a boost-air temperature of 80°C it was the ortho-compound of isomeric xylenes that allowed least supercharging among aromatic mixtures in the BMW 132 - monocylinder. In the cases examined supercharging could be increased as the number and length of side-chains of the benzene-nucleus increases (fig. 10). Among 2 highly aromatic fuels therefore the one containing aromatic compounds of higher boiling point could be used for greater supercharging. The octane number gave a different result from the supercharge test (55).

The generally interesting ring-sticking tendency of oils was investigated and the following result obtained: the running-time in one motor using one fuels and lubricant mainly depends on the temperature in the ring groove.

Page 13

Lubricants

Fig. 11 shows the temperature dependence of various oils. It should be particularly emphasized that the minima for the lubricants differ largely (58). For these experiments it is necessary to keep the operating conditions, especially the temperature, exactly constant. To achieve this one had first to make a careful study of the temperatures occurring in the engine under the most varied conditions (59). In this connection measurement of the temperature of the piston during operation gave the result that the temperatures in the region of the piston ring do not by any means remain constant under similar external conditions. The influence of the heat transfer from piston to cylinder is of far greater importance in these ring-sticking experiments then had so far been generally assumed (60): the heat transfer in turn depends on the formation of residues, the plays, the oil film adhesion and the oil film sealing capacity. All the same a well-defined connection could be found between external conditions and the temperature of the piston.

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Development of Test Methods

In order to simplify and cheapen the investigation it was tried to develop a suitable test method by a large number of runs on small engines (500 cc. and less) (73,74). It became apparent however that these engines were not sufficiently loaded thermally: for test-methods they would therefore have to be altered. The instant when ring-sticking starts was ascertained only with difficulty. Fundamental dangers in the piston did lead to success in this direction. The construction was however apparently liable to lead to faulty results. Among other things the residues deposited in the piston skirt produced misleading results (75).

A novel test-method for measurement of the tendency for ring-sticking was also developed with a small engine. Here the uppermost groove of the piston was provided with small holes running into the interior so that at the start of the experiments the combustion gases can flow past the piston ring into the crank case, a very low performance resulting. The passages were blocked to an increasing extent by the slow formation of residues, less gas blows through the holes which is linked up with a rising performance of the engine. The velocity of the increase in performance (expressed as the gradient of the performance-time curve) could be taken as the direct measure of the tendency for residue formation of the fuel under test (76). Fig. 13 shows that there is a certain connection between the results found in the BMW 132 oil test engine and those in the present test method. It is most important that inversion of the curves is found at higher temperatures in both cases. This method which now offers the measurement of piston temperatures (81) should now be made to register continuously and the reproducibility be thus improved.

For the determination of lubricating qualities several test-methods were used. Experiments were carried out with the aim of applying the instrument developed by the PTR on behalf of the DVL, to the measurement of lubricating qualities. This met with a certain measure of success only when one sector of the revolving cast-iron plate (which had been lapped very exactly) was covered with the oil under test and another one with the reference oil so that the contact pin moved alternately in the two oils (41). On the whole the measuring range turned out to be insufficient in comparison with the scattering of results. Pronouncements on the differences between lubricants could thus be made only with reservation. The instrument is thus more useful in the classification of the constructional materials. The wear at various pressures in the region below the seizing limit was measured by means of a four-ball apparatus of particular construction for the region of greater loads (78); measurements were made with four typical gear oils. The result was different for each oil when the load varied: in the upper region the results agree with practical gear oil tests (79) (fig. 14). The classification of the same oils after 2½ secs. seizing load (method of Beerlage) gives yet another grading as does the determination of the welding point load (method of Rhenania-Ossag and of the Heereswaffenamt). Thus for each method it is necessary to find out to what practical conditions it corresponds and for what cases of loading inferences may be allowed.

Figures

Fig. 1 - Ignition delays of Benzene, Iso-octane and heptane according to Jost and Teichmann.
Fig. 2 - Ignition delays of n-Heptane as a function of final compression temperature (according to Scheuermeyer).
Fig. 3 - Pressure and temperature diagram with the ranges of spontaneous ignition entered in it (according to Teichmann).
Fig. 5 - Simplified plan of oxygen-combination detected in an aged oil.
Fig. 6 - Sulphur content and anti-wear number of a few oils.
Fig.10 - The extent to which supercharging may be carried with some aromatic compounds if mixed with lead gasoline as a function of the boiling point (50% point).
Fig.13 - Testing of lubricants according to two different methods.
Fig.14 - Wear test of typical engine oils of equal viscosity in the DVL four-ball oil test apparatus.

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I.G. FARBENINDUSTRIE AKTIENGESELLSCHAFT
Cognate Specification for Foreign Application based on
Le 2457, 2520, 2521, 2918, 2942, 2979, 2980
3727, 2728, 3729.

LEVERKUSEN-I.G. WERK, 26.2.1943.

Process for production of polymerisation products of tetrahydrofurane.

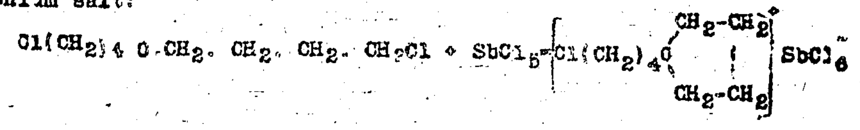
According to previous methods, one of the most important conditions for the polymerisation of organic compounds (in the true sense of the word) is either the presence of unsaturated linkages or else of unstable, easily broken up ring systems. Thus it is well known that ethylene oxide, under the catalytic action of Caustic potash, trimethylamine, tin tetrachloride and similar substances, easily forms high-molecular products, so-called polyethylene oxides. Epichlorohydrine may also be polymerised by dropping in concentrated hydrofluoric acid. On the other hand, the saturated cyclic ethers, with five and six membered rings, were hitherto considered to be extremely stable compounds which, like the aliphatic ethers, could be broken up only by very powerful agents, e.g. by heating with fuming hydrobromic acid, and are therefore unsuitable for polymerisation proper.

It has now been found that contras to expectations that tetrahydrofurane can be converted easily and at low temperatures into high-molecular, partly viscous and partly solid substances. The polymerisation of tetrahydrofurane takes place particularly easily and smoothly under the influence of tertiary oxonium salts of halogen acids, e.g. oxonium salts with the ions BF_4, $SbCl_6$, $FeCl_4$ or $AlCl_4$. These tertiary oxonium salts may easily be obtained according to the processes described by H. Meerwein and his collaborators (Journ. pr. Chemi 2, 147, 257, 1937); G. Willfang (Dissertaion Marburg 1937); H. Gold, Dissertation Marburg 1939 by the action of oxygen compounds, e.g. ethylene oxide, on the ethereal solutions of metallic and non-metallic haloid etherates.

The quantity of tertiary oxonium salt required for the polymerisation of the tetrahydrofurane is very small. In the case of the oxonium salts of antimony chloride and boron fluoride it only amounts to fractions of a Mol percent. The oxonium salts of ferric chloride, aluminium chloride and tin chloride are less active.

In order to carry out polymerisation, it is not necessary to start with the completed oxonium salts; the latter can be produced by the aforementioned process in a solution of tetrahydrofurane. Thus for example boron fluoride may be added to tetrahydrofurane in the proportion of 1-2 mol percent and the equivalent amount of epichlorhydrin added to the resulting solution. Polymerisation will occur almost immediately, which can be recognised by the occurrence of increase in temperature and increasing viscosity of the solution, will set in.

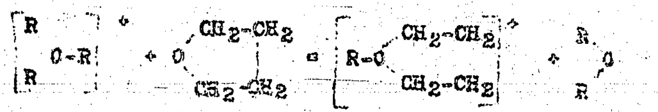
A further method for obtaining tertiary oxonium salts consists, as was found, in the action of electrophile metal haloids, e.g. $SbCl_5$ $FeCl_3$ of BF_3 on : β, γ, δ or ε halogen alkyl ethers or esters e.g./ the δ, δ' dichlordi butyl ether with antimony pentachloride furnishes an excellent crystalline oxonium salt:



In order to effect polymerisation, the isolation of the tertiary oxonium salts produced in accordance with this equation is not necessary. Usually the metallic or non-metallic haloid is dissolved in the halogen alkyl ether or ester, and the mixture of the reaction is allowed to stand for some time until the tertiary oxonium salt has formed, the tetrahydrofurane is then added Polymerisation then sets in at once. In certain cases it is possible to produce the tertiary oxonium salt by this process direct in the tetrahydrofurane solution. The alkyl ethers halogenated in the β, γ and ε positions and the alkyl esters possess a slight tendency to form tertiary oxonium salts and therefore have only a very week polymerising effect in the presence of electrophile metallic and non-metallic haloids.

Regarding the mechanism of the polymerising effect of the tertiary oxonium salts, the following statement, based on experiment, may be made:

In the tertiary oxonium salts, the oxygen atom is very loosely held so that in chemical reactions it frequently behaves as a free alkyl ions, much as the hydroxonium ion shows the properties of the free hydrogen ion. In the action of tertiary oxonium ions on excess tetrahydrofurane a new oxonium ion is formed, in which the linkage between the oxygen atom and the CH_2 group is particularly loose according to the following reaction:



The oxonium ion therefore behaves like the alkyl cation:

$$RO-CH_2-CH_2-CH_2-CH_2{}^{+}$$

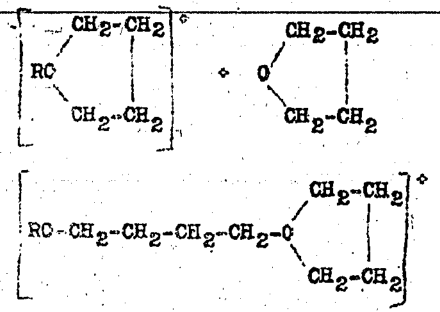
If an easily polarised anion with the tendency to attach itself on the C-atom to form a homopolar compound is present in the reaction medium a neutral molecule is formed by the seizure of this anion. This is the case, for instance in the presence of chlorine and hydroxyl ions when, as shown experimentally, the compounds

$$RO-CH_2-CH_2-CH_2-CH_2Cl$$

or

$$RO-CH_2-CH_2-CH_2-CH_2OH$$

are produced. With the oxonium salts having anions which are difficult to polarise, such a reaction with the tertiary oxonium ions does not take place, or takes place slowly. The latter thus have the opportunity to join a tetrahydrofurane molecule, forming a new tertiary oxonium ion as followings:



which now behaves in chemical reactions like an alkyl cation with the formula

$$RO(CH_2)_4\ O-CH_2-CH_2-CH_2-CH_2^+$$

The reaction proceeds as described until there are produced high molecular, linear polymerisation products of tetrahydrofurane (ionic chain reaction). The termination of the chain takes place either by reaction with the easily polarisable anions, which are contained or are produced in small quantities in the reaction medium, or else by a dissociation of the naturally unstable halogen acid ions. The more stable the halogen acid ion, i.e. the more difficult it is to polarise, the longer will be the reaction chain and therefore the greater the molecular weight of the products of polymerisation.

It has also been found that instead of the tertiary oxonium salts of halogen acids, generally speaking any compounds which have the ability to add onto oxygenated compounds to form oxonium salts may be used for polymerising the tetrahydrofurane. These include:

1. Alkyl fluorides.

2. Functional derivatives of aliphatic and aromatic oxygen compounds, with 1 mol alcohol and 1 mol of an organic or inorganic acid, or 2 mol of similar or different organic or inorganic acids respectively, such as for example chloromethyl ether, dichlorodimethylether, benzal chloride, methylene glycol-methyl-ether-acetate, methylene glycol diacetate, benzophenone chloride.

3. Acid haloids or acid anhydrides, such as acetyl chloride or fluoride, adipic acid dichloride, benzoyl chloride, phthalic acid dichloride, thionyl chloride, sulphuryl chloride methane-chlorosulphonate, benzol sulphuryl-chloride, phosphorusoxychloride, acetic anhydride, succinic anhydride, phthalic anhydride etc.

4. Hydrolysable halogen compounds, which strictly speaking cannot be termed acid haloids, because the compounds produced on their hydrolysis do not possess the number of ionisable H-atoms to correspond to the hydrolysed halogen atoms, e.g. S_2Cl_2, SCl_2, PCl_3, PBr_3, PCl_5, $AsCl_3$, $SbCl_3$, $SiCl_4$, BCl_3, benzotrichloride.

5. Acids with difficulty polarizable anions, such as perchloric acid, chlorosulphonic acid, fluorosulphonic acid, pyrosulphuric acid and the complex halogen acids, or mixtures of halogen hydrides with electrophile metallic and non-metallic haloids may be used.

6. Esters of strong acids having the ability of adding to tertiary amines to form quaternary ammonium salts, e.g. dimethyl sulphate aryl sulphonic acid ester, alkyl rhodanide and the like.

7. Diazonium haloids. –

With the foregoing polymerisation agents with the exception of those mentioned under 5, in general it is necessary to have the simultaneous action of additional substances, which by forming complex compounds facilitate the addition of the polymerising agent on the tetrahydrofurane with the formation of oxonium salts (cf. H. Meerwein and Maier-Hüser, J. pr. 134, 82.64), and at the same time enhance the stability of the anion, which is essential for polymerisation. Such additional substances are: electrophile metallic and non-metallic haloids, such as boron fluoride, aluminium chloride, iron chloride, antimony pentachloride, tin tetrachloride, also sulphur trioxide and very strong acids such as perchloric acid, iodic acid, sulpho acids, sulphuric acid.

Of the many possible compounds which can be employed for polymerising tetrahydrofurance the following will be given as characteristic examples.

1.- Ethyl fluoride and boron fluoride

2.- Mono and dichloro-dimethyl ether, α chloroethyl ether, 2.3 dichloro-tetrahydrofurance methoxy methyl acetate, methylene glycol diacetate, benzal chloride combined with antimony pentachloride, iron chloride or aluminium chloride.

3.- Acetyl fluoride and borom fluoride; acetyl chloride or other aliphatic and aromatic carboxylic acid chlorides and ferric chloride, aluminium chloride, tin tetrachloride zirconium tetrachloride or sulphur trioxide; acetic anhydride, succinic anhydride or other anhydrides of organic carboxylic acids, together with ferric chloride or other haloids, perchloric acid, iodic acid or sulphuric acid; methane chlor-sulphonic acid, benzene chlor-sulphonic acid, sulphuryl chloride, or thionyl achloride together with ferric chloride, aluminium chloride etc, or sulphur trioxide; phosphorisoxy-chloride and iron chloride or sulphur trioxide.

4.- S_2Cl_2, SCl_2, PCl_3, PBr_3, PCl_5, $AsCl_3$, $SbCl_3$, $SiCl_4$, BCl_3, benzo trichloride in combination with antimony pentachloride, ferric chloride, aluminium chloride, stannic chloride.

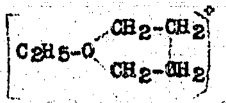
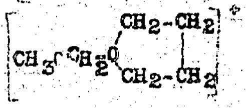
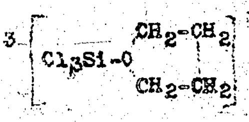
6.- Dimethyl sulphate, aryl sulphonic acid ester, together with ferric chloride or sulphur trioxide; alkyl rhodanides and sulphur trioxide.

7.- Aryldiazonium chloride and ferric chloride.

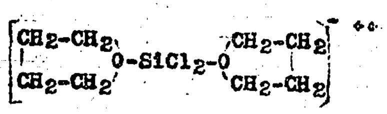
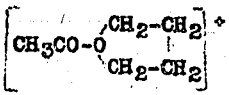
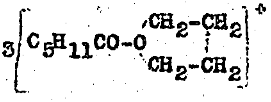
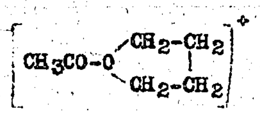
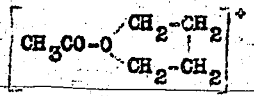
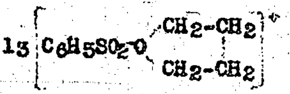
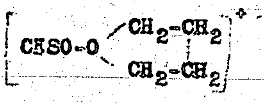
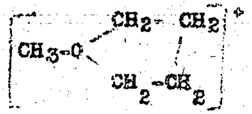
Instead of using the compounds specified above, the process can be carried out in such a way that the active substances, i.e. the polymerising agents and additional substances are produced in the reaction mixture. For example hydrochloric acid and 2.3-dichlorotetrahydrofurane are produced by the action of small quantities of chlorine or chlorinating substances, such as N.-chloroacetanilide on tetrahydrofurane. Both substances are able to polymerise, along with metallic haloids, the tetrahydrofurane acid haloids and hydrochloric acid are easily formed from thionylchloride or other inorganic chlorine compounds and carboxylic acids. Both the reaction products are polymerising agents. From benzyl chloride under the influence of metal haloids one can obtain resins and free hydrochloric acid. If this reaction takes place in the presence of tetrahydrofurane the hydrochloric acid together with the metallic haloid effects the polymerisation. Pyrosulphuric acid may be produced using sulphur trioxide and sulphuric acid.

The probable reaction process of the polymerisation will be explained by means of a few examples:

The polymerising agent first forms, in conjunction with the additional substance a tertiary oxonium salt with tetrahydrofurane, which reacts in a similar way to the formulae on pages 2 4 with further molecules of tetrahydrofurane to form high molecular weights linear polymerisation products. For instance, when using the various polymerising agents and addition agents, the following tertiary oxonium salts are obtained:

Polymerising agent	Admixture	Tertiary oxonium salt	
		Cation	Complex anion
C_2H_5F	BF_3		$[BF_4]^-$
$ClCH_2OCH_3$	$FeCl_3$		$[FeCl_4]^-$
$SiCl_4$	$FeCl_3$		$[FeCl_4]^-$

or:

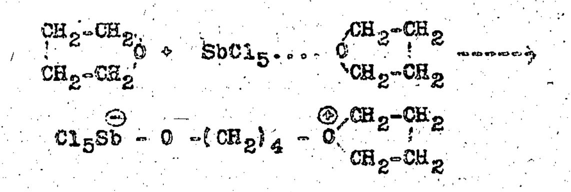
Polymerising agent	**Admixture**	**Tertiary oxonium salt** **cation**	 **complex anion**
			
CH_3COF	BF_3		$[BF_4]^-$
$C_5H_{11}COCl$	$AlCl_3$		$[AlCl_4]^-$
CH_3COCl	SO_3		$[ClSO_3]^-$
$(CH_3CO)_2O$	$HClO_4$		$[CH_3COO$ $HClO_4]$
$C_6H_5SO_2Cl$	$FeCl_3$		$[FeCl_4]^-$
$SOCl_2$	$FeCl_3$		$[FeCl_4]^-$
$(CH_3)_2SO_4$	SO_3		$[CH_3SO_4$ $SO_3]$

If strong acids and halogen acids are used as polymerisation agents (Case 5), the primary product of the reaction is a secondary oxonium salt, which first reacts with a second tetrahydrofurane molecule to form a tertiary oxonium salt. In polymerisation with acid anhydrides, e.g. acetic anhydride, it is doubtful whether they act in all cases as such, or whether they react with part of the metallic or non-metallic haloids to form acyl haloids. It is likewise uncertain whether in using acid anhydrides in the presence of strong acids, the complex compounds formed from the two components or the mixed anhydrides of the acids used from the actual polymerisation agent. (Cf. Bergmann and Radt, Ber. 54 1652, 1921).

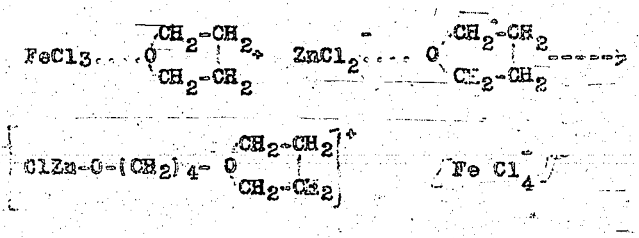
Finally, the electrophile metallic and non-metallic haloids also have a polymerising effect, to some extent, on the tetrahydrofurane. In the case of the antimony pentachloride the polymerising action takes place with the same tertiary oxonium salts. In other cases, e.g. boron fluoride and tin tetrachloride, the action is slight. It was found that these can be considerably increased by using mixtures of haloids. By way of suitable mixtures, we may mention:

Aluminium chloride - tin tetrachloride
Iron Chloride - Titanium tetrachloride
Iron Chloride - Zirconium tetrachloride
Iron Chloride - Zinc chloride

Polymerisation with the aid of electrophile metallic and non-metallic haloids, alone or mixed together, would have to be formulated by assuming the production of tertiary oxonium salts from ethylene oxides and metallic and non-metallic haloid etherates, as follows:



or



In the foregoing sections we have dealt exclusively with the polymerisation of tetrahydrofurane. According to a method to be described below, the polymerisation of tetrahydrofurane is carried out with the catalysts described above in the presence of 1.2 oxygen compounds. It was then found that mixed polymerisates of tetrahydrofurane and 1.2 oxygen compounds were obtained. Suitable 1.2-oxyo-compounds are, for example:

Ethylene oxide
1.2-propylene oxide
alpha or beta butylene oxide
Epichlorohydrine
1-phenoxy-2,3-propene oxide
Butadiene dioxide
Resorcin-bis glycid ether and others.

For the preparation of the mixed polymerisates, the polymerising agents described above for tetrahydrofurane polymerisation may be used. It is a great advantage to see that one of the difficultly deformable halogen acid anions BF_4, $FeCl_4$ or $SbCl_6$ is formed in the reaction mixture.

It was also found that in its behaviour to polymerisation agents, trimethylene oxide (1.3-propylene oxide) comes between ethylene oxide and tetrahydrofurane. It polymerises by itself, but not so powerfully as ethylene oxide and it produces mixed polymerisates with tetrahydrofurane.

As will be seen from the foregoing, there are many possibilities of polymerising tetrahydrofurane alone or in combination with 1.2 or 1.3 oxygen compounds. In the following explanation and description of the reaction conditions for the sake of simplicity, only the polymerisation of tetrahydrofurane is discussed the same remarks also apply in a similer manner to mixed polymerisation.

The progress of polymerisation will be recognised externally by the increasing viscosity of the reaction mixture. The final state is reached in hours or days according to the composition of the reaction mixture.

Polymerisation of tetrahydrofurane is in some cases reversible, and always when electrophile metallic or non-metallic haloids are used as the polymerising agent or addition substance. In these cases it would appear that the polymerisation brings about equilibrium between tetrahydrofurane and the polymerisate, which in working without diluents lies at about 70-80% polymerisation. If the equilibrium is interfered with by the polymerisate crystallising out, the reaction may produce a yield of 95% polymerisate. The reversibility of polymerisation also necessitates destruction or removal of the polymerising agent and the addition substance from the polymerisate, in order to obtain stable polymerisates.

If prepared oxonium salts or other polmerising agents which can take effect at once without admixture, e.g. chlorosulphonic acid are used for indicting polymerization the speed and degree of polymerisation are dependent on the quantity of catalyst used. If a polymerising agent and an addition substance are used for polymerising the tetrahydrofurane the speed of polymerisation will be determined by the type and quantity of the addition substance, while the degree of polymerisation depends on the quantity of the polymerising agent. Indeed, if an excess of polymerising agent is used compared with the addition substance there will occur both a premature termination of the polymerization chains and a breakdown of the polymerisate already formed, owing to the reversibility of polymerisation and also partly owing to the ether splitting effect of the polymerising agent (cf. Meerwein-Maier Hüser, J. pr. 134, 51 et seqq.). Thus, when polymerisation is complete the degree of polymerisation can be reduced by adding sufficient polymerising agent and the same final product obtained as would be formed, if polymerisation had been started with large amounts of polymerisation agent.

Conditions of polymerisation may vary within wide limits as regards temperature and pressure. Since the stability of the anions decreased with rising temperature, raising the temperature should only be resorted to for increasing the speed of reaction in the case of the relatively stable anions. For example, the polymerisation of tetrahydrofurane with acetic anhydride in the presence of BF_3 or $FeCl_3$ at 90° in an autoclave takes place in very much shorter time than at room temperature. The use of diluents may be of advantage in order to moderate too violent a polymerisation or for the manufacture of polymerisates with high molecular weight.

According to the reaction mechanism explained above, the polymerisation products obtained are not, strictly speaking, to be regarded as true polymers of tetrahydrofurane with the composition $(C_4H_8O)n$. They tend to have the following general formula:

$$X(CH_2)_4O[(CH_2)_4O]_n(CH_2)_4Y$$

in which the nature of the end groups X and Y depends on the polymerising agents used and the secondary changes that may take place during preparation (saponification of ester groups, splitting off of sulpho groups etc.).

In the case of products of lower molecular weight produced by large amounts of polymerising agent, the nature of the end groups may have a decisive influence on the physical and chemical properties of the polymerisation products obtained. Thus, for example, the product with the formula

$$Cl(CH_2)_4O[(CH_2)_4O]_n(CH_2)_4O \cdot SO_3H (n<20)$$

which has a low molecular weight and is produced by the polmerisation of the tetrahydrofurane with chloro-sulphonic acid, is easily soluble in water owing to the final sulpho group, whereas the product with a high molecular weight, produced with a small quantity of chloro- or fluoro-sulphonic acid, is not soluble, in water, but is soluble in benzene.

The molecular structure of the pure tetrahydrofurane polymerisates in the form of unbranched chains, enables the molecules to assume a parallel arrangement, so that the products which are oily and viscous to beging with, generally "crystallise" and become solid on standing. The speed of crystallisation is, however, low, and the softening point below 60°. The products are soluble in aromatic hydrocarbons, aliphatic chloroinated-hydro-carbons, in many ethers, esters and ketones but are difficultly soluble in aliphatic and cycloaliphatic hydrocarbons. Solubility decreases with increasing molecular weight.

Products with low molecular weights remain liquid at room temperatures.

Their consistency in the solid state is, in the case of products of medium molecular weight, like that of vaseline or wax, and in those of high molecular weight, more viscous and horny.

In the case of the mixed polymerisates from tetrahydrofurane and ethylene oxide derivatives the solidifying point is reduced. The mixed polymerisates are chiefly oils. They show similar solubility properties to the pure tetrahydrofurane polymerisates, but their solubility in aliphatic and cycloaliphatic hydrocarbons with increasing oxygen content is still less than in the case of the pure tetrahydrofurane polymerisates. With mixed polymerisates from tetrahydrofurane and ethylene oxide, with increasing ethylene oxide proportion water soluble polymerisates are obtained exclusively. Mixed polymerisates containing polymerised compounds having several ethylene oxide groups such as butadiene dioxide or resorcin-bis-glycid ether, are cross linked. They are not soluble in organic solvents and have lost their plasticity.

The "parts" given in the following examples are parts by weight.

Example 1.

In 43.2 parts of tetrahydrofurane (0.6 mol) were dissolved 0.38 parts triethyl oxonium-boro -fluoride (0.002 Mol) and the temperature was kept down to about 10° by water-cooling; after 5 hours the mass became a viscous fluid. After 24 hours it was treated with water and small amounts of unchanged tetrahydrofurane were removed off by steam distillation. The water was decanted from the solid mass obtained after cooling and the product was dried at 110°. After cooling it formed an almost colourless, solid, rather hard mass. By a similar process, from 72 parts tetrahydrofurane by the action of 6 parts triethyloxonium tetrachloroferriate, a very thick oil was obtained which is slow in solidifying; on treatment with 1 part triethyloxonium hexachloroantimoniate, an almost colourless, hard reaction product was obtained with about 85% yield.

Example 2.

1.8 parts iron chloride were dissolved in 2 parts δ-chlorobutyl acetate, the solution was allowed to stand for 24 hours and then 7.2 parts tetrahydrofurane were added. After 4 days, the reaction mixture was steam distilled with the admixture of concentrated tartaric acid, and the polymerisate, which separated out as a solid in the distillation residue was isolated. Yield: 5 parts of a solid, slightly yellowish product.

Similarly from 3.2 parts iron chloride, 10 parts δ δ-dichlorodibutyl ether and 29.8 parts tetrahydrofurane 18 parts of a thick, brownish oil were obtained, which solidified quickly on cooling.

Example 3.

To 43.2 parts tetrahydrofurane (0.6 mol) were added 0.85 parts of the boron-fluoride compound of tetrahydrofurane (boiling point 14mm 92), and 0.55 parts epichlorohydrine (0.006 mol). The mixture was then treated as described in Example 1 and reaction product and yield were about the same as in that example.

Instead of 0.55 parts epichlorohydrine, equivalent amounts of ethylene oxide, propylene oxide, butylene oxide, cyclohexene oxide, phenoxypropene oxide or dodecylphenoxypropene oxide may be used with similar results.

Example 4.

In 72 parts tetrahydrofurane 2.66 parts aluminium chloride were dissolved and 1.85 epichlorohydrine added; the whole was meanwhile cooled. After 24 hours, this was treated with dilute tartaric acid. The residual polymerisation product formed a colourless, rather thin oil, which on being allowed to stand, partly solidified and formed crystals.

Example 5.

A mixture of 72 parts tetrahydrofurane and 132 parts ethylene oxide was allowed to drop into a mixture of 45 parts carbon tetrachloride and 3 parts of the boron fluoride compound of the tetrahydrofurane. While this was being done, the temperature was kept to 50-60° by efficient cooling. The apparatus was fitted with a reflux condenser, so that no ethylene oxide could escape. Duration of dropping process: 1½ hours. The reaction mixture was kept for 4 hours at 50-60°, then it was diluted with 450 parts carbon tetrachloride and neutralised with slaked lime. After filtering the solvent was distilled away, and the residue was then dried for 2 hours at 150° in a vacuum. 160 parts of a slightly brownish oil, miscible in any proportion with cold water were obtained.

By using instead of the foregoing mixture of 72 parts tetrahydrofurane 132 parts ethylene oxide a mixture of 108 parts tetrahydrofurane and 38 parts ethylene oxide the method employed being the same, 174 parts of a very viscous fluid oil, miscible with cold water were obtained.

In like manner, from a mixture of 108 parts tetrahydrofurane and 75 parts 2',3'-oxydopropyloxybenzene under the action of 6 parts antimony pentachloride, a viscous polymerisate was obtained in a yield of 151 parts.

To a reaction mixture of 72 parts tetrahydrofurane, 2.9 parts of the boron fluoride compound of tetrahydrofurane and 24 parts epichlorohydrine, after polymerisation had set in, and the mixture had become viscous, a solution of 1.35 parts 1.3-Di-(2',3'-oxydopropyl)-oxybenzene and 72 parts tetrahydrofurane were added and a sticky, rubberoid polymerisate, was obtained which at first was transparent, but after standing for some time became opaque. In this case, it is recommended to treat the polymerisate in the crushed st te with cold soda lye, in order to dissolve out the catalyst and neutralise the acid produced from it during hydrolysis.

By the action of 0.23 parts of the addition compound of boron fluoride and tetrahydrofurane on 10 parts butadiene dioxide and 10 parts tetrahydrofurane a hard glassy mixed polymerisate was obtained. By working under conditions which were otherwise the same, with a mixture of 2.5 parts butadiene dioxide and 47.5 parts tetrahydrofurane a viscous mass that becomes solid on standing was obtained.

Oily mixed polymerisates of tetrahydrofurane and propylene oxide, e.g. in the ratio 5 : 1, can be produced very advantageously by replacing first of all 1 part tetrahydrofurane with 0.4 parts iron chloride, then 0.3 parts thionyl chloride, adding at the same time 7 parts thionyl chloride and a mixture of 34 parts tetrahydrofurane and 7 parts propylene oxide, the whole being allowed to react for 48 hours.

Example 6.

72 parts tetrahydrofurane were mixed under cool conditions with 2.99 parts antimony pentachloride. The temperature was kept at 25°. After half an hour the mass became thick. After 24 hours it was treated as in Example 1. 57 parts of a hard, colourless polymerisation product were obtained.

Example 7

288 parts tetrahydrofurane were mixed with 27 parts aluminium chloride and 26 parts tin tetrachloride. In the course of 24 hours no polymerisation was perceptible. 16.2 parts of iron chloride were added. Polymerisation at once set in and was recognised by the heat tone (Wärmetönung) and increasing viscosity. After 6 days it was diluted with toluol and treated as usual 172 parts of a solid polymerisate were obtained. In the foregoing mixture, there can be used with the same success as catalysts a mixture of 16.2 parts iron chloride + 38 parts titanium tetrachloride or 16.2 parts iron chloride + 25 parts zirconium tetrachloride, or 32.4 parts iron chloride + 27.2 parts zinc chloride.

Example 8

9 parts tetrahydrofurane were enclosed in an ampoule with 1 part of the boron fluoride compound of the tetrhydrofurane and 0.7 parts δ-fluorobutyl-ethyl ether. After 5 hours the contents of the tube already showed the

consistency of glycerine. After 12 hours the product was solid. After the usual treatment, 7 parts solid polymerisate were obtained.

If instead of 0.7 parts fluorobutylethyl ether, 1 part of fluoro-ether of the following formula is used:

$$F.CH_2.CH_2.CH_2.CH_2.O.CH_2.CH_2.CH_2.CH_2.O.CH_2.CH_3$$

the yield will amount to 7.5 parts solid polymerisate.

Example 9

144 parts tetrahydrofurane were mixed with 8.1 parts iron chloride and 8.1 parts monochlorodimethylether. After 2 days the mixture was decomposed with water and soda, the unchanged tetrahydrofurane and water were filtered off and distilled. The yield amounted to 105 parts of an oily polymerisate.

With 48.6 parts monochlorodimethylether and 8.1. parts iron chloride, 135 parts of a thin oil were obtained.

In like manner tetrahydrofurane may be polmerised by iron chloride and 2.3-dichlorotetrahydrofurane; the latter can be produced in the reaction mixture itself by the addition of chlorine or by the action of chlorine donors, such as N-chloracetamide.

The same applies to mixed polymerisation. Thus from 144 parts tetrahydrofurane and 185 parts epichlorhydrine, by the action of 16.2 parts iron chloride and 8.1 parts monochlorodimethylether, 297 parts of an oily mixed polymerisate were obtained. In a similar way and with the aid of the same catalysts mixed polymerisates were obtained from tetrahydrofurane and ethylene oxide. Here the iron chloride may be replaced by antimony pentachloride.

Example 10

288 parts tetrahydrofurane were mixed with 16.3 parts iron chloride and 21 parts methyleneglycol methylether acetate. After a period of reaction lasting 8 days at the normal temperature, it was treated in the usual way. 147 parts of a solid polymerisate were obtained.

In like manner a reaction mixture of 144 parts tetrahydrofurane 16.3 parts iron chloride and 27 parts methylene glycol diacetate gave, a yield of 73 parts. When instead of the methylene glycol diacetate, 32.2 parts benzal chloride were used, a polymerisation yield of 97 parts was obtained.

These admixtures may likewise be used successfully for the mixed polymerisation, for instance, 72 parts tetrahydrofurane were mixed with 28 parts iron chloride and 27 parts methylene glycol diacetate, and after 2 hours a mixture of 144 parts tetrahydrofurane 58 parts propylene oxide and 27 parts methylene glycol diacetate were added at a temperature of 30°. An oily polymerisate was obtained.

Example 11

72 parts tetrahydrofurane were mixed with 4.5 parts acetyl chloride and 8 parts iron chloride. After 4 days this was treated in the usual way. The polymerisation product was a slowly solidifying oil. The yield was about 60 parts = 79% in relation to the original materials (72 parts + 4.5 parts). When benzoyl chloride was used in place of acetyl chloride, 77% was obtained, and with benzol-sulpho-chloride, 63.5%.

In the above mixture, the iron chloride may be replaced with equal success by 6.6 parts aluminium chloride.

Furthermore, the following may be used as catalysts admixtures: aluminium chloride + adipic acid chloride, the boro-fluoro-compound of tetrahydrofurane + acetyl fluoride, sulphur trioxide + benzoyl chloride, sulphur trioxide + phosgene. In a method of applying the latter case 36 parts of tetrahydrofurane were mixed with a solution of 1.2 parts sulphur trioxide in 7.7 parts carbon tetrachloride. The two latter substances reacted and formed phosgene, and the catalyst mixture was produced from phosgene and sulphur trioxide. A solid, colourless polymerisate was obtained.

Example 12.

A mixture of 72 parts tetrahydrofurane with 5.6 parts acectic acid was treated with 7.2 parts perchloric acid (70%) for a period of reaction lasting 7 days at normal temperature, and then worked up in the usual manner. The polymerisate amounted to 54.5 parts.

The perchloric acid may also be produced in the reaction mixture from sodium perchlorate and sulphuric acid or benzene sulphonic acid. Instead of perchloric acid, iodic acid may also be used.

When 72 parts tetrahydrofurane were mixed with 2 parts acetic anhydride and 0.7 parts perchloric acid, a polymerisate was obtained with an essentially higher molecular weight in a yield of 47 parts, which solidified to form a viscous, horny mass.

When on the other hand large quantities of acetic anhydride were used in the said mixture, e.g. 41 parts with 3.2 parts perchloric acid (70%), oily polymerisates were obtained. Other acid anhydrides may be used instead of acetic anhydride with equal success, e.g. propionic anhydride, benzoic anhydride, succinic anhydride, maleic anhydride and phthalic anhydride.

Furthermore, the following admixtures have been used successfully in place of perchloric acid: antimony pentachloride, iron chloride and boron fluoride. Mixed polymerisates may also be produced with these catalysts, for instance, 162 parts tetrahydrofurane were mixed with 34.5 parts acetic anhydride and 100 parts antimony pentachloride, and then a mixture of 2160 parts tetrahydrofurane and 440 parts ethylene oxide was added. A further 1734 parts of acetic anhydride were then added. The reaction product was a thin oil.

Example 13

5.5 parts acetyl chloride were mixed with 6.1 parts sodium perchlorate and mixed during cooling with 72 parts tetrahydrofurane. After 5 hours the reaction mixture became viscous. After 2 days it was treated and the polymerisate was isolated in a yield of 76%.

Example 14

720 parts tetrahydrofurane 238 parts thionyl chloride and 67.5 parts iron chloride were allowed to stand for three days at the normal temperature. 600 parts of an oily, sulphur free polymerisate were obtained. By adopting a higher reaction temperature (e.g. 60°), the time of the reaction may be considerably curtailed.

When in the above mixture 600 parts thionyl chloride were used and the whole was allowed to completethe reaction over 6 days at 30° there were obtained 1005 parts of a limpid liquid polymerisate, consisting mainly of dichlorodibutylether (80%) and as by-products dichlorobutene and trimer-dichloroether.

As in the case of iron chloride, sulphur trioxide makes a good addition substance to thionyl chloride. Mixtures of phosphorus oxychloride may also be used.

Example 15

The following is a description of a suitable method for continuous operation which permits of a large production in small reaction chambers. The catalysts used may of course be replaced by others.

The process was carried out in three vessels (A, B and C). Vessel A contained a catalyst solution consisting of 288 parts tetrahydrofurane 97 parts iron chloride and 65 parts chloromethyl ether. Vessel B contained a mixture of 2016 parts tetrahydrofurane 923 parts ethylene oxide and 794 parts chloromethylether. The two vessels A and B were connected with the actual reaction vessel C, which had a capacity of 1500 volumetric parts by run in devices; vessel C had a bottom outlet. After the reaction vessel C was charged with 150 parts of the catalyst solution from Vessel A, about 1000 parts were added from Vessel B with vigorous stirring and steady cooling, so that temperature of the reaction was kept at 20-25°. 500 parts of the reaction product were then run off through the drain cock (1st running), 35 parts were added from Vessel A and a further 500 parts of the mixture were run in from Vessel B. A further 500 parts of the reaction product were run off (2nd running). After the addition of 35 parts catalyst solution, polymerisation was repeated and so on. The quantities described will furnish 8 runnings, which were worked up individually after 5 days. The yields and properties of the oily; rather limpid liquid polymerisates are the same.

The reaction vessel may also be fitted with an overflow, and the reaction product may be allowed to run off continuously.

Example 16.

288 parts tetrahydrofurane were mixed with 16.2 parts iron chloride and 12 parts boron chloride with good cooling. Polymerisation at once set in with powerful heat toning (Warmetonung). By cooling the temperature was kept below 25°. After standing for two days at the normal temperature and after the usual treatment 185 parts (= 64.3% of the original substances) of an oily polymerisate were obtained.

The process can be carried out similarly with mixtures of iron chloride and arsenic trichloride, iron chloride and sulphur mono-chloride, iron chloride and sulphur dichloride, iron chloride and silicon tetrachloride, iron chloride and tin tetrachloride or aluminium chloride and silicon tetrachloride.

If mixtures of iron chloride and phosphorus trichloride are used in the process, with alkaline treatment anhydrous polymerisates may be obtained, which may be regarded as monoesters of the phosphoric acid. Thus the reaction mixture of 720 parts tetrahydrofurane, 16.2 parts iron chloride and 137.5 parts phosphorus trichloride produced a yield of 443 parts of an anhydrous product, which could easily be separated from the aqueous solutions.

Example 17.

288 parts tetrahydrofurane were mixed with 28.4 parts 1-chloromercapto-2.4.6- trichlorobenzol and 16.2 parts iron chloride. After standing for 2 days, it was treated in the usual way. Solid polymerisate yield: 209 parts.

Similarly, a reaction mixture of 144 parts tetrahydrofurane, 7.8 parts benzo-trichloride and 19.5 parts iron chloride gave a solid polymerisate in a yield of 82 parts.

Example 18.

To a mixture of 720 parts tetrahydrofurane and 720 parts chloroform, 164 parts chloro-sulphonic acid were added in 2 minutes at a temperature of 10°. The temperature rose to 38°. The whole was allowed to stand for a day at the normal temperature. The reaction mixture was then allowed to flow into the prepared diluted soda lye, stirring all the time. The reaction was kept faintly alkaline. The chloroform and unchanged tetrahydrofurane were expelled by means of steam. There remained a clear, aqueous solution, containing 54% of the original tetrahydrofurane in the polymerised state. The reaction product was salted out.

If the operation is carried out without dilution and with chloroform, the addition of chloro-sulphonic acid should take place over a much longer time. It is preferable in such cases to keep the temperature at 20°.

Example 19

To 5 parts by volume of fuming sulphuric acid (45% SO_3 content) which had been cooled to -20°, 72 parts of tetrahydrofurane cooled to -10° were added with constant stirring and the mixture was stirred while cooling until the fuming sulphuric acid was completely dissolved. The clear, yellow solution was allowed to stand for 12 hours in the cooling mixture and 8 days at room temperature. It was then mixed with water and the unchanged tetrahydrofurane was distilled away from the strongly foaming solution. The polymerisation product was separated, and the aqueous solution extracted with methylene chloride. After drying and removing the methylene chloride by distilling, 47 parts polymerisation product were obtained in the form of a yellow oil, which after a few days solidified to form a waxy mass.

Example 20.

A solution of 1.8 parts gaseous hydrochloric acid in 72 parts tetrahydrofurane were mixed with 8 parts ferric chloride. Polymerisation at once set in, and was indicated by the rise in temperature and the increasing viscosity of the solution. After 2 days, unchanged tetrahydrofurane was blown off with steam and the non-volatile polymerisation product, a slowly solidifying brownish oil, was isolated in the usual way. Yield: 48 parts = 67% of theory.

A similar result was obtained by using hydrochloric acid and aluminium chloride. The polymerisation product was liquid.

In the above reaction mixture, the hydrochloric acid may be replaced with equal success by 12.8 parts benzyl chloride or 17 parts benzyl bromide, respectively from which halogen hydride is released by the action of the iron chloride.

Example 21.

72 parts tetrahydrofurane were mixed with 11.2 parts dimethyl sulphate and 2.8 parts of the boron-fluoride compound of tetrahydrofurane. The thickly fluid reaction mixture was treated after 12 days by adding excess diluted soda lye with steam. The polymerisate became solid on cooling. Yield: 43 parts of a colourless solid.

When five times the amount of dimethyl sulphate were used (56 parts), the mixture and method being otherwise the same, a glycerine-like, fluid polymerisate was obtained.

A similar effect was obtained with mixtures of toluene sulphonic acid methylester and iron chloride, or methyl rhodanide and iron chloride. Mixed polymerisates were so made with these catalysts, first of all by allowing e.g. 180 parts tetrahydrofurane to react for 2 hours on 66 parts iron chloride and 57 parts dimethyl sulphate, then adding a mixture of 1080 parts tetrahydrofurane 290 parts propylene oxide and 240 parts dimethyl sulphate at 30° 1200 parts of an oily polymerisate were obtained.

Similarly, sulphur trioxide lends itself as an admixture for the polymerisation of the tetrahydrofurane by means of the esters of strong acids such as dimethyl sulphate.

Example 22.

144 parts tetrahydrofurane were mixed with 42 parts acetic anhydride and 12 parts by volume of the boron-fluoride compound of tetrahydrofurane. The mixture was kept in the autoclave for 40 hours at 90° and treated as usual. The yield amounted to 95 parts of an oily polymerisate.

When instead of the boron-fluoride compound, 1 part by volume of a 70% aqueous perchloric acid were used, 140 parts of oily polymerisate were obtained.

When instead of the boron-fluoride compound 10 parts pure sulphuric acid were used, a yield of 53 parts oily polymerisate was obtained.

Example 23.

144 parts tetrahydrofurane were mixed with 65 parts benzene diazonium chloride-zinc chloride double salt and 16.2 parts iron chloride. After 2 days, this was treated in the usual way. Yield: 90 parts

Patent Claims

1. Process for the polymerisation of tetrahydrofurane by itself or in admixture with 1.2-or 1.3- oxygenated compounds, characterised by reaction with tertiary oxonium salts with

an anion that is difficult to polymerise, the quantity being chosen so that the mean degree of polymerisation of the reaction products amounts to a minimum of 2.

2. Process according to Claim 1, the characteristic of which is that the tertiary oxonium salts are produced by the action of electrophile metallic or non-metallic haloids on halogenalklether orhalogenalkylester.

3. Process according to Claim 1and 2, characterised by the feature that the tertiary oxonium salts are produced in the reaction medium.

4. Process according to Claims 1 and 3, characterised by the fact that tertiary oxonium salts are generated in the reaction medium from 1.2 oxide compounds and electrophile metallic and non-metallic haloids, whose etherates are able to form tertiary oxonium salts.

5. Process according to Claims 1 and 3, characterised by the use of halogen alkyl ether or halogen alkyl ester in the presence of electrophile metallic or non-metallic haloids.

6. Process according to Claims 1 and 3, characterised in that tertiary oxonium salts are produced in the reaction medium by the action of electrophile metallic or non-metallic haloids or mixtures of the same on tetrahydrofurane.

7. Process according to Claims 1 and 3, characterised in that compounds possessing the ability to attach themselves to oxygen containing compounds, if necessary in the presence of admixtures, to form oxonium salts are caused to act on the cyclic ether if necessary in the presence of addition substances such as electrophile metallic haloids, sulphur trioxide or strong acids.

8. Process according to Claims 1, 3 and 7, characterised in that organic fluorine compounds are used with the metallic or non-metallic haloids addition substances.

9. Process according to Claims 1, 3 and 7, characterised by the use of functional derivatives of oxygenated compounds with 1 mol alcohol and 1 mol of an organic or inorganic acid, or 2 mols of the same or different organic or inorganic acids in the presence of addition substances.

10. Process according to Claims 1, 3 and 7, characterised by the use of haloids and anhydrides of organic or inorganic acids in the presence of addition substances.

11. Process according to Claims 1, 3 and 7, characterised by the use, in the presence of addition substances of halogen compounds which can be hydrolysed, but which, strictly speaking, cannot be termed acid haloids, since the products of their hydrolysis do not contain the number

of ionisable H-atoms corresponding to the number of hydrolysed halogen atoms.

12 Process according to Claims 1, 3 and 7, characterised by the use of acids with difficultly polarizable anions and in which in the case of the halogen acids, the components, the electrophile metallic or non-metallic haloids and the halogen hydride, can be caused to react.

13. Process according to Claims 1, 3 and 7, characterised by the use of those esters of strong acids which possess the ability to add or to tertiary amines to form quaternary ammonium salts, in the presence of addition substances.

14. Method in accordance with Claims 1, 3 and 7, characterised by the use of diazonium haloids in the presence of addition substances.

Note From the text claim 1 should have been re-written as below:

1. A process for the polymerization of tetrahydrofurane alone or in admixture with a 1,2 or 1,3 oxygenated compound, characterised in that the tetrahydrofurane or the mixture is reacted with a tertiary oxonium salt having a difficultly polymerizable anion in such quantity that the average degree of polymerization of the reaction products is at least 2.

Ref. FD 4975/45 - Folder III

Memo from Leuna dated 10.6.41

On the Conference of the Ministry of Economic Expansion of the 8th and 9th July 1941

Present from the Reichsamt: Dr. Kranepuhl
Dr. Öhinger
Dr.I. Hübner

Present from the I.G.: Dr. Christmann, Ludwigshafen
Dr. Zorn, Leuna
Dr. Becker, Ludwigshafen (intermittently)

Subject of the conference was the preparation of a lubricating oil production programme for the New Goering plan. According to this plan the aero-engine fuel and lubricant production will have to be increased fourfold. As starting point the lubricant production existing at the end of the year 1941 was chosen. This amounts to :

10,000 tons per year SS 906, Leuna
15,000 " " " SS 1106, Pölitz
12,500 " " " mineral oil (low viscosity) Oslebshausen
12,500 " " " " " " " Koln
10,000 " " " " " high " Rhenania and Lutzkendorf
60,000 " " " of finished aero-engine oil.

This production has to be increased to 240,000 tons per year. New plants have to l erected for 180,000 tons per year. As wax cannot be released for lubricating oil synthesis, only ethylene and propylene can be considered for this purpose. The polymers of ethylene, the SS 900 oils, are tested very thoroughly and we have found that in consideration of the existing ethylene or ethane production these polymers can be fully utilised for our plan. The propylene polymers are up to date tested only in single cylinder runs; however the I.G. will have to propose testing these on a large scale to the RLM immediately.

They are prepared as products of very high viscosity of 9-10°E, at 100°C with a viscosity index value of 80. Low viscosity products cannot be used in the engine, as they give too high oil consumptions. In order to produce from these highly viscous oil an aero-engine oil of 3°E at 100°, they have to be mixed in a ratio of 1:2 (polymerisation product: mineral oil). In other words for this polymerisation product a large quantity of low viscosity mineral oil is necessary. As the plant equipment is very unsuitable for the production of mineral oils of superior quality and low viscosity, the proposal of Dr. Zorn was accepted to prepare the ethylene polymerisation products with the aero-oil viscosity of 3°E at 100° and not to mix it with mineral oil. These purel synthetic SS 903 oils are more suitable for the aero engine designs which are at presen being developed. (cf. file note on the conference in the RLM of 8.7.1941).

Table 1 (tons per year)

	Ethane	Propane	Butene
Magdeburg	17,000	22,000	44,000
Wesslingen	(31,000)	39,000	65,000
Blechhammer	45,000	64,000	81,000
Schelven	6,300	6,400	6,300
	(26,000)	(28,000)	(31,000)
Leuna	4,300	45,000	72,000
	(18,500)		
Moosbierbaum	15,400	16,000	11,700
Pölitz	(33,000)	56,000	138,000
Ludwigshafen	12,000		
	(9,600)	21,600	-
Brüx-I (300,000)	8,000	18,500	26,500

The numbers in brackets are not available for the lubricating oil plan as these gas quantities are already disposed of.

On the basis of these production figures the following plan (table 2) was made. For this the following basic yields were set down :-

For C_2 - polymerisation product = 1 ton ethene --- 0.5 tons polymerisation product dehydrogenation according to the method of Dr. Klein (partial oxidation of ethane) and concentration of the C_2H_4 by the Linde process. In place of the Klein process the Häuber process can possibly be used and the Linde plant can perhaps be replaced by washing with copper lye. About this at present tests are still being carried out.

For C_3 - polymerisation product = 1 ton propane --- 0.8 tons polymerisation product dehydrogenating by the chlorination method of Dr. Bähr.

Altogether this summary gives the following picture: 46,200 tons per year purely synthetic ethylene polymerisate, 132,000 tons per year mixer oils from propylene polymerisate and mineral oil 1:2.

Table 2 (tons per year)

Place of production	C_2- polym. product SS 903	Ethene quantity required	C_3- polym. product	propane quantity required	Mineral oil quantity required
Heydebreck	22,500	45,000	-	-	-
Moosbierbaum	7,700	15,400	10,000	12,500	20,000
Pölitz	-	-	17,000	21,000	34,000
Ludwigshafen	6,000	12,000	17,000	21,000	34,000
Schkopau	10,000	12000 C_2H_4 from C_2H_2	-	-	-
TOTALS	46,200	84,400	44,000	54,500	88,000

For special purposes (cold-starting oils) part of the ethylene polymerisation compounds must be mixed with an ester. To this end two ester-units have been planned, for 3,300 tons per year each, at Schkopau and Auschwitz.

Thus the following picture is obtained :-

26,000 tons per year special oils (C_2 - polymerisate + ester)
26,200 " " " C_2-polymerisate
52,200 " " "
132,000 " " " mixed oils (C_3-polymerisate + mineral oil 1:2)

Altogether: 184,000 tons per year; this corresponds to the extra production required by the Goering plan.

The material, staff and capital required for the C_2-polymerisation plants was put before the Reichsamt in accordance with the values given in Table 3.

The corresponding figures for the two small ester plants, for the C_3-polymerisation compounds and for the mineral oil units were not discussed at the conference. For the two ester plants the amount of iron required was estimated at about 500 tons each and the amount of capital to about 4-500,000 RM. For the C_3-polymerisation plants the amount of iron required was estimated at about 44,000 tons and the capital required at about 40,000,000 RM. For the 88,000 tons per year mineral oil estimates have not yet been made.

Table 3

Material, staff and capital required for the C_2-polymerisation compound plants

	Tons per year polymerisation compounds			
	Ludwigs-hafen(2) 6000	Moosbier-baum(3) 7700	Schkopau(1) 10,000	Heyde-breck(4) 22,500
A) C_2H_4 production				
Iron for the apparatus, tons	1300	1725	400	4200
Constructional iron work	300	375	30	900
Sicromal	120	150	-	330
Copper	60	75	40	100
Building worker	300	375	60	1000
Montage worker	180	225	50	600
Process worker	120	150	36	200
Cost in mill. RM.	3.8	4.7	0.52	12.2
B) C_2H_4 polymerisation				
Iron for apparatus, tons	700			
High pressure-material	220	375	1000	2000
Hg-autoclaves *	310	265	310	640
Constructional iron work	300	390	440	900
Building worker	240	375	420	350
Montage worker	140	300	350	620
Process worker	70	185	200	300
Cost in mill. RM.	2.8	3.5	4.0	7.0

Total Iron: 20,345 tons
Total capital: 38.5 mill. RM.

* each 1000 tons polymerisation compound 1 autoclave.
(1) Translators addition and note - ethylene obtained from acetylene.
(2) Translator's addition
(3) "
(4)

In respect of production the following possibilities were discussed :-

From Rhenanie	30,000 tons per year
From the Baden oil in Oppau	10,000 tons per year
From Ostmakr oil in Pressburg	10,000 tons per year
From hydro plants using mineral oil	38,000 tons per year
	88,000 tons per year

Further the aluminium chloride plants in Ludwigshafen and Schkopau have to be erected in such a manner that the following production is assumed :-

280 tons per month for C_2-polymerisation compounds
220 tons per month for C_3- " "

It has also to be found out whether for the works in question the gas separation units possess the requisite capacity.

Leuna, 25th July 1941

File Note

On the discussions re SS 900 oil plants at Leuna on 24.7.41

The following were present :-

From Schkopau: Obering Schuhmacker
Dip.Ing. Wintermeyer

" Heydebreck: Obering Wällnitz

" Oppau: Obering Giehne
Dr. Beckmann
Dr. Häuber

" Gendorf: Dr. Wittwer

" Moosbierbaum: Dr. Ober
Obering Rudloff

" Leuna and
Auschwitz: Dir.Dr. v. Staden)
" " Strombeck) from time to time
" " Zorn
" " Hofmann
" " Sackmann
Dip.Ing. Mayer)
" " Happe) for Uhde, Dr. Köhler
" " Hutter) from time to time
Dr. Korn

The subject of discussion was the organisation required for the six new SS 900 plants to be set up under the new Goering plan. First, Dr. Zorn and Dr. Hofmann briefly described the process, see Appendices 1 and 2. It should also be mentioned that in accordance with a decree of the German Air Ministry the process is subject to the official Secrecy Regulations. Agreement was reached on the following points :-

1) The oil polymerisation plants will be centrally controlled by the Uhde construction bureau, under the direction of Herr D.I. Mayer. The individual factories will receive from here the necessary plans for setting up the plant. The most important apparatus will be purchased centrally for the account of the factory in question. All the documents required for the building certificate will be forwarded to R.W.A. by the works which are erecting the building.

2) The steps to be taken for ethylene production are divided up as follows:

a) The production of ethylene from acetylene by catalytic hydrogenation followed by washing and concentration in a Linde plant for the plants at Schkopau and Auschwitz will be the responsibility of Schkopau.

b) The production of ethylene from alcohol and its purification and concentration, if the splitting furnaces at Schkopau and Heydebreck are electrically heated, will be the work of Schkopau. If Heydebreck decide on gas heating, they will set up their own plant.

c) The production of ethylene by the thermal splitting of ethane by the Häuber process for the works at Heydebreck, Oppau and Moosbierbaum, including the erection of Linde plants or copper lye washing plans, will be done by Ludwigshafen.

Individual producers will get into touch with Herr. D.I. Meyer for the purpose of arranging for the Linde plants and the compressors for compressing the purified and concentrated ethylenes.

3) The producer will order for the account of the constructing works, and will receive from it, the overall quota for the iron required. The producer will request and fill in the metal certificate.

The electrical part of each plant will be planned and ordered by the authority for whom it is being built on the basis of the plans prepared for him by the producer.

The contracts for the buildings required for the plant will be placed by the authority for whom they are being built on the basis of clear written instructions by the producer, and their erection will be supervised by the former.

In order that these projects shall be carried through without friction, it is agreed that the constructional works, assembling, electrical, and building engineers shall maintain contact with the competent producer. The names of the gentlemen in question are set out in Appendix 3.

4) On the basis of the dates fixed for the gas-producing plants, the following order of precedence was fixed for the setting up of the polymerisation plants :

a) Gondorf: from 1.1.42, 24-25,000 tons per annum will be available.

b) At the end of 1942 2500 tons per annum of ethylene will be available from Saar gas, and also 2000 tons per annum of ethane from Saar gas. A Häuber furnace is to be set up for the latter by the above date. The rest of the ethylene required for 6000 tons per annum of SS 900 oil is to be covered by alcohol, until such time as ethane from the DHD plant is available.

c) Schkopau: the ethylene from acetylene will be available not earlier than the beginning of 1943, provided that the transformer is delivered punctually.

d) At the beginning of 1943, 39,000 tons of ethane from Blechhammer will be available.

e) Moosbierbaum: from the middle of 1943, about 4000 tons per annum of ethane and from the middle of 1943 14,000 tons per annum of ethane will be available.

f) Auschwitz: unable to deliver ethylene before the middle of 1943.

5) Supply of catalysts and auxiliary products:

a) The amounts required for polymerisation by all the plants are 700 tons per month = 8400 tons per annum of $AlCl_3$. Schkopau will communicate with Ludwigshafen about the possibility of producing $AlCl_3$, will make the application for the metal required to HWA, and will inform Herr D.I. Meyer of the fact.

b) It will probably be possible to provide the alcohol catalyst at Ludwigshafen.

c) The acetylene hydrogenation catalyst, and the acetylene cleaning catalyst will be supplied by Leuna.

Moosbierbaum will provide the fuller's earth required for refining the oil, to the amount of 800 tons per annum. Herr Dr. Ober will go into the possibility of production, will order the iron required from HWA, and will inform Herr D.I. Meyer.

APPENDIX I

SS 900 oil - description of the process

25 atü of pure ethylene which has been compressed to 100-200 atü are run into an

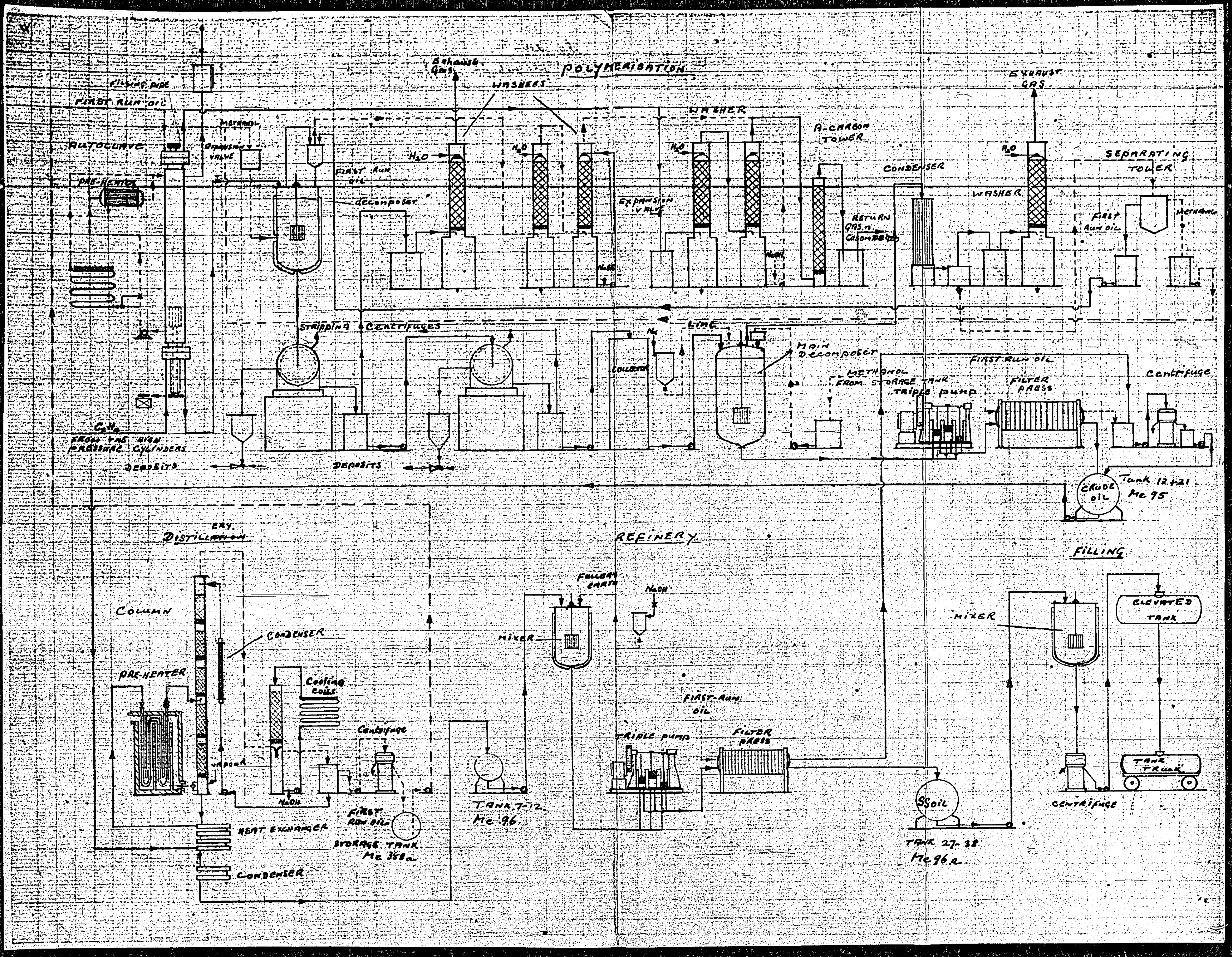
autoclave (800 x 9000) filled with 1400 litres of first run oil and 125 kg. of water-free $AlCl_3$ which contains iron. The contents of the autoclave are brought by external heating to about 100°. A vigorous reaction sets in, the internal temperature rising to 160-250°. The internal temperature is brought down to 120° by cooling with warm water, and then ethylene is run in while external cooling goes on (about 300 m^3/hour). After about 8-10 hours the autoclave is full. The contents are allowed to expand in a pre-decomposer, where it is stirred while methanol is fed in. The product after this treatment then runs through two centrifuges connected in series. The $AlCl_3$, oil, and sludge are separated here. The oil is passed, when thus purified, to the main decomposer and neutralised with methanol and chalk. The sludge is separated in an extraction-filter compressor. The oil so obtained is separated by atmospheric distillation with water vapour into first run oil and residual oil. The residual oil is refined with fuller's earth and then adjusted to the required viscosity. The first run oil is freed from water by centrifuging and then once more applied to polymerisation. The release gascontaining ethylene content pass back via a washing and adsorption plant to the gas-producing apparatus (recycle gas). Raw material and energy required per ton of SS 900 oil:-

Ethylene	1250 kg.
Aluminium chloride	76 kg.
Methanol	43 kg.
slaked lime	24 kg.
fuller's earth	7 kg.
Heating gas	228 m^3
High pressure steam	1.5 tons
Low pressure steam	5 tons
Water	140 m^3
Low tension	130 K.W.

(Appendix 2 missing)

APPENDIX 3

	Constructional Engineers	Electrical Engineers	Building Engineers
Schkopau	D.I. Wintermeier	Obering Bechtold	D.I. Reinhart
Moosbierbaum	D.I. Hutter	Dr. Viereck	D.I. Mann
Heydebreck	Obering Wöllintz	—	D.I. Holzapfel
Oppau	Obering Giehne Dr. Heckmann		Obering Will
Auschwitz	D.I. v.Lom	D.I. Frey D.I. Müller Dr. Viereck	Dr. Sitzenstuhl


POLYMERISATION
Exhaust Gas
WASHERS
FILLING PIPE
FIRST RUN OIL
METHANOL
AUTOCLAVE
EXPANSION VALVE
FIRST RUN OIL
PRE-HEATER
decomposer
H_2O
H_2O
NaOH
WASHER
H_2O
EXPANSION VALVE
NaOH
A-CARBON TOWER
RETURN GAS n. GASOMETER
CONDENSER
EXHAUST GAS
H_2O
WASHER
SEPARATING TOWER
FIRST RUN OIL
METHANOL
C_2H_4
FROM THE HIGH PRESSURE CYLINDERS
STRIPPING CENTRIFUGES
DEPOSITS
DEPOSITS
COLLECTOR
N_2
LIME
MAIN DECOMPOSER
METHANOL FROM STORAGE TANK
TRIPLE PUMP
FIRST RUN OIL
FILTER PRESS
Centrifuge
CRUDE OIL
Tank 12+21
Me 95
ERY.
DISTILL~~ATION~~
COLUMN
CONDENSER
PRE-HEATER
Cooling coils
VAPOUR
NaOH
Centrifuge
FIRST RUN OIL
STORAGE TANK
Me 388a
HEAT EXCHANGER
CONDENSER
TANK 7-12
Me 96.
REFINERY
FULLERS EARTH
NaOH
MIXER
FIRST-RUN OIL
TRIPLE PUMP
FILTER PRESS
SS OIL
TANK 27-38
Me 96a
FILLING
MIXER
ELEVATED TANK
TANK TRUCK
CENTRIFUGE

Letter from I.G.
to
Ammoniakwerk Merseburg
attention: Dr. Zorn

4.2.44

Re: ethylene for lubricating oil SS 900

With your letter of 30.8.43 you informed us about the general situation of the field of lubricating oils. For our up-to-date global study of the ethylene position we should now ask you to let us know the ethylene quantity required for lubricating oils in 1944.

To our knowledge Merseburg works to its capacity of 10000 tons per year: its ethylene requirement is therefore 12,500 tons per year.

From the Schkopau production plan we see a production of 200 tons is foreseen for January, 300 tons each for February and March, 400 tons for April and 500 tons monthly of SS oil from May onwards. We wish you would check whether these figures tally with your information: also inform us of the starting dates foreseen according to latest data for Leuna II, Heydebreck I and II, Oppau and Moosbierbaum and the corresponding production figures. We assume that the conversion ratio 125 parts of ethylene for 100 parts of lubricating oil still applies.

letter to I.G.
attention Dr. Alt
Ludwigshafen

10.2.44

With reference to your letter of the 4th inst. we give you the ethylene requirement for the lubricants section:

1) Leuna I: 12,500 tons per year of ethylene from the cracking of ethane for 10,000 tons per year lubricating oil.

2) Leuna II: Starting date, 1.10.44. 9000 tons per year of ethylene from the cracking of ethane for 7,200 tons per year lubricating oil

3) Schkopau: Target for February 200 tons, March 300 tons, April 400 tons, May 500 tons: full production (800 tons/month of lubricating oil) should be attained in June.

4) Heydebreck I: Starting date 1.7.44. 20,000 tons per year of ethylene from the cracking of ethane for 16,000 tons per year lubricating oil. This quantity is lower as compared with our schedule of 30.8.43, because the ethane supplies from Blechhammer had to be cut as a result of the cancellation of the DHD extension in Blechhammer

5) Heydebreck II: Starting date 1.1.45. 12,750 tons per year of ethylene from coke plants for 10,000 tons per year lubricating oils.

6) Moosbierbaum: Starting date 1.6.44. 4,500 tons per year of ethylene from the cracking of ethane for 3,600 tons per year lubricating oil.

7) Oppau: According to a decision of the planning division of the armament ministry the lubricating oil project Oppau has been shelved, with the result that the Saar gas ethylene is now available for other purposes.

Letter from I.G. Ludwigshafen
to Ammoniewerk Merseburg
attention Dr. Zorn

18.8.43

Re: Lubricating oil S 900

We have been entrusted by Dr. Ambros with the preparation of a global balance sheet for ethylene, shewing the production and consumption of the ethylene supplies now and after the execution of the planned expansions. This blance sheet should also contain the ethylene consumption for lubricating oils and we quote the latest figures. The following are the data available:-

Present position: 12,500 tons per year ethylene from cracking in Merseburg for 10,000 tons per year lubricating oil.

Final plan:

Merseburg I
12,500 tons per year ethylene from cracking for 10,000 tons per year lubricating oil.

Merseburg II
9000 tons per year ethylene from cracking for 7200 tons per year lubricating oil.

Schkopau
12,500 tons per year ethylene from hydrogenation for 10,000 tons per year lubricating oil.

Heydebreck I
27,750 tons per year ethylene from cracking for 22,200 tons per year lubricating oil

Heydebreck II
12,750 tons per year ethylene from cracking for 10,200 tons per year lubricating oil

Oppau
2475 tons per year ethylene from coke gas for 1980 tons per year lubricating oil

Moosbierbaum
4500 tons per year ethylene from cracking for 3600 tons per year lubricating oil

We ask you to check whether these figures still hold good and, if the case may be, to send us a rectification. Likewise we should be grateful for the indication of the probable starting dates for the new plants, as well as for the information whether the conversion ratio of 125 parts of ethylene for 100 parts of lubricating oil still stands.

	Production tons p.a.	Ethane requirements	Ethylene requirements	Estimated date for commencing production
Leuna I	10,000	20,000	-	-
Leuna II	7,000	14,000	-	1.4.1944
Schkopau	10,000	-	12,500 from C_2H_2	1.4.1943
Heydebreck I	22,000	37,000	-	1.1.1944
Heydebreck II	10,000	-	12,500 from coking gas	1.10.1944
Moosbierbaum	3,500	6,000	-	1.3.1944
Oppau	2,000	-	2,500 from coking gas	1.4.1944
Pölitz	12,500	17,000	2,500 from coking gas	1.10.1944
	77,000	148,000	30,000	
for the Army	12,500	17,000	2,500	
for the Air Force	64,500	131,000	27,500	

Of the 64,500 tons of SS oil, 13,900 tons are required for the manufacture of 18,500 t of low temperature aero engine oil, so that only 50,600 tons are available for mixing with mineral oils.
If the 18,500 tons of low temperature aero engine oils were produced as ethylene-oxide ester oils, this would require 7,500 tons of ethane (= 4,500 tons of SS oil). In this case the volumes of lubricating oil at the disposal of the Air Force would be as follows :-

64,500 - 4,500 = 60,000 tons p.a. SS 906

+18,500 " " Ethylene-oxide - Ester oils

78,500 " "

+26,000 " " paraffin

+77,000 " " mineral oil

181,500 " "

	Additional SS Oil production in tons per annum	Ethylene required in tons per annum	Spirit reqd.	Iron reqd. for building purposes	Iron reqd. for machinery	Millions RM Capital expenditure for Building	Millions RM Capital expenditure for Machinery	Building workers	Fitters
Leuna	-	-	-	-	-	-	-	-	-
Schkopau	1800	2400	5,400	-	-	-	-	-	-
Moosbierbaum	3500	4700	10,400	480	1720	0.48	1.72	130	140
Heydebreck	6700	8900	19,800	800	3000	0.80	3.00	220	250
	12,000	16,000	35,600	1280	4720	1.28	4.72	350	390

A special project is to be set on foot so that production can begin on the following dates:

Moosbierbaum from 1.7.1943
Heydebreck I " 1.7.1943
Leuna II
(first half) " 1.7.1943

The production plan for Army SS oil for the year ending 31.12.1943 is then as follows:

	Total production in tons per month	Luftwaffe in tons per mth.	Army tons per month	Beginning of Army production	No. of working months	Total production	Tons per annum from Ethane	Tons per annum from Spirit	Total spirit reqd.	Tons per month from 1.9.42	or from 1.8.43
Leuna I	850	850									
Leuna II	150	-	150	1.9.42	16	2400	-	3200	7100	445	
Schkopau	1000	850	150	1.7.43	6	900	1200	-	-		
Moosbierbaum	580	-	580	1.8.43	5	2900	1935	1935	4300		850
Heydebreck I	2390	790	1600	1.9.43	4	6400	3580	4970	6600		1240
						12,400	6715	10,105	18,000		

	1942				1943				1944				1945			
Pölitz	-	500	2000	4000	5000	5000	5000	5000	5000	5000	5000	5000	5000	5000	5000	5000
Rhenania	-	200	300	600	1000	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500
Ruhrchemie	-	-	-	-	-	-	-	-	1000	2000	3000	3000	3000	3000	3000	3000
Leuna	1800	2500	2500	2500	2500	2500	2500	2500	2500	2500	2500	2500	2500	2500	2500	2500
Schkopau	-	-	-	-	-	500	1500	2500	2500	2500	2500	2500	2500	2500	2500	2500
Heydebreck I	-	-	-	-	-	-	-	-	500	1500	3000	5500	5500	5500	5500	5500
Heydebreck II	-	-	-	-	-	-	-	-	-	-	-	500	1500	2500	2500	2500
Moosbierbaum	-	-	-	-	-	-	-	300	500	750	750	750	750	750	750	750
Oppau	-	-	-	-	-	-	-	200	500	500	500	500	500	500	500	500
	1800	3200	4800	7100	8500	9500	10500	12000	14000	16250	18750	21750	22750	23750	23750	23750
	16,900				40,500				70,750				94,000			
Mineral oil	21,500				44,200				51,000				51,000			

A) **General Information**

1. Name and Description of plant	Ester oil plant Auschwitz I
Exact address	I.G. Farbenindustrie, Auschwitz, Upper Silesia
Telephone	Building Inspectorate of I.G. Farbenindustrie A.G., Myslowitz 22371/72, Auschwitz 36 and 37, and Merseburg 3831.
2. Location of the plant	2 Kms. east of Auschwitz
3. Authority for whom the plant is being built	I.G. Farbenindustrie A.G. Frankfurt/Main
4. Export in charge	Dr. Dürrfeld, Ammoniakwerk Merseburg, G.m.b.H.

B) A new ester oil plant will be set up in conjunction with the fuel works (Todt, No. O.T, Breslau 7).

Power, water supply, canalisation, railway station, and traffic facilities will be used jointly by the ester oil plant and the fuel works.

Applicants are reminded that buildings must, in accordance with the orders of the Reichsmarschall of 20 June 1941, be constructed in the simplest form, full use being made of structural aids. All outlay which is not absolutely necessary such as for finely finished work, architectural refinements, decorations, etc., are prohibited.

Capacities of the plant to build :p

Products: ~~1600 tons per annum of Ester 426~~
2400 tons per annum of Ester 504

Raw Materials: 7300 tons per annum of higher alcohols
440 tons per annum of P_3
1200 tons per annum methyladipic acid
120 tons per annum soap/fatty acid

Number of working days per year

330 days of 24 hours.

Reason for the project

The above project is for the purpose of manufacturing Ester lubricating oils, which, together with SS 900 oils, are used to produce low temperature lutricating oils.

C) **Short description of the process**

The E oils are produced by esterfying organic acids with higher alcohols.

The basis of Ester 426 is P_3, which can be drawn from Leuna, and Leuna carboxylic acid (branched monocarboxylic acid C_8-H_{14}). The carboxylic acids are obtained by bath conversion of higher alcohols from the isobutanol synthesis. The carboxylic acid is released with sulphuric acid, and purified by distillation.

The esterfying is done in batches. The raw ester is washed with soda lye and water, freed of neutral oil and water by distillation under vacuum, and refined with fuller's earth.

The basis of Ester 504 is higher alcohols from the synthesis of isobutyl oil, and