2nd Batch (received 12.10.1943)

BA. 3a	Sonde 21	EPG Gösting
BA. 7a		van Sickle
BA. 10a	" ST.U.63	Neusiedl
BA. 13	" " 37	DEA Neusiedl
BA. 19a	" 24	" "
BA. 33		EPG Gösting
		van Sickle
BA. 34a	" ST.U.67	Neusiedl
GA. 7	" GA 7	DEA Neusiedl
GA. 17	" GA 17	RAG Zistersdorf
GA. 35	" GA 35	" "
GA. 40	" GA 40	" "
GA. 42	" GA 42	" "
GA. 59	" GA 59	" "
		" "

3rd Batch (received 18.12.1943)

Hau 16	vom Hauskirchnerfeld der Itag
Hau 17	" " " "
Hau 22	" " " "
Hau 29	" " " "

The samples could only be arranged according in order of increasing numerals because no data on the geological origin of the various samples are available at present. It must be left to a later date to classify the samples according to gelogical considerations.

The crude oil samples were greenish black or quite black viscous oil throughout, in many cases containing appreciable amount of emulsified water.

The samples of the first delivery contained an unusual amount of water (up to 80%); these oils could therefore not be examined so thoroughly.

C. The methods of investigation

The majority of the tests were carried out with the usual methods. The cases quoted here will be restricted to methods which are not generally known, or new methods, or those for which detailed instructions do not exist, or those in which existing methods have been modified.

The "basis" of the raw oils was determined from the specific weight of the so-called key-fraction at 15.6° according to the following table (key fraction 1 from 250 to 275° at 760 mm. Hg and key fraction 2 from 275 to 300° at 40 mm. Hg)

	paraffin base	mixed base	naphthene base
$d_{15.6}$ of key fraction 1	up to 0.8250	0.8250-0.8602	over 0.8602
$d_{15.6}$ of key fraction 2	up to 0.8762	0.8732-0.9340	over 0.9340

The key fractions were separated by means of a Widner column with a spiral 150 mm. long. The specific gravity of key fraction 1 was determined at 15.6 by means of pylmometer of 25 cc. volume. The key fraction 2 on the other hand was mainly solid at the above temperature; its density was therefore found at 40° and 50° and it had then to be extrapolated to 15.6°.

The content of solid paraffin in the whole of the raw oil was determined by distilling a sample over from a 50 cc. flask. The solid paraffin in the distillate was then determined according to the Butanon method at -15°.

The separation of the gasolines was carried out in a column 1 m. high of diameter 35 mm., filled withRaschigringens of diameter 4 mm.

The separation of the middle oils was carried out by means of a Widmer column with a spiral 150 mm. long at an average pressure of 150 mm. Hg.

The aromatics in the gasolines were estimated together with the olefines by shaking for 15 minutes with 5 times its volume of 98% sulfuric acid at 0°C. The content of olefines was obtained from the Bromine number (according to Winkler).

The proportion of naphthenes and paraffins was calculated from the aniline point of the sample, freed of olefines and aromatic compounds, according to the Garner diagram.

D. Experimental results

The numerous single experimental data have been represented in the following diagrams for the sake of simplicity:

Sheet 1: crude oils
2: gasolines up to 200°
3: middle oils 200-350
3a " " 200-400

The following should be added to the method of experimentation and the use of the diagrams.

The crude oils can be classified in groups with similar data after only a few characteristic data had been determined. In order to be able to cope with the mass of material, one representative of each group was investigated thoroughly; the result thus obtained was also assumed for the other oils in this group. In the diagrams these thoroughly investigated oils of the single groups have been underlined. In the case of data which were measured for all the crude oils, e.g. the density, none of the oils has been underlined.

The graphical representations are no more than an arrangement of the various data of the analysis according to their magnitude by plotting them on an inclined straight line. The scale of each of these ordinates is given at the side of the sheet.

1) Raw oils

The densities of the raw oils depend on the most varied factors; these include chemical make-up on the one hand and on the other the boiling point curve (proportion of gasoline, etc.). Therefore a more detailed classification of the oils is not feasible on the basis of the densities. All the same the graphical representation shows three distinct regions of accumulation viz. one series of oils of relatively low density in the range from 0.850 to 0.86, one of mean density between 0.880 and 0.900 and one with relatively high density between 0.910 and 0.93

The classification of the raw oils according to their "basis" is much more conclusive and clear since the basis derives from the "key-fractions" thus eliminating the factor of the boiling point curve.

The samples of raw oil wereceived at first were mostly too small to carry out the tests on all of these. All the oils were shown to be of mixed-base type with the exception of the oils BA 19a, GA 7, GA 17, GA 33, GA 40, GA 42 and GA 59 whose key fraction I (250 to 275°/760 mm.) just touch the naphthene base region. Thus the oils to a large extent have similar chemical characters.

For the sake of completeness the solidifying points and the content of solid paraffin are given apart from the densities. These data, which naturally shows a certain parallelism, are dependent on factors which overlap to a larger or smaller extent. They thus do not really qualify for characterising the oils.

The quite usual observation that oils of a more paraffinic type have greater proportions of gasoline is incidentally confirmed here (e.g. BA 10a, Hau 16, 17, 22, 29, BA 7a, 13, 33 have more gasoline content than those with a naphthene-like character such as GA 7, 17, 35, 40, 42, BA 19a, GA 59.

The proportion of middle oil (200-350) varies between 33 and 38% by weight. For Hau 10a, 28, 35, 40 it is particularly low (28%).

The proportion of middle oil 200-400 varies between 44 and 60% by weight. The oils BA 51, 59, EPO 62, 66 and 67 contain a particularly low proportion of middle oil (33-38%).

It was observed that oils of higher gasoline content have a relatively small content of middle oil 200-350 (e.g. Hau 16, 17, 22, 29, BA 10a, 7a, 13, 33 ----) and that those which contain less gasoline contain more middle oil 200-350, e.g. GA 59, 7, 17, 35, 40, 42. The proportion of residual oil above 350° remains constant within relatively narrow limits (50-59% by weight of raw oil). Compare the graphical summary on page 3.

It is not feasible to say any more about the crude oils since this would be connected with corresponding uncertainties. We now consider the results of the examination of particular fractions.

2) Gasolines up to 200° (compare sheet 2)

The following should be said about the specific gravity of gasolines up to 200°. The greater proportion of gasoline in the crude the lighter is the product and the smaller the proportion of gasoline the heavier is the product. A chemical analysis showed that the chemical character of the fraction is in general more paraffinic for high gasoline content and more naphthenic for lower gasoline content.

BA 10a constitutes an exception, containing little paraffin but very many naphthenes and comparatively high proportions of aromatics in spite of high gasoline content. The gasoline rich crude BA 34a contains in the gasoline a particularly large amount of aromatics besides many paraffins and is distinctly more heavy.

BA 2 and BA 19a also provide exceptions. The fraction from BA 2, in spite of constituting a small proportion of the total crude oil, contains very many paraffins and relatively few olfines apart from many aromatics but no naphthenes; the fraction thus has a lower density, in contradiction to the above rule. BA 19a gives a paraffinic fraction in-spite of its low gasoline content.

The gasolines from GA 7, 17, 35, 40, 42 as well as GA 59 represent a transition between heavy and light gasolines. They do still contain quite a large amount of paraffins, but the rising proportion of naphthenes and aromatics already has a significant effect on the density.

One can draw up the following diagram:

I Gasoline rich gasoline: low boiling paraffinic low density	transition	II Gasoline poor gasoline: high boiling naphthenic high density
BA 7a, 13, 33, 28, 35, 40; Hau 16, 17, 22, 29	GA 7, 17, 35, 40, 42, 59	BA 8, 21, 55, 41, 3a
Exceptions: BA 10a, 34a		Exceptions: BA 2, 19a

The following should be added with regard to the chemical composition of the gasolines.

The proportion of paraffin hydrocarbons lies between 0 and 50%. Some accumulation is observed between 34 and 38%. As a rule, the above proportion increases with increasing proportion of gasoline of the corresponding raw oil. A particularly high proportion is found for the fractions from BA 2 and BA 19a which have already been characterised as exceptions.

The naphthene content is mostly round about 50% as is shown by the diagrammatic representation. The fractions from PA 8, 21, 55, 41, 3a are particularly rich in naphthenes. The most paraffinic fraction from BA 2a is quite free of naphthenes, consisting of 68% paraffins, aromatics 28% and 4% of olefines.

The proportion of aromatic compounds remain within narrow limits for most gasolines viz. between 10 and 15%. The sample richest in aromatics is BA 2; others which are fairly rich are the fractions from BA 34a and GA 59 which like BA 2 contain mainly paraffin hydrocarbons in addition.

All the gasolines contain but a small proportion of olefines which is generally below 1% by volume. The BA 2 fraction already mentioned contains most olefines with 4% by volume.

The gasolines have no particular interest for the fuel chemists; mainly they are of low antiknock quality. (Because of the limited quantities the octane numbers could not be determined). The only gasolines interesting in this respect, i.e. those with a higher proportion of naphthenes and aromatics are only an extremely small percentage of the crude oils.

Evidently they are more or less suitable for a catalytic after-treatment. Detailed investigations as to their suitability could not be carried out because of the small amounts available.

3) Middle oils

The results of the examinations of the middle oils 200-350° have been summarised graphically on sheet 3, the results of those originally separated between 200 and 400° on sheet 3a.

With middle oils the differences caused by chemical constitution recede more into the background as would be expected from the higher molecular regions. The graphical representation of the densities, aniline points and cetane numbers are satisfactorily consistent with the physical connections of these data: there does not seem to be any middle oil which has an exceptional chemical character. The middle oils 200-350° from BA 7a, 13, 33, 10a; Hau 16, 17, 22, 29 incline to the side of the paraffins and have correspondingly high aniline points and cetane numbers. These middle oils would be relatively suitable for sulfochlorination for instance (Mersol-production).

GA 59, BA 19a, GA 7, 17, 35, 40, 42 give middle oils which are rich in aromatics and have the correspondingly low aniline points and cetane numbers.

The state of affairs for the middle oils separated from 200-400° is similar except for their higher olefine content.

The middle oil from BA 2 has the highest bromine number (proportion of olefine about 20-25%). High bromine numbers are also shown by EPG 54, 62, 65. Most of the oils have an olefine content of 5 to 10%.

The middle oils rich in olefines might be of interest for chemical reactions such as the Oxo process or sufation. The middle oils from 200-350 have bromine numbers below 2 without exception and may be regarded as practically olefin-free.

Probably the middle oils from BA 28, 35, 40, 41, 3a, 19a, 34 and GA 7, 17, 35, 40, 42, 59, would be rather suitable for catalytic cracking; for all other usual middle oils a medium suitability is to be expected.

The Conradson cokes are small for all the middle oils; they very within the limits of 0.005 to 0.035% by weight.

4) Elementary analysis

a) Carbon and Hydrogen

The raw oils have a relatively high carbon content corresponding to their bases, the content lying between 86.20 and 87.50% by weight. The hydrogen content varies within the medium limits of 12.0 and 13.4% by weight.

The gasolines up to 200° contain 85.5-86.10% by weight and 13.45 to 14.45% of hydrogen. They thus keep within the limits of distilled gasolines.

The middle oils 200-350 and 200-400° contain percentages of carbon and hydrogen which are also within the limits known from the Diesel fuels from mineral oils, the greater part of the values lying somewhat nearer to the upper limit. The contents of carbon vary between 86.10 and 87.40% by weight, the contents of hydrogen between 12.50 and 13.70% by weight.

b) Sulfur content

All the raw oils have a low sulfur content which varies between 0.1 and 0.3% by weight, only a few exceptions having a higher sulfur content, going up to a maximum of 0.6% by weight.

Consequently the sulfur content of the middle oils is also very low, viz. 0.03-0.20% by weight. The sulfur content of gasolice may be neglected in practice.

E. Summary and Classification

The Austrian petroleum oils examined so far may roughly be divided into three groups.

Group I is the most homogeneous and comprises the following oils : BA 28, 35, 40, 7a, 13, 33, 10a, 34a, Hau 16, 17, 22, 29. The oils of this group have a relatively high proportion of gasoline (14-16% by weight of gasoline up to 200°); its character is paraffinoid.

Group II is not so homogeneous any more. It comprises the oils BA 3a, 41, 19a, GA 7, 17, 35, 40, 42, 59; these contain a medium proportion of gasoline (5-9% by weight of gasoline up to 200°). The character of the oils varies between paraffinoid and naphthenoid, naphthenoid being the more frequent one.

Group III comprises BA 8, 21, 58, 51, 59, 67, 68, 70, 76, 77, 78, EPG 54, 57, 62, 65. These oils have a particularly low content of gasoline (1-5% by weight of gasoline up to 200°). Because of the small amounts available, the gasolines could only partially be examined thoroughly. The oils have a naphthenic character.

The oil BA 2 represents a type by itself. The high proportion of aromatic compounds and the absence of naphthenes in the gasoline boiling range are characteristic. The middle oils 200-400° has an increased content of olefines (20-25%).

F. Prospects

The present report is only the first part of a continuing investigation: we have also been authoritatively informed that the selection of the samples sent to us, particularly the first 20, could not yet be carried out according to any consistent plan. We therefore believe that the present report will help to assure that the further samples shall be selected more systematically.

Furthermore we hope that the present picture may be completed as further samples from the borings already examined, continue to come in, if the borings are economically important. We also hope that our report may have given some interesting clues to the geologists in the task that we shall have to tackle in combination with them.

The particularly interesting final aim of these investigations is to uncover connections between the chemical characteristics and the geological position and origin of the raw oils.

Sheet 1 - Examination of Austrian petroleum crude oils

Horizontal inscriptions:

Density @ 20°; Density @ 15.6; Key fraction 1; Density @ 15.6; Key fraction 2; Solidifying point; paraffin content

Wt. % gas. up to 200°; 1m. column; Wt. % middle oil; 200-350 30 cm. Widmark; Wt. % middle oil 200-400 30 cm. Widmark

The oils investigated thoroughly within a group or by themselves have been underlined

Sheet 2 - Investigation of Austrian Petroleum: gasolines (up to 200°)

Horizontal inscriptions:

Density 20°; Aniline point I; 10% vol. acc. to Engler; Vol. % olefine*; Vol. % aromatics; vol. % paraffins

* gasolines containing less than 1% of olefines have not entered

Sheet 3 - Investigation of Austrian petroleum: middle oils

Horizontal inscriptions:

Density @ 20°; Aniline Pt.; Cetane No.; Solidifying Pt.; Bromine No.*; Wt. % residue above 350°

* Bromine numbers from 0 to 2 have not been entered

3379/109

Ammonia Works Co. Ltd. Merseburg
Report No. 758 / II 10.12.40/26.6.41

Laboratory Experiments for Obtaining Adipic Acid And Alkyl Adipic Acids.

Dr. Ing. Fröhlich

In February 1938 the first plant for obtaining adipic acid was taken into commission at Leuna. In previous laboratory experiments the most favourable conditions had been ascertained under which the oxidation of cyclohexanol can be carried out with nitric acid. The optimum yield of about 87-89% of theoretical is obtained if 1 mol. cyclohexanol is allowed to flow into 8 mols. 62% nitric acid, which has been pre-heated to at least 60°, stirring well, so that on simultaneous cooling the temperature of the reaction does not exceed 80°C. After the addition of the cyclohexanol has been completed and the nitric oxide production has died down, the adipic acid will crystallise out to a great extent when the solution has cooled to 15°C. Its solubility in the acid, which still contains about 40% HNO_3 after the reaction, is only 0.47%. After filtering, washing in ice-cold water and recrystallisation, a pure white acid is obtained which, after drying, possesses a melting point of 151°C.

In the course of these investigations a number of problems cropped up, which had to be answered by laboratory experiments. This experimental work may be divided into two groups:

A. Experiments called for by the operating requirements.
B. Experiments which aimed at replacing the basic raw material "Phenol" by "Benzol".

A. Laboratory experiments required by operations.

1. Gas analytical investigation of cyclohexanol oxidation.

The oxidation conditions mentioned at the outset, in contrast to those indicated in technical literature or elsewhere, produced far better yields.

Thus, for example, Bouveault and Loquin (Bl. (4) 3, 438) recommend adding 300 gr. cyclohexanol to 1620 gr. commercial, boiling nitric acid for hours, keeping the reaction mixture at boiling point for a further 10 minutes. By this method, the adipic acid yield is said to be 52% d.Th.

Holleman, van der Laan and Slijper (R.24,23) run into 1000 gr. boiling nitric acid, spec. weight 1.2-32.3%, 100 gr of the mixture resulting from the reduction of phenol with hydrogen in the presence of nickel, a mixture consisting of much cyclohexanol and little cyclohexanon. The boiling point of this nitric acid is + 108°C.

The attempts made by Dr. Kögler, Leuna, to ascertain the ideal oxidation conditions showed that temperatures of over 80°C reduce the yield. The use of weaker acids than 62% HNO_3 had the same effect.

Object of the gas analyses.

In these experiments, the course of the oxidation reaction was investigated as regards the adipic acid yield. In addition to this important question for utilising the raw material (cyclohexanol), the transformation of the oxidising agent (HNO_3) and a possible more extensive oxidising decomposition was of interest, also the formation of lower aliphatic acids. These questions could only be answered by an analysis of the gases produced by the reaction. To carry out the investigations with this end in view, use was made of a modified Ruff apparatus, the construction of which is shown in the accompanying sketch.

Oxidation apparatus.

Into the 500 ccm retort, fitted with gas tight Jena stirring rod, thermometer and drop funnel, and long back-flow cooler, a determined quantity of nitric acid was run, where in many experiments the oxidising catalyst was dissolved or in suspension. For each experiment 15.0 gr cyclohexanol or SR II mixture (approximate composition: 50% cyclohexanol, 30% methylanol and 20% dimethylanol) were weighed out into the drop-funnel, while the acid in the retort was heated to 60°C by means of a water-bath. At the same time the gas apparatus was thoroughly evacuated by the water-jet and mercury pump. At the point S, both apparatus could be connected together.

Description of the gas apparatus.

The apparatus for analysing the gas mixture produced by the oxidisation process can be divided into two main parts, separated from each other by the cock H1. The part on the left side of the cock H1 serves for making the vacuum and possesses, besides the two pumps, a mercury gauge, connected with the jacket of the glass spring gauge used as a zero instrument. The part to the right of the cock H1 is for receiving the gas mixture and is connected with the inner space of the glass spring gauge. Measurement of pressure with the aid of a zero instrument requires the presence of nitrogen dioxide, which attacks mercury. The glass blubs P1 and P2, required for distilling and condensing the gases , the pressure tube DK, a glass bulb K provided with means of freezing, and three gas-traps F1, F2 and F3, are connected together by means of standard clamps and a length of tube. The right-hand distillation portion of the apparatus may be evacuated direct by the mercury or water-jet pump, by-passing the spring gauge.

The volume of the glass flask K, including the condenser trap KF up to the joint at the cock H4, was determined by weighing with water. In the same way, the volume of the specific gravity flask DK, used for determining the molecular weight of a gas fraction was ascertained in a number of experiments. On the basis of the Boyle-Mariotte law, p.v. = const, the various partial volumes of the distillation apparatus were ascertained from the known volume of the specific gravity flask and the glass flask. The sensitivity of the glass spring gauge made it possible to effect these volumetric determinations with an accuracy of 0.5%.

After the oxidation apparatus, as described above, had been made ready and the gas apparatus evacuated, a current of nitrogen was passed through the stirring flask for some time in order to remove the atmospheric oxygen. The apparatus A and B were then connected together by the ground joint S. B was therefore first filled with nitrogen at 1 atmosphere. The next step was to begin dropping in slowly the cyclohexanol or the alkylanol. The oxidation reaction at once set in, brown gases were generated and the pressure rose; this could be checked from the U-gauge filled with acetylene bromide, situated in the gas pipeline. By careful opening and closing of the capillary cock placed on the ground joint S, exactly the same amount of gas was drawn into the evacuated gas apparatus as corresponded to precisely one atmosphere prevailing in the oxidation apparatus. Spraying with cold water ensured that the reaction temperature did not exceed + 70° in the stirring flask. On an average, the dropping in of 15.0 gr. cyclohexanol or alkylanol was completed in 25 minutes. Stirring was continued for a further 25 minutes to complete the secondary reaction, and then, by means of the nitrometer(azotometer) connected with the oxidation apparatus, an exactly measured quantity of nitrogen was passed through the apparatus, until the gas-chamber had become colourless. The amount of gas to be determined, increased by the known quantity of nitrogen used for rinsing, was now in the exactly known volume of the distillation apparatus, confined by the cocks H1, H3 and S. The volume of nitrogen remaining after the experiment in the oxidation apparatus need no longer be considered, as the apparatus was filled with 1 atm N2 before the experiment. By carefully opening the capillary cock H5, the pressure in the glass spring gauge was exactly compensated, and from the pressure read off on the Hg-gauge, the temperature and the known volume of the apparatus, the total quantity of gas could be calculated. The quantity of nitrogen. reduced to 0°C and 760 mm, was deducted so that the quantity of gas produced by oxidation remained.

The three evacuated gas traps, F1, F2 and F3 are now cooled with Dewar-vessels containing liquid nitrogen. Then by carefully and slowly opening the cock H3, the whole gas mixture is drawn through the three gas-traps, when the condensable components of the gas, such as NO, NO_2, N_2O and CO_2 are retained, while the non-condensable nitrogen is drawn off through the pumps. The Dewar vessels filled with liquid nitrogen are removed from the three gas traps and the bulb P1 is cooled. Now everything that could be condensed was distilled to P1. The cock H3 was closed and the condensate was allowed to evaporate in the known volume of the apparatus. From the pressure and temperature measurements, the total amount of the condensable gas components was calculated. The difference between the total amount of gas (deducting the cleansing nitrogen) and the condensable matter gave the amount of nitrogen produced during the oxidation reaction.

Next, the gas trap KF connected with the flask K was cooled with liquid N_2. The condensable matter previously filling the apparatus space H1, FN, P1, S, H3 and K was thereby deposited in KF.

The end of each distillation can naturally be recognised by the fact that on conclusion, the original vacuum must be adjusted once more in the apparatus. If this is not the case, uncondensable components are present, which must first be removed by fresh pumping across several gas traps cooled with liquid N2.

After the evaporation of the condensable matter in the flask K and the trap KF, the flask at cock H4 of the dist. apparatus was removed. A measured quantity of a 20% potassium lye was then sucked in; its CO_2 content must be known and was therefore checked from time to time. By vigorously shaking the flask, the brown colour of the gas, derived from the NO_2 gradually vanished. After a while the flask was once more attached to the cock H4, and the residual gas consisting of N_2O and NO (in so far as the latter was present in the original mixture in the proportion of NO : NO_2 equal 1 : 1) was slowly sucked through the three gas-traps F1, F2 and F3, cooled with liquid N2. The condensate retained in the traps now consisted of ice, N_2O and NO. After the original vacuum had been restored in the apparatus, the flask containing the KOH was removed, the potassium lye was placed quantitatively in a measuring flask and rinsed with water free from CO_2. A CO_2 determination was then carried out for the KOH solution, as well as a total nitrogen determination with Arndt's alloy, and a nitrite-nitrogen determination with N/20 $KMnO_4$ solution.

Calculating the composition of the gas.

For calculating the composition of the gas on the basis of an analysis of the KOH, the following three cases should be borne in mind:

1.- NO and NO_2 are present in the gas mixture exactly in the molar ratio 1 : 1 and N_2O_3 is formed. In this case, the N_2O_3 reacts with the KOH in accordance with the equation

$$NO + NO_2 + 2\ KOH = 2KNO_2 + H_2O$$

i.e. only nitrite is formed and no nitrate.

The NO_2 - N-value found in the $KMnO_4$ titration must therefore agree with the total nitrogen value.

2.- An excess of NO is present over and above the molar ratio required for forming N_2O_3. For the formation of the N_2O_3, the required part of the NO is removed from the gas chamber. The remainder stays over the potash lye as residual gas. Once more, only nitrite is formed in the KOH.

3.- An excess of NO_2 is present. In this case, part of the NO_2 reacts, according to the amount of NO present, in the form of N_2O_3 in accordance with the equation (1) $N_2O_3 + 2\ KOH = 2\ KNO_2) + H_2O$; the remainder of the NO_2, i.e. the excess over and above that in combination as N_2O_3, then reacts in accordance with the equation (2) $2\ NO_2 + 2\ KOH = KNO_3 + KNO_2 + H_2O$. For this case, the calculation of the NO and NO_2 content is as follows: From the total amount of nitrogen, there is first of all deducted the nitrite-nitrogen calculated from the $KMnO_4$ titration. The difference corresponds to the nitrate-nitrogen. But since, in accordance with equation (2), during the absorption of the NO_2, the same quantity NO_2 - N is produced as NO_3-N, the amount present corresponding to the NO which has been present in the gas chamber may be calculated from the difference between titrated NO_2-N and NO_3-N. To elucidate this, an example is given. By the analysis of KOH there have been determined: 1.58 gr. total N and 1.045 gr. nitrite N. Therefore 1.580 gr. total N less 1.045 gr nitrite N equal 0.535 gr. nitrate N. From this wemay calculate:

$$2 \times 14\ mg\ N = 2 \times 22.4\ ccm\ NO_2$$
$$2 \times 535\ mg\ N = 2 \times 856\ ccm\ NO_2$$

On the basis of Equation 2

1.045 gr. nitrite N (total)
less 0.535 gr. nitrite N (corresp. to NO_2) equals
0.510 gr. nitrite N (corresp. to NO)

28 mg N = 22.4 ccm NO and 22.4 ccm NO_2

510 mg N = 408 ccm NO and 408 ccm NO_2

$$\text{Result: } \left.\begin{matrix} 856 \\ 408 + 856 \\ 408 \end{matrix}\right) = 2120\ ccm\ NO_2 + 408\ ccm\ NO$$

Analysis of the residual gas from the absorption of KOH

The residual gas in the three traps F1, F2 and F3 now consisted of a mixture of NO and N_2O containing water vapour. By distillation, the whole of the residual gas was first collected in the trap F3. Next, two pentane baths, adjusted to -40°C, were placed below the traps F1 and F2 and the residual gas was slowly distilled through these traps towards the bulb F1. With this slow distillation, the total moisture was retained in the two traps cooled to - 40°C.

For separating the NO from the N_2O, a pentane bath set to -150°C was placed below the bulb P1. The boiling point of N_2O is 88.7°C and that of the NO, - 151.8°C, i.e. the N_2O possesses at -160°C practically no vapour pressure, while the NO already exerts one atmosphere pressure. If NO were present, therefore, considerable pressure would ensue, the bulb P2 would be cooled with liquid N_2 and the NO would be distilled over. The end of distillation was ascertained by a drop in the pressure to 0. The whole of the N_2O was now in P1 and the NO in P2. The quantity of each fraction and its molecular weight was determined, first of all by the entire gas fraction being evaporated into the known volume consisting of bulb, specific gravity flask and apparatus volume, and determined quantitatively by measuring the pressure and temperature. The weight of the portion of gas in the specific gravity flask was then ascertained, whence the formula:

$$M = \frac{62400.T.G}{P.V}$$

giving the molecular weight.
G is the weight of the gas in the density flask, T the absolute temperature, p the gas pressure in mm Hg and V the volume of the density flask.

Example of a gas analysis

Placed in the stirring flask: 126 gr. 62% HNO_3 and 100 mg V_2O_5. Added at 60°C: 15.0 gr. cyclohexanol in 20 mins. react. 20 mins. Quantity of rinsing nitrogen used: 947.0 ccm; p = 744.0 mm; t: 24.2°C.

$$v_o = \frac{744 - 947.273}{760.297.2} = 852.0 \text{ ccm } N_2 \text{ rinse at N.T.P.}$$

Total quantity of gas obtained: p = 408 mm; v = 11171.21 ccm; t = 24.4°C

$$v_o = \frac{408.11171.273}{760 . 297.4}$$

i.e. 5505 ccm less 852 ccm equals 4653 ccm, total amount of gas produced by the reaction.

Determining the condensable material: p = 306.5; v = 11171.21; t = 20.7°C.

$$v_o = \frac{306.5 \; . \; 11171.21 \; . \; 273}{760 \; . \; 293.7} = \underline{4190 \text{ ccm condensable gas}}$$

Accordingly : 4653-4190 = 463 ccm nitrogen = 9.95% N_2.

Used for absorption: 195 ccm KOH, which from a blank determination already contained 106.8 mg CO_2.

Analysis of the KOH by absorption: ascertained, 1.0200 gr. CO_2
614 mg nitrite-N and 861 mg total -N

$$\begin{array}{lllll}
\underline{CO_2} : & 1,0200 \text{ g } CO_2 & & & \\
 & \underline{0,1068 \text{ g } ''} & & & \\
 & 0,9132 \text{ g } CO_2 \; ; & 44 \text{ mg } CO_2 & = 22,4 & \text{ccm } CO_2 \\
 & & 913,2 \text{ mg } '' & = \underline{465} & \underline{\text{ccm } CO_2}
\end{array}$$

861 mg Total - N
-614 mg NO_2 ' - N 14 mg N = 22,4 ccm NO_2
247 mg NO_3 ' - N 247 mg N = 395,6 ccm NO_2

614 mg NO_2 '-N- total
- 247mg NO_2 '-N, corresp. to the NO_2 28 mg N = 22,4 ccm NO u. 22,4 ccm NO_2
367 mg NO_2 '-N; 367 mg N = 294 ccm NO u. 294 ccm NO_2

Determination of the residual gas after KOH absorption.

At - 150° C no vapour pressure, i.e. only N_2O present.
p = 633.5 mg Hg; t = 22°C; v = 3612.29 ccm.

$$v_0 = \frac{633.5 \cdot 3612.29 \cdot 273}{760 \cdot 295} = 2785 \text{ ccm}$$

Determination of the molar weight: gravity flask Gas: 90. 8510 gr.
" empty : 90. 5900 gr.
0. 2610 gr.

Volume of the gravity flask: 171.79 ccm

$$\text{Molar weight } M = \frac{62400 \cdot 295 \cdot 0.261}{633.5 \cdot 171.79} = 44.1$$

i.e. pure laughing gas (N_2O = 44.02) is present.

Composition:

465.0	ccm	CO_2
689.5	"	NO_2
294.0	"	NO
2975.0	"	N_2O
4283.5	"	Condensable.

i.e. the quantity of condensable material calculated on the basis of the KOH analysis and the determination of the residual gas differs from that actually measured by 43.5 ccm, i.e. 1.03%.

465.0	ccm CO_2	=	9.9%	CO_2
689.5	" NO_2	=	14.68%	NO_2
294.0	" NO	=	6.26%	NO
2785.0	" N_2O	=	59.30%	N_2O
463.0	" NO_2	=	9.86%	NO_2
4696.5	ccm		100.00%	

In the oxidation of 15.0 gr. anol, after drying 18.50 gr of dry crude adipic acid were obtained. An analysis of the acid showed: 99.7% adipic acid, 0.14% N being contained in it. Yield 84.5% of theory of filtrate, 95 ccm = 123.60 gr were obtained. It contained 43.7% HNO_3 and 9.4% organic acid (calculated as adipic acid).

For ascertaining the recoverable nitrogen, the distribution of the nitrogen employed was calculated on the basis of an analysis of the adipic acid and the filtrate. For this purpose, all the gas components containing nitrogen were converted into gr. of nitrogen.
Quantity used : 125 gr 62% HNO_3 = 17.22 gr. N.
The reaction products contained nitrogen:

Loss N			Recoverable N		
Adipic Acid:	0.026 g N =	0.15% N	Filtrate :	12.01 g N =	69.80 % N
gasf. N_2 :	0.579 g N =	3.36% N	NO:	0.184g N =	1.07 % N
Laughing gas :	3.485 g N	20.24% N	NO_2:	0.431g N =	2.66 % N
		23.75% N			73.45 % N

The ratio of the recoverable nitrogen to the nitrogen lost is in the gas phase

NO :	0.184 g N	N_2 :	0.579 g N
NO_2:	0.431 g N	N_2O:	3.485 g N
	0.615 g N		4.064 g N

i.e. 13. 15% N recoverable.

It will be seen from the foregoing that the main bulk of the nitrogen (~ 70%) is in the filtrate of the adipic acid. On this account, the method was soon adopted of concentrating the HNO_3 content of the filtrate to the figure of 62% required for a fresh oxidation, by passing in nitrogen oxides and air. On a manufacturing scale it has been found that this method may be repeated until the crystallisation and filtering of the adipic acid becomes very difficult owing to the production and concentration of organic acids such as succinic and glutaric acids, which are secondary products. If the amount of extraneous acid in the filtrate amounts to approximately 10-11%, the adipic acid crystallises out in such fine granules that difficulties attend the passage of the acid into the suction filter. In this case the quantity of extraneous acid may be lowered by giving up part of the filtrate and adding fresh 62% HNO_3, and the process of concentration can now becarried out repeatedly.

The results of a series of similar gas analyses are shown in Tables I and II.

It will be seen clearly that the said oxidation experiments at plus 60 degrees, using 62% HNO_3 produce the greatest yield in the molar ratio of 8 : 1. These working conditions are also applied on a large scale and will in future be regarded as the standard conditions. A higher temperature and thinner acid are extremely detrimental to the yield. Furthermore, the favourable influence of the oxidation catalysts in accordance with German Patent 473960 - Dehydag and more especially V_2O_5. The CO_2 content of the waste gases is in inverse proportion to the yields attainable with the various conditions of oxidation. With falling yield, the CO_2 content rises in the gas phase. This is to be attributed to the formation of low molecular secondary products. Whereas under normal conditions the total amount of gas amounts to about 6 L, and the recoverable nitrogen amounts to is between 13 and 18%, with higher temperature and thinner acid the latter lies between 25 and 30%, while the total amount of gas increases to 8 L. The simultaneous losses of organic matter are expressed by a rise in the CO_2 content.

The oxidation of the alkyl-cyclohexanols shows precisely the same course, so it is superfluous to devote any space to the results.

The experiment designated in Table I as V 13 refers to the analysis of samples of gas obtained from a semi-technical, continuous oxidation plant. In contrast to the discontinuous method, in these processes nitric acid and cyclohexanol were placed together under pressure in a mixing nozzle and the oxidation reaction proper takes place in a heated pipe. The secondary reaction takes place in a larger receptacle connected with the former and the adipic acid crystallises out from the completed reaction mixture on cooling. The composition of the gas was shown by analysis to be more unfavourable than with the discontinuous method. The higher CO_2 content of the waste gases implies the occurrence of undesirable secondary reactions and therefore smaller yields.

To sum up, it may be said that the results of the gas analyses confirmed previous experience gained in other directions regarding optimum oxidation conditions and moreover showed that allowance must be made for a nitrogen loss of about 25% of the total nitrogen used.

The possibilities of using the laughing gas generated have not yet been explored. By recovering the N_2O, the nitrogen losses could be kept down to 4-5%.

2. Experiments for obtaining alkyl adipic acids.

After the oxidation of an anol mixture, consisting of about 50% cyclohexanol, 30% methyl anol and 20% dimethyl anol, which was obtained from SR II phenol oil, on cooling only the adipic acid corresponding to the cyclohexanol crystallises out. Methyl and dimethyl adipic acid remain in solution. It has been found that the direct production of the two soluble alkyl adipic acids by evaporation under atmospheric pressure, resulted in dark coloured, greasy products. For this reason, the process was soon adopted of carrying out the evaporation in a vacuum. The evaporation apparatus used was a normal Claisen flask, on one of whose necks was placed a T-piece with dropping funnel and the boiling capillaries, by means of standard ground joints. Connected to the flask were a long Liebig cooler and a round flask, ice-cooled. The vacuum was produced by an efficient water-jet pump, checked continuously by a U-gauge.

In order to explain the process of evaporation, equal fractions of the distillate were drawn off during distillation and analysed. The HNO_3 content was obtained by titrating with phenolphthalein. By deducting from the total amount of NaOH consumed the NaOH corresponding to the nitric acid, the content of organic acid was calculated. As dibasic organic acids are not volatile in steam, the acids in the present case must have been monocarbonic acids. The quantity of solution evaporated was accurately analysed beforehand in the Claisen flask and determined volumetrically, so that the quantity of nitric acid first added was known. From a determination of the quantity of HNO_3 that has passed into various fractions, the nitric acid remaining in the flask during the various phases of evaporation could be computed.

These experiments led to the following results:-
If the filtrate of the adipic acid which was evaporated had to begin with 43% HNO_3, a 17% acid first of all passed over; the concentration of the acid remaining in the flask gradually increased. At the moment when this attained about 50%, large quantities of nitrogen oxides were generated,

evidently owing to the action of the nitric acid on organic substances. The pressure change involved was so violent that the lower pressure in the apparatus was almost neutralised. The product obtained by this method of evaporation was also a dark coloured mass, which was very much more consistent than that obtained under atmospheric pressure. In addition to the vigorous generation of NO_2, powerful frothing occurred in the substance contained in the distilling flask, so that often portions of the contents were carried along.

In order to remedy all these troubles, an attempt was first of all made to add small amounts of water shortly before the occurrence of frothing, in order to lower the concentration of the nitric acid in the flask. The desired effect was indeed achieved, the generation of NO_2 and frothing ceased at once, but the duration of distillation was considerably prolonged by this measure, so that the course was adopted of blowing steam into the flask during distillation, in place of water. The use of steam did not, however, bring about the desired shortening of the time of the experiment, so that as regards the final effect it was immaterial whether steam or small quantities of water were added. In the laboratory experiments, the course followed that first of all evaporation took place without admixture until the commencement of slight generation of NO_2, when about 5% of the volume of fluid originally used during the distillation was slowly dropped in. Evaporation was then continued until the generation of NO_2 showed signs of beginning, when a second portion of 5% water was dropped in. This measure was continued until with further evaporation there was no more generation of gas and a product, yellow and viscous when warm, was obtained, which solidified on cooling to form a yellow, almost solid mass, having approximately the consistency of margarine. The concentration ratios of the nitric acid in the distillate and in the distillation still for this type of distillation, as well as the progress of the method will be seen from the accompanying curve. It was found from a number of experiments that to obtain the effect described above, the necessary minimum of water must be about 22% of the initial volume of the fluid to be evaporated.

With a vacuum of 20 mm Hg, the dilute nitric acid will distill at 44°C, but the distillation temperature gradually rises to 55°C; at this temperature the main bulk will be distilled. Towards the end of distillation, in order to obtain the last portions of water or dilute acid from the already viscous mass, the bath temperature of the distilling flask must be slowly brought to a maximum temperature of plus 110°C. If this temperature is exceeded, the product will always acquire a brown colour. It is moreover most important not to break the vacuum to fill the product until the temperature of the mass has dropped below 60°C, as otherwise widespread decomposition and discolouration of the alkyl adipic acids will be the result.

At 55°C to 60°C, the mass is still molten and can be poured. Example: 200 gr of a SR II-phenol-mixture were oxidised with 1634 gr 61.7 nitric acid at 60°C. After cooling the reaction solution, 139.5 gr crude adipic acid (90.62% adipic acid) were separated and filtered off. The filtrate from the adipic acid separation 1565.3 gr (d_{20} = 1.301) with 44.1% HNO_3 was evaporated for 20 minutes with the addition of 22% water (in relation to the volume of liquid to be evaporated). 133 gr. of a light yellow, quickly solidifying residue were obtained, containing slight amounts of succinic and glutaric acid and consisting mainly of methyl and dimethyl adipic acid.

3. Experiments for purifying nitric waste acids and alkyl adipic acids.

In suction-filtering the adipic acid from the nitric reaction mixture there accumulate relatively large amounts of waste acids with a content of about 38-40% HNO_3. These are mainly eliminated by transformation to calcium nitrate. The waste acids contain substances which prejudice the solution of lime by violent frothing, and the quality of the calcium nitrate is impaired by yellow discoloration. No exact knowledge was available as to the nature of these impurities, but organic nitro-compounds were suspected. Absorption and reduction experiments were conducted to eliminate these disturbances, which occurred irregularly and to varying degrees.

The direct addition of A-carbon to the nitric filtrate of the adipic acid separation was not practicable, as even with a dilution of the filtrate with water in the ratio of 1 : 50, there occurred a lively reaction with the A-carbon, accompanied by the production of gas. Thereupon a special bleaching carbon, "Carboraffin carbon" was used, which indeed reacted only very slightly with the nitric filtrate, but had no bleaching effect. Even after boiling away the "Nitrose," the addition of C-carbon did not clarify the colour at all. It was assumed, as already stated, that the yellow colour of the filtrate, as well as that of the evaporation residue, were caused by organic nitro-compounds. These should change by reduction into amino-compounds. For this reason, after removing the "Nitrose" by boiling, reducing agents, such as iron filings, zinc powder, formaldehyde and sulphurous acids, were used for treating the filtrate. All these attempts failed, however, in the presence of nitric acid. If the solution was accurately neutralised with lye or ammonia water, its colour was strengthened and the addition of A or C carbon silica gel/etc. had no effect whatever.

Experiments for purifying the yellowish alkyl adipic acids were initiated with the aid of reducing agents. Thus, for instance, 150 gr. crude evaporated residue was dissolved in a little water and the solution was treated with 40% soda lye with a pH of 7.0. About 32 gr of Arndt's alloy were then added and the whole boiled for a few hours, when large quantities of ammonia were given off. After this, the solution was acidified with conc. hydrochloric acid and evaporated in a vacuum until dry. The residue was boiled in the reflux cooler for 2 hours with propyl ether, when the solution was filtered and the ether distilled off in a vacuum. There remained 63.0 gr of a yellowish residue, which only contained 0.00978% N.

In spite of the great drop in the nitrogen content, no difference could be discerned between the colour of the starting material and that of the treated product.

The addition of SO_2 to the melted evaporation residue was likewise unsuccessful; in fact, the colour was, if anything, darker.

Since the reduction experiments were unsuccessful, an attempt was made to remove the yellow colour from the residue by means of selectively active solvents. In this connection it was found that ether, acetic ester, acetone and alochol readily dissolve the whole substance without residue. Pentane, petrol and carbon disulphide on the other hand, have no solvent action.

A special position is occupied by benzol and chloroform, as both these solvents dissolve only methyl and dimethyl adipic acid, but not adipic acid. The substances responsible for the yellow colour are also dissolved, so that a white adipic acid remained in the residue. The benzol or $CHCl_3$ solution of the alklyl adipic acids naturally produced on evaporating the solvent residues that were very yellow in colour. On the basis of an analysis of the adipic acid remaining in the residue on extraction with benzol or chloroform, it was found that for separating the adipic acid in the purest possible form, chloroform is the more appropriate solvent. Even with extraction with cold $CHCl_3$, the acids may successfully be separated.

The actual effect aimed at, viz, the elimination of the coloured impurities, was not successful by this means.

An attempt was next made to bleach the alkyl adipic acids after separating the adipic acid, by means of $CHCl_3$ extraction and vacuum distillation. With this in view, 200 gr. evaporation residue were twice extracted in the cold with 200 ccm chloroform in each case. The residue amounted to 70 gr (= 35%) of pure adipic acid with a melting point of 151°C.

The chloroform solution of the alkyl adipic acids was first concentrated at atmospheric pressure, then the remainder of the chloroform was removed in a vacuum. The residue thus produced was distilled at 1 mm by means of a mercury pump. At 73°C, a bright yellow distillate was obtained, which remained fluid at room temperature. Between 100-200° the rest of the residue was distilled, without any steadying of the distillation thermometer being observed. This distillate (125.7 gr) solidified on cooling to form a crystallisable, only slightly yellowish product. 125.7 gr. = 62.8%.

There remained in the distillation flask a carbon residue of 7 gr.

The condition for the success of the vacuum distillation of alkyl adipic acids is : 1) - the prior separation of adipic acid by chloroform extraction, as the latter, owing to its high boiling point, is more difficult to distil and tends to crack. 2) the use of a good vacuum. The pressure of 10-12 mm Hg abs. obtainable with a good water-jet pump is not sufficient, as at least 1 mm or less must be attained in order to prevent a thermal decomposition of the organic substance.

4. Distillation analyses of the cyclohexanol and SR II mixture used as starting substance.

In order to confirm the assumption that nitro compounds are responsible for the yellow impurities in alkyl adipic acids, compounds which may be produced by the action of nitric acid on the phenols present in the cyclohexanol or alkylanol mixture, a few comparative boiling analyses of different starting materials were carried out, whose individual fractions were then subjected to oxidation. The best distillation device for this purpose was found to be the familiar Widmer column. The latter was 260 mm long and furnished, with slow distillation, excellent results, as shown by the check distillations of mixtures of known composition. The fine distillation column recommended in recent technical literature by H. Grosse-Oetringhaus (Oel und Kohle 16/35, 1939, 599) was also tested, but it has the disadvantage that it requires relatively large amounts of substance and moreover retains too large a portion of the final fraction in the 850 mm long distillation tube. The manipulation of the Widmer column is very much simpler, and with a little practice and careful distillation it furnished at least equally good results.

The assessment of the various distillation fractions was effected by these being oxidised separately with nitric acid; the adipic acid was then filtered off, and with the nitric filtrate, samples of calcium nitrate were made, whose colours were compared together.

In treating an anol mixture obtained from phenol oil SR II, it was found, for instance:

Column	Amount used : 724.7g		Colour of calcium nitrate
1. Fraction : 97-160°C	14.4g	= 1.9%	Pure White
2. " :162-164°C	497.4g	= 67.0%	"
3. " :164-171°C	163.2g	= 22.0%	Slightly Yellow
4. " :171-201°C	51.2g	= 6.9%	Very Yellow
Residue:	8.5g	= 1.1%	
		98.9%	

The alkyl adipic acids obtained from the filtrates of the adipic acid with the addition of water in a vacuum, presented the same aspect in regard to colour as the calcium nitrate samples.

This confirmed the assumption that the phenol impurities, boiling at 180° or above (or also their hydration products), in the starting materials are responsible for the yellow colour of the products and the waste acids.

On the basis of these results, care was now taken that the cyclohexanols and alkyl anols oxidised were subjected to previous distillation. This eliminated to a great extent the difficulties in making the calcium nitrate mentioned above. At the same time the intense yellow colour of the evaporation residue of the alkyl adipic acids disappeared. The reaction products were normally only faintly yellow.

B. Experiments for replacing the fundamental raw material hitherto used. "Phenol" by "Benzol".

The older processes for obtaining adipic acid are largely based on the raw material phenol, which on being hydrated produces cyclohexanol. Since phenol is not a cheap substance and is required for many other productions, laboratory experiments were first of all directed towards the possibility of avoiding phenol and using other compounds instead. The simplest way was found to be the oxidation of cyclohexane or its derivatives. In the course of work on this problem, the following possibilities of reaction were investigated:

1.
Benzol
Cyclohexane
Adipic Acid

2.
Benzol
Nitrobenzol
Cyclohexylamine
Adipic Acid

3.
Benzol
Cyclohexane
Cyclohexylchloride
Adipic Acid

4.
Benzol
Cyclohexane
Cyclohexylchloride
Cyclohexene
Adipic Acid

5.
Benzol
Cyclohexane
Cyclohexylchloride
Cyclohexene
Cyclohexylester
Adipic Acid

Benzol
Cyclohexane
Cyclohexylchloride
Cyclohexene
Cyclohexanol
Adipic Acid

1. Attempts to oxidise cyclohexane with nitric acid.

Literature.

Practically simultaneously, work was published by Markownikoff (Ann. 302, 1898, 34) and Aschan (Ber. 32, 1899? 1771) on the oxidation of cyclohexane (hexanaphthene) by means of nitric acid. The results of all this work are highly unsatisfactory having regard to the adipic acid yields obtained. Markownikoff indicates as the most prolific method the oxidation of hexanaphthene with nitric acid of spec. weight 1.236 in sealed tubes and thus obtaines 32% adipic acid. If the oxidation was carried out under reflux on the water-bath, 6 volumes of nitric acid, S.G. 1.510 = 98%, were used to one volume hydrocarbon and the mixture was heated for 10 hours until it started to boil. Out of 20 gr. hydrocarbon, 3.5. gr. were unchanged; from the 16.5 gr. involved in the reaction, 3.32 gr pure adipic acid were obtained, which corresponds to a yield of only 11.6% of theory.

Aschan (lc.), in his work published one year later, improved Markownikoff's method and evolved an economical method of making the adipic acid. He heated the hydrocarbon with 10 times the amount of nitric acid of specific gravity 1.42 = 69% for 50-60 hours. The temperature is not stated. The evaporation residue is then purified as the ammonium salt of the adipic acid, from which, by acidifying with concentrated hydrochloric acid, pure adipic acid is obtained. Aschan states that in this way he obtained 17-18 gr. adipic acid from 100 gr. hydrocarbon. The yield was thus only 10%.

Oxidation experiments.

When the cyclohexane was dropped into nitric acid at 80°, of S.G. 1.38, no action by the acid on the hydrocarbon could beascertained. In order to increase the disintegration of the cyclohexane in the acid, a device known as the "sintered glass tube" apparatus was selected, consisting of a Jena glass tube 50 mm wide and 650 mm long, to the top end of which was attached a spherical extension, holding 1.5 litres and on this again, by means of ground joints, a reflux condenser. At the lower end a Jena No.2. sintered glass plate was fused in and the lower, tapering part of the tube was fitted with a T-piece and cock. In this way, any condensate forming could be drained off. To the T-piece was attached a glass tube bent upwards, passing through the heating or cooling jacket covering the entire reaction tube, after which it ran horizontally and was connected with a triple neck round flask of 250 ccm. This round flask served to vaporise the material to be oxidised. On the centre tube was placed, by means of a standard ground joint, a reflux condenser fitted with a cock. Through the right-hand outer joint of the flask a gas inlet tube was inserted to the bottom of the flask. The round flask was placed in a heated water bath, whose temperature was adjusted so as to be close to or even above the boiling point of the hydrocarbon to be vaporised. At the same time a stream of nitrogen or carbon-dioxide was passed through the flask, the intensity of which was measured by the number of gas bubbles occurring in a mercury dipper.

Whereas when the cock of the reflux condenser was first opened only a very small part of the boiling hydrocarbon was taken along with the N_2 of CO_2 stream, according to the adjustment of the cock aperture the quantity of hydrocarbon reaching the sintered plate could be regulated. Two thirds of the height of the reaction tube was filled with warm nitric acid, which had to be traversed by the carrier gas laden with hydrocarbon, in fine distribution.

Thus, for example, 700 ccm 62% nitric acid are heated in the fritted tube to 95°C. Then, 16 ccm cyclohexane are vaporised at 84°C in the current of N_2 and taken through the hot acid. No reaction occurred and at the end of the experiment, the cyclohexane separated unchanged from the nitric acid.

Additives of Hg salts, $Fe(NO_3)\ 39H_2O$, V_2O_5, MnO_2 as catalysts had no effect. Varying quantities of conc. sulphuric acid were also unable to set the reaction going. Even an increase in the nitric acid concentration to 99% acid did not bring about any satisfactory result: Into 600 gr. 99% HNO_3 were dropped at 80°C and with vigorous stirring, 25 ccm cyclohexane. The temperature was maintained for 6 hours. On cooling, 22 ccm of unconverted cyclohexane were separated off. After evaporating the acid in a vacuum, 13 gr of a dark brown, greasy residue were obtained, smelling strongly of organic nitro-compounds and having none of the properties of adipic acid.

All the experiments showed that cyclohexane is extremely stable in the presence of nitric acid in various concentrations. In order to make the cyclohexane molecule more ready to react, substituents were added, viz. NH_2, Cl etc. The experiments carried out with these combinations produced the following result:

2. Oxidation of cyclohexylamine.

In a 600 ccm round flask provided with stirrer, dropping funnel and reflux condenser, 280 gr of 62% nitric acid were placed. A few drops of cyclohexylamine were then added from the dropping funnel and stirred. This brought about a white cloudiness and the generation of considerable heat. When the amine was dropped in quickly, flame phenomena were observed in some cases and carbon was deposited on the walls of the flask. When the dropping-tube was lengthened until it was submerged in the acid, further explosive decomposition was prevented. Nevertheless, the amine had to be added very slowly and carefully in order to moderate the neutralisation reaction. After thewhole amount of 20 gr. $C_6H_{11}NH_2$ had been added, the solution was slowly heated. It had been ascertained in preliminary experiments that the oxidation of cyclohexylamine only proceeded at adequate speed at temperatures of 90°C. It is true that at 70°C, after a little while, there was weak generation of nitrogen oxides, but the reaction at this temperature was too sluggish. The nitric acid-cyclohexylamine nitrate solution was therefore stirred and heated to 90°, when the nitrogen oxides were only given off regularly after stirring for $\frac{1}{2}$-$\frac{3}{4}$ hour. After about 15 to 20 hours, the generation of gas slackened off considerably, and on cooling the solution to 15°C, the resultant adipic acid was separated off, after which it was filtered, weighed and analysed. In the filtrate the HNO_3 - nitrogen content was determined, and by titrating with phenolphthalein the organic acids as well, calculated as adipic acid.

Results of the experiments.

In the following table, a few experiments have been collated. The most striking phenomenon in the oxidation of cyclohexylaminwas found to be the following: In contrast to the oxidation of cyclohexanol, it was only possible on rare occasions to obtain results that agreed at all from two experiments carried out under exactly the same conditions. The discrepancies in the yield were sometimes between 20 and 30 per cent.

Whereas in the oxidation of cyclohexanol, higher temperatures than 70°C were found to lessen the yield, for the oxidation of cyclohexylamine the temperature must be at least 90° in order to keep the reaction going sufficiently. All the same, reactions lasting at least 15-20 hours cannot be avoided, as a premature interruption impairs the yield very appreciably. These reaction times thus amount to 10 times those required for oxidising the anol.

Regarding the machinery of the reaction, it was tempting to assume that the cyclohexylaminenitrate which is first of all formed is diazotised by traces of nitrous acid; the diazonium salt is at once saponified, cyclohexanol is formed and this is then oxidised by the nitric acid to form adipic acid. In this manner the slow progress of the reaction may be explained, as in the 62% nitric acid extremely little HNO_2 is present, which, according to the above view, is the only part that reacts to begin with. When the oxidation gradually advances in the cyclohexanol, more nitrous acid is formed to the same extent, so that larger quantities of the amino nitrate can be attacked. This view finds confirmation in the fact that it was possible, by adding 0.5 gr. sodium nitrite to the nitric acid solution of the cyclohexylamine, to start the reaction at once, while without this additive, at least $\frac{1}{2}$ - $\frac{3}{4}$ hour passed before the first signs of incipient oxidation were observed.

Experiments with cyclohexylamine Oxidation.

	Oxidation conditions		Temp. in °C	Reaction time in hours.	Yield %
62%	HNO_3		90 -100	28	53
"	"		100	20	46
"	"		"	27	60
"	"	+ 0.5 g $NaNO_2$ + V_2O_5	95 -100	25	66
"	"	+ 15 g $NaNO_2$	98	17	46
"	"	+ 3 % N_2O_4 + V_2O_5	100	56	61
"	"	+ platinised balls	105	20	39
"	"	+ 0.5 g Hg $(NO_3)_2$	"	39	43
73%	"	without additive	95	20	54
76%	"	+ V_2O_5	90	"	65
"	"	+ platinised balls	100	22	51
82%	"	+ V_2O_5	118	26	61 x).
85%	"	without additive	100	18	55
98%	"	" "	10	Explosion	
		after max.	(70) (114)	(3.5) (12)	46.6

x) on dropping in flame phenomenon & formation of soot

All experimental results refer to use of
20.0 g $C_6H_{11}NH_2$

In addition to the sodium nitrite as the initial reagent, various catalysts were used, which had already shown a favourable influence on oxidation in the case of cyclohexanol, e.g. MnO_2, V_2O_5, Hg $(NO_3)_2$ $\frac{1}{2}H_2O$ and platinised porcelain balls. However, these catalysts did not bring about any shortening of the long reaction times, but only a slight increase in the adipic acid yield of about 5 -10%.

The use of a higher acid concentration than 62% caused a slighter improvement in the yield than corresponded to theexpenditure of stronger acid. Moreover it was more difficult to bring the cyclohexylamine into the stronger acid. With concentrations of about 85%, explosions occured on some occasions.

The extremely long times of reaction, the poor yield, the unreliable degree of repoductibility and the trouble involved by working at temperatures over 90° were the reasons why the experiments with cyclohexylamine as a starting material were discontinued.

The method referred to by Hoechst on 28.4.39 - "Adipic acid and Cyclohexylamine" by Dr. Hilpert and Dr. Bostian was followed in a few experiments, but the yields mentioned by the writers could not be attained. The Hoechst experiments differ from the present ones described above in that one mol of cyclohexylaminonitrate (formed beforehand) is acted on by 1-2 mols sodium nitrate at a low temperature, then it is cooled and the requisite nitric acid is added for oxidising, and finally, by subsequent heating, towards the end of the reaction and even up to boiling temperature, the oxidation reaction is carried out. 71.3% of the theoretical amount should be obtained. In subsequent treatment, never more than 50% of the theoretical amount was obtained.

Oxidation experiments with cyclohexyl chloride

The cyclohexane monochloride, which is easy to make in accordance with reaction diagram 3 by chlorinating the cyclohexane was only subjected to oxidation with nitric acid in a few tentative experiments. The course of the reaction resembled that of the oxidation of cyclohexylamine, as the reaction likewise only started at temperatures of about 90°C. At 60 - 70°C, no action could be ascertained. Up to the completion of the nitrogen oxide generation, reaction times of 15 - 20 hours were also needed for 35 gr. $C_6H_{11}Cl$. The yield was about 20% of the theory, and in no case were better results obtained. In a final experiment, into 62% HNO_3 at 90-100° cyclohexane was dropped and at the same time gaseous chlorine was passed through. No reaction could be observed, the chlorine left the apparatus unchanged and the cyclohexane was deposited in the nitric acid after stirring had ceased.

Since cyclohexyl chloride seemed unsuitable as a starting material, not only owing to its resistance to nitric acid, but also owing to material difficulties in extending the process to an industrial scale, the very much more promising cyclohexane was used.

Experiments with cyclohexene.

The direct oxidation of cyclohexene. Cyclohexene may be prepared in accordance with German Patent 264 473 of the B.A.S.F. by passing cyclohexane monochloride over catalysts such as $BaCl_2$ and Al_2O_3 at temperatures of 300 - 400°C or in accordance with Russian patent No. 42 550 by separating off HCl from cyclohexyl chloride by means of activated vegetable or animal carbon. In the Russian process, yields of cyclohexene up to 92.3% are said to be obtainable.

Regarding the action of nitric acid on cyclohexene, Markownikoff (Ann. 302, 1898, 28) states that "fuming acid reacts violently with cyclohexene. If the naphthylene is added drop by drop to the nitric acid, it will oxidise explosively with the copious generation of nitrogen dioxide, which enters into combination (crystallisable as needles) with the naphthylene passing through. After heating for several hours in sealed tubes at 100°C with an excess of nitric acid and the subsequent complete evaporation of the acid, very little adipic acid, in the main only a syrupy substance, is obtained, which is readily soluble in ether and water and has a melting point of 137 to 139°."

Before commencing the quantitative examination of the oxidation of cyclohexene, a few test tube experiments showed the qualitative behaviour of the olefin with nitric acid at various temperatures and in different concentrations. It was found that 40% boiling nitric acid does not readily attack cyclohexene. 65% acid has to be heated to 70-80° before the reaction starts. With 62% HNO_3 a preheating to 55-60 degrees is sufficient. The oxidation reaction showed the following process in the test tube: Into the 62% HNO_3, which was heated to 60°, a few drops of cyclohexene were added, which coalesced to form a yellow layer on the acid. After a short time, a few gas bubbles began to rise from the surfaces of contact acid/hydrocarbon, and the C_6H_{10} turned an intense green. The generation of gas became intensified and suddenly large quantities of nitrogen dioxide were given off, when the green layer gradually disappeared. After concentrating and cooling the nitric acid solution, some adipic acid separated out. Furthermore, the occurrence of yellowish-brown drops of oil was frequently observed; at 0° these solidified to form a brown, not readily crystallising mass, which became liquid again at room temperature.

Quantitative experiments.

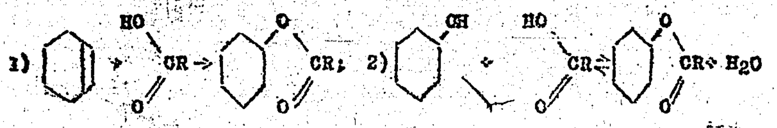
In the following quantitative oxidation experiments, to 1 mol cyclohexene, 10 mols 62% nitric acid were used. In the stirring apparatus already described, 184.6 gr. 62.6% HNO_3, to which 200 mg V_2O_5 had been added, were heated to 70°. 16 gr. cyclohexene were then added slowly during stirring. In order to prevent the reaction from becoming violent, the addition of the 16 gr. C_6H_{10} had to be spread over 5/4 hour. The heat generated by the reaction was neutralised by cooling. When, after stopping the cooling for a time, the temperature in the flask exceeded 80°, there was found in the lower part of the cooler an intense green, oily distillate, which gradually disappeared giving off abundant NO_2. When the reaction was over, and on cooling to 12°, 7.0 gr of 77% adipic acid were obtained. In the mother lye were found 3.0 gr. acid, so that altogether 8.4 gr. pure adipic acid were produced, which corresponds to a yield of 31.4% of the theoretical amount.

In other similar experiments, additives such as MnO_2, $Co(NO_3)_2\,6H_2O$ and $Hg(NO_3)_2\,\frac{1}{2}H_2O$ were used, which, however, showed no noticeable effect on the progress of the reaction. In these experiments, yields of between 30 and 33% of the theoretical amount were obtained. The gaseous oxidation of cyclohexene in the fritted tube described under Cyclohexane, did not bring any improvement in the yield, still 30% only was obtained. However, the quantity of the yellowish, oily by-product was rather more in this type of reaction. No attempt was made to identify this substance, which probably consisted of a nitro or nitroso combination of the cyclohexene. The oil could not be made to enter into further reaction with fresh, 62%, boiling nitric acid.

The direct oxidation of the cyclohexene was now dropped, and investigations were started with the capacity for oxidation of cyclohexene derivatives (Figure 5 of the reaction diagram).

Preparation and oxidation of cyclohexyl esters.

"On heating cyclohexene with organic acids to higher temperatures, the esters of cyclohexanol will be produced". (Brunel. Anal. d. Chim. et de Phys. 8 6. 215).



While the formation of these cyclohexyl esters from cyclohexanol and acid represents a true esterification reaction, since ester and water are produced, when they are obtained from cyclohexene, the acid only attaches itself to the double bond of the olefin, without elimination of water. The esters produced are, however, the same in both cases. If cyclohexyl esters obtained by one or the other method are subjected to saponification in the familiar way, the same products are always produced, viz. cyclohexanol and acid. For this reason, there was justification for the assumption that by the action of nitric acid on the esters for oxidation purposes, cyclohexanol is first of all released, and is then changed into a good yield of adipic acid.

To decide this problem, the addition compound of acetic acid with cyclohexene, cyclohexyl acetate, was used. To simplify the method of preparation, the ester was merely prepared from cyclohexanol and acetic anhydride. The crude product was rectified, BP_{17} : 64-65°C.

Oxidation of the cyclohexyl acetate.

Into 447 gr. 62% HNO_3, mixed with a little V_2O_5, 62.5 gr. pure cyclohexyl acetate were dropped at 75°. The reaction at once set in and showed development agreeing with the oxidation of anol. After cooling to 12° and filtering, a pure white adipic acid was obtained. 56.22 gr. adipic acid = 87.6% of the theoretical amount. This excellent result was able to to confirmed in several experiments so that the fundamental question as to whether cyclohexyl ester can be oxidised equally as well as cyclohexanol, was thereby answered. The next task was to test the manufacturing processes of cyclohexylesters, as given in technical literature, and improve them so that satisfactory yields can be attained with some reliability.

Experiments for preparing various cyclohexyl esters.

The method indicated by Brunel (l.c.) was at once discarded, as it produced too small yields and has been surpassed by more recent literary references. Brunel heated organic acids, e.g. acetic acid, together with cyclohexene for 48 hours to 180-230°. Only very small amounts of the corresponding esters were formed "less than on thirtieth of the theoretical quantities".. On the other hand, the method published in the Berichten 64 (1931) 2104, by Friese, gives a yield of 89.9% of the theoreticalamount of cyclohexyl acetate. Further research with this method made it possible to obtain yields of 95.6% of the theoretical amount.

"To a solution of 16.4 gr. cyclohexene and 75 gr. iced acetic were added 12 ccm sulphuric acid, when only slight heating took place. After standing overnight, it was warmed for 30 minutes on the boiling waterbath, the reaction solution was poured into 150 cc. iced water and extracted with ether, the etherial extract was purged of acid components by a solution of sodium carbonate, and the residue was fractionated after the ether had been evaporated. First of all at 82-84°, 5.5 gr unchanged original material is obtained, while the main fraction (25.5 gr) boils between 169 and 171° at 720 mm".

This method was now varied in a number of experiments as regards sulphuric acid concentration, reaction temperature and the sequence of adding the substances. Also, other catalysts, such as $H_3\ PO_4$, fuming hydrochloric acid, gaseous HCl, trichloroacetic acid, $ZnCl_2$ and 70% perchloric acid were used. All these catalysts were found to be completely unserviceable and only sulphuric acid, in the form of the 98% acid alone, produced good results.

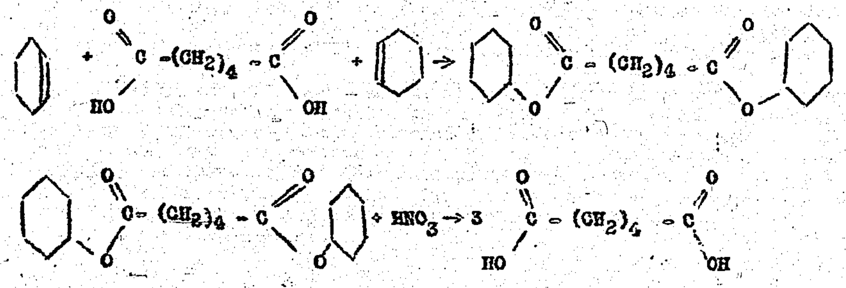
In Vol. I of the "Chemie der Petroleum-Kohlenwasserstoffe" by Ellis (1937), page 331, the assumption is voiced that the esterification of cyclohexene takes place through the sulphuric acid half ester. The total picture of the many different esterification experiments in our laboratory entirely confirmed this assumption. The deductions made from this fact will be still more clearly seen from the following chapter, which deals with the hydration of cyclohexene.

As already stated, sulphuric acid was found to be the only serviceable catalyst, but it had to be used in the form of concentrated acid for the esterification or addition of organic acids. Whereas with 98% H_2SO_4, yields of 89-93% were obtained, with 80% H_2SO_4 the yield dropped to 60.6% and with 60% acid to ~50%. With the additional amount of water corresponding to the rising dilution of the sulphuric acid, the percentage of unchanged cyclohexene proceeded on parallel lines. Furthermore, the necessity was able to be confirmed of the excess of iced acetic over and above the quantity required in theory, as Friese also indicated.

The oxidation of cyclohexyl acetate with nitric acid, as described above, produced a perfectly satisfactory result as regards the adipic acid yield, but certain faults were found in applying the method on a technical scale: 1) The treatment of the waste acid for re-use of the nitric acid and the separation of the acetic acid is difficult and 2) the necessity for using 98% sulphuric acid makes the process an expensive one. During the process of esterification, the sulphuric acid is diluted to 15%, and had then to be concentrated again to 98%.

In order to obviate these difficulties, an attempt was made to start off with the dicyclohexyl ester of adipic acid. In the oxidation of this product, only anitric acid adipic acid solution was to be expected. One part, therefore, of the final product produced by the method is used as an aid to the reaction, no extraneous acids need be used and there is therefore no necessity to recover these again by secondary processes.

The first thing to be found was whether the oxidation of dicyclohexyl adipate with nitric acid could be carried out equally as well as that of cyclohexyl acetate. From one mol of ester, in theory three mols of adipic acid were to be expected in accordance with the reaction equations:-



(Mol. Wt. 310)

40 gr. pure, distilled dicyclohexyl ester of the adipic acid were made from cyclohexanol and adipic acid with 211 gr. 62% HNO_3 (molar ratio 1 : 8) at 70°.

Obtained: 49.02 gr. adipic acid, which after crystallising once from water had a melting point of 150°.

Yield: 87% of the theoretical amount.

Experiments for preparing cyclohexyl adipic acid esters.

It was ascertained in preliminary experiments that without the help of sulphuric acid, the addition of adipic acid to cyclohexenes, even with a long period of reaction, can be secured neither at room temperature nor even at higher temperatures.

Further experiments were undertaken by means of the experimental conditions (which were found to be satisfactory in the cyclohexene-iced acetic process), using sulphuric acid as catalyst. 70 gr. adipic acid, finely ground in an agate mortar were suspended in 30 gr. 98% H_2SO_4, and to this suspension were added, stirring well, 70 gr. cyclohexene. The mixture was then stirred for 22 Hours at 80°C and then allowed to cool, the unchanged adipic acid was filtered off and the filtrate poured into iced water. After extracting the aqueous layer, with ether the ethereal solution was dried with $MgSO_4$ and the ether together with the unchanged cyclohexene distilled off. There was obtained in this way a dark-coloured crude ester residue of 80.0 gr, consisting of cyclohexene polymerisate and dicyclohexyl adipate. In order to ascertain the ester content, the crude ester residues produced in the many esterification experiments were not distilled in a vacuum; instead, preference was given to the very much simpler determination of the oxidation yield. An aliquot part of the crude ester was oxidised with 62% nitric acid, the quantity of adipic acid already placed in the ester was deducted from the adipic acid obtained, and from the residual quantity of acid, the yield was calculated in relation to the cyclohexene used for esterification.

The aforementioned esterification experiment thus produced a yield of 25% of theory, i.e. if the oxidation yield is estimated at 87%, only 29% of the cyclohexene used passed into the ester, 10% was not altered and 61% was polymerised. In the many experiments that followed, the sulphuric acid concentration, the reaction temperature and the sequence of adding the substances were varied. The adipic acid yields thus obtained, in relation to the cyclohexene employed, in the most favourable case only amounted to 42% of the theoretical amount. The H_2SO_4 concentration used was 54%, the reaction temperature 78-80° and the duration of stirring 15 hours. The addition of $AgNO_3$ or Ag_2SO_4 as catalysts, as normally used successfully in esterification, afforded no improvement.

Finally, attempts were made to attach cyclohexene to adipic acid under pressure, using solid catalysts, such as 80% phosphoric acid on asbestos or $ZnHPO_4$, the reaction being carried out in the stirrer autoclave at 180°C and 7-8 atm. excess pressure. The yields thus obtained were, however, only 10% and less, so that the experiments were suspended. As a final possibility of obtaining adipic acids from cyclohexane, experiments were conducted for making cyclohexene into cyclohexanol by hydration, Figure 6 of the reaction diagram.

Experiments for preparing cyclohexanol by hydrating cyclohexene.

The industrial manufacture of cyclohexanol is usually carried out by hydrogenating carbolic acid over nickel contacts. The further possibility, of attaching water to cyclohexene to make cyclohexanol, has indeed been described in patent literature, but the methods concerned have not yet found a practical application.

Thereason for this may be sought in the maximum yields of only 65-75% of the theoretical amount obtained. With the familiar addition of water to olefins, by the action of sulphuric acid of a definite concentration, the use of complex heavy metal compounds of the observance of certain temperatures are given as the characteristics on which the patents are founded. An examination of these patents in a number of experiments, yields of only 60 to at most 65 per cent of the theoretical amount were obtained.

The difficulty of the problem to be solved, the polymarisation of the cyclohexene being restrained as far as possible, consisted in finding conditions for the reaction in which the hydration of the cyclohexene was not impaired by the reaction of the separation of water from the cyclohexanol formed; with concentrated sulphuric acid or some other dehydrating agent cyclohexene can very easily be obtained from cyclohexanol. I t was therefore to be assumed that a temperature and concentration zone must exist within narrow limits, wherein the hydrating reaction predominates.

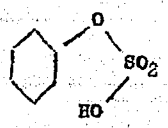
The experimental arrangement and method of operation was as follows:

Into a round flask fitted with ground stirrer, thermometer, dropping funnel and reflux condenser was placed a certain quantity of sulphuric acid of known concentration; the acid was well stirred and a weighed out amount of cyclohexene was slowly dropped in through the dropping funnel. After the absorption of the first drops of cyclohexene, the acid acquired a red colour which gradually became more intense, finally turning brown and even black, fairly rapidly according to the conditions of the experiment. At the same time the contents of the flask heated up considerably, and had to be cooled in order to keep to a definite temperature of reaction. At temperatures of over 60°C, the mass became considerably darker in colour and, as found out subsequently, the polymerisation of the cyclohexesthereby attained a higher figure that a low temperatures. The speed of the dark discoloration as well as its intensity served as a visual indication for the polymerisation of the cyclohexene and therefore for evaluating an experiment, while it was still in progress.

When the cyclohexene had all been dropped in, the stirring of the reaction product, which had now become dark and viscous, was continued for a while at room temperature; the mass was then stirred and slowly poured into a determined amount of iced water and subjected to steam distillation. Cyclohexanol, water and unchanged cyclohexene were then distilled off. In the residue was an oily, dark-coloured cyclohexene polymiserate layer, which floated on the diluted sulphuric acid and on cooling solidified to form a viscous rubber-like mass.

From the distillate there was separated off in the separatory funnel the aqueous distillate, which was extracted separately with ether. After purifying this ethereal extract with the cyclohexanol cyclohexene layer, the whole solution was fractionated in the Widmer column.

The first experiments determined first of all the optimum sulphuric acid concentration. It was found that relatively good yields were only obtained by the use of 80% H_2SO_4. Stronger concentrations brought about more advanced polymerisation and with concentrations below 75%, the percentage of unchanged cyclohexene was greater. As regards the quantity of 80% H_2SO_4 to be used, it was found that for forming the H_2SO_4- half ester



the amount theoretically required was sufficient.

Under these conditions the following mean value was obtained: anol yield ~50%, unchanged C_6H_{10} ~20% and polymerisation loss ~30%.

In order to find out the effect of steam distillation on the formation of anol, a few distillations were carried out under reduced pressure, e.g. at 630 mm Hg and 60°C. The conversion of the cyclohexene thus was reduced to 30%. To all appearances, the temperature of 60° was insufficient to decompose the half ester into cyclohexanol and dilute sulphuric acid. Since the formation of ester takes place with considerable generation of heat, the reaction of splitting the ester must be an endothermal reaction. To find out the requisite temperature, the half ester was heated with a sufficient quantity of water to only 60° and 80° C, extracted with ether and then the ethereal solution was fractionated. Only 20-30% of the cyclohexene was thus converted into anol. In the same way direct distillation of the reaction product, diluted with water, produced very poor yields, as in this case the sulphuric acid had a disintegrating effect on the organic substance, large amounts of SO_2 were given off and the solution acquired a greenish-black colour. This showed that steam distillation is absolutely essential for the complete decomposition of the ester.

The following steam distillations were again carried out under atmospheric pressure, and the steam was superheated. The quantity of anol formed now reached the previous level of 60-65%, while the polymerisation loss was diminished, although it still amounted to ~20% of the cyclohexene used.

The results previously obtained pointed to the fact that the cause of the cyclohexene losses, or for the poor conversion to anol, was not to be sought in the steam distillation process, as possibly the retrograde reaction of the splitting off of the water from the anol thus formed occurred through the action of the sulphuric acid and the high temperature, but rather that the conditions prevailing in the preparation of the half - ester were of decisive importance.

In order to ascertain the effect of temperature on the polymerisation of cyclohexene, in some experiments the half ester was prepared at 0° and -15°C. Even at these low temperatures, the solution was discoloured at the same rate as at higher temperatures. At the same time it was noticed that the rate at which the cyclohexene was absorbed by the sulphuric acid, dropped considerably, so that longer periods were required for conversion.

The approximate dependence of polymerisation and anol formation on temperature will be seen from the accompanying table. According to the latter, the favourable temperature range appears to be 35-45°C.

The polymerisation loss increased correspondingly as the temperature of the reaction rose above 45°, while below 45° it was fairly constant.

The amount of unchanged cyclohexene, on the other hand, increased with falling temperature.

From this it appeared that the temperature was not the only deciding factor in the polymerisation of cyclohexene. Attempts were therefore made, by altering the physical conditions, to influence polymerisation in the preparation of the half ester itself. By dint of intensive stirring, a reduction of ~5% in the polmerisation loss could be obtained. By adding emulgents such as mepasine sulpho acid etc, attempts were made to produce a sulphuric acid-cyclohexene emulsion. The poor stability of the emulsion first produced, brought about by the 80% acid and the increased temperature, prevented the desired effect from being obtained. On the other hand, if a good emulsion was produced, consisting of cyclohexene + emulgent and a small amount of water, and then dropped into the required amount of concentracted sulphuric acid for forming the half ester, the emulsion was preserved for a time, the weaker polymerisation made itself noticeable by a lighter colour of the reaction product, and the results achieved in this way are best illustrated by the experiment described below:

80 gr. cyclohexene were treated with 1 ccm mepasine sulpho acid; to this solution were added, stirring well, 30 ccm water, whereby a white emulsion was produced. Within 1 hour 100 gr. conc. sulphuric acid were then dropped in, the reaction product was stirred for a further ½ hour and allowed to stand overnight. Next morning, the reddish-brown solution was poured on to 300 gr ice and distilled with superheated steam. After separating the aqueous condensate, the latter was extracted with ether in the separating funnel and, after drying with $MgSO_4$ the ethereal solution was fractionated.

The cyclohexanol thus produced was combined with the anol made by the fractional distillation of the hydrocarbon layer, and then weighed. The first runnings obtained at 83° consisted of unchanged cyclohexene.

Definitions.

1. Conversion = 100% - % unchanged cyclohexene.
2. Anol yield = anol formation in % of cyclohexene employed.
3. Anol formation = % anol from converted cyclohexene.
4. Polmerisation = conversion - anol yield.

There were obtained:

53.6 gr anol and 22.0 gr cyclohexene = 27.5% unchanged C_6H_{10}.

The conversion thus amounts to 72.5% i.e. 58.0 gr. C_6H_{10} converted, which should theoretically give 70.8 gr. anol; since only 53.6 gr anol were obtained, the formation of anol is 75.7%.

The total amount of 80 gr. cyclohexene used give in theory 97.6 gr. anol.

The anol yield is therefore 55%.

The loss caused by polymerisation is thus calculated from the difference between conversion and anol yield:

Conversion : 72.5 %
- anol yield 55.0%
17.5% polymerisation loss

Such a method, viz the splitting up of the requisite 80% H_2SO_4 into 98% H_2SO_4 and water, which is required for preparing the emulsion, involved however the serious drawback that the sulphuric acid, diluted to about 25-30% after steam distillation, had to be concentrated, not to 80% but to 98%. This signified a very much greater expenditure of heat.

On this account, the following experiments were conducted with 80% acid without emulgent, when, in lieu of the emulgent, an aliphatic or aromatic solvent that is proof against sulphuric acid, was used. The object of this was to make the cyclohexene react with the sulphuric acid in dilute form.

As will be seen from the reaction diagram No. 6, for obtaining cyclohexene, cyclohexane is required as an intermediate product. As it is an advantage to pursue the chlorination of the cyclohexane only as far as a diluted cyclohexyl chloride, in order to avoid the occurrence of highly chlorinated products, by fractional distillation a cyclohexyl chloride-cyclohexane solution of any desired concentration can be produced which, after parting with the hydrogen chloride, furnishes a solution of cyclohexene in cyclohexane of the same or similar solution.

It was therefore an obvious conclusion to use cyclohexane as a diluent. Cyclohexane was found to be suitable for this purpose, in contrast to toluol, xylol, benzene and gasoline, as it does not engage in any reaction with sulphuric acid.

The following experiments were carried out in such a way that the cyclohexene-cyclohexane solution (to be referred to as C.C. sol. for short) in various concentrations was placed in a cylindrical vessel fitted with a stirrer and heated to at least 30°C; then the amount of 80% sulphuric acid required theoretically was added drop by drop, stirring vigorously. The formation of half-ester took place with the generation of considerable heat, and the reaction product acquired a brownish colour, becoming viscous. When all the sulphuric acid had been added, stirring was continued for a while.

When C.C. solutions of $>70\%$ C_6H_{10} in C_6H_{12} were used, the reaction product was a stable, viscous emulsion; with concentrations of $<70\%$, on completion of stirring the C.C. layer was separated. Both layers were poured into iced water and distilled with superheated steam. The subsequent treatment was precisely the same as described above. With steam distillation in the laboratory, about 10-12 times the volume of anol accumulated in aqueous condensate. By extraction with ether, on an average 12% of the total anol formed was obtained from the aqueous condensate.

As the boiling point of cyclohexane (Kp 80°) and cyclohexene (Kp 82°) only differ by 2°, in fractionating the C.C. layer, a fraction was obtained between 75 and 82°, containing some water, cyclohexane and the unchanged cyclohexene. The latter was determined by titrating with a solution of potassium bromate.

Experiments to account for the esterification reaction.

In the various experiments following, the temperature of the reaction and the degree of dilution of the hydrocarbon solution were varied. The results may be seen from the accompanying tables. It was found that here again the experience previously gained was confirmed, namely that the reaction temperature must be between 30 and 40° in order to obtain a sufficiently rapid and complete reaction with the sulphuric acid.

At lower temperatures the amount of unchanged cyclohexene increases, while at temperature over 40°, polymerisation comes to the fore. Up to 35° the latter has a fairly constant value, so that the process of forming the half-ester at lower temperatures and correspondingly longer times of conversion affords no advantage.

Regarding the most favourable concentration of the hydrocarbon solution, it will be seen from the illustration that solutions between 80 and 90% cyclohexene in cyclohexane furnished the best results. The conversion is 78%, the formation of anol 95%. 22% of the cyclohexene used was recovered, while 3% passed into polymerisate.

Dependence of decomposition, Anol yield, polymerisation and Anol formation on concentration of hydrocarbon solution.

Exper. No	% conc. of hydro-carbon Sol.	Non-decomposed C_6H_{10} %	Decompo-sition %	Anol yield	Polymer-isate %	Anol formation %
165	100	7.8	92.2	78.9	13.8	85.6
180 B	89	22.55	77.5	74.8	2.65	96.4
162 a	75.4	16.14	84	77.7	6.16	92.6
160	50	24.25	75.8	66.4	9.35	87.8
176 b	40.6	31	69	62.5	6.5	91.6
153	34	29	71	63.8	7.7	89.3
158	31	26.8	73.3	65.0	8.25	88.8
154 b	11	59.9	40	29.1	11.0	72.6

It was also of interest to ascertain whether, by using more diluted hydrocarbon solutions, which at the end of the reaction with sulphuric acid or half ester solution form two layers, a separation of the residual H.C. layer and mere steam distillation of the half ester layer, involves a reduction in the anol yields. The latter was the case. Thus, for instance, by using a 32% H.C. solution, separation of the residual H.C. layer and mere steam distillation of the half ester solution, the normal conversion of 65% fell to 57%. It was then assumed that a small portion of the cyclohexene might be present as sulphuric acid diester, which should be considerably more soluble in the H.C. layer than, for instance, the half-ester, owing to the absence of a free OH group.

To confirm this assumption, the H.C. solution was rinsed several times with sodium bicarbonate solution to remove the free sulphuric acid and dried with $MgSO_4$. From the sulphur index obtained by combustion analysis, the diester content was secured, and from this again the corresponding amount of cyclohexene or anol was calculated. It was found that with a 33% H.C. sol., after the reaction about 5-6% of the cyclohexene used was present as diester in the residual H.C. layer. On separating the layer before steam distillation, the diester was thus prevented from being saponified, and therefore a decrease in conversion or anol formation of at least 5% must occur.

As already stated, the best yields were obtained with 88-90% H.C. solutions. With concentrations such as these, after the formation of half-ester is complete, an immediate separation of the cyclohexane layer from the half-ester layer does not occur.

In order to determine the conversion, i.e. to what extent the cyclohexene used is converted into half-ester or diester, a half-ester solution made with 89% hydrocarbon solution was shaken up several times with cyclohexane. The cyclohexane solutions obtained were combined and rinsed with sodium bicarbonate solution to remove the free sulphuric acid and the sulphurous acids. Titration with potassium bromate yielded a cyclohexene content corresponding to 2% of the C_6H_{10} solution. Thus 98% was converted into half-ester or diester.

The half-ester solution freed from unchanged cyclohexene was distilled with steam, when 20% of the cyclohexene used was recovered.

The conversion was thus reduced from 98% after the half-ester formation to 78% after saponification.

To explain this phenomenon, two possibilities are conceivable:

1. Retrograde disintegration of the cyclohexyl ester into cyclohexene and sulphuric acid or
2. Water separating action of the sulphuric acid on anol that had already been formed.

In the specimen experiment, a quantity of pure anol, corresponding to conditions in a laboratory steam distillation, was distilled with 27% sulphuric acid and steam. About 5% anol was converted into cyclohexene. In previous experiments, on saponifying the half-ester, four times the amount of cyclohexene, compared with the specimen experiment indeed become free, but it may be assumed that the anol released in statu nascendi is more reactive and submits more easily to the dehydrating action of the sulphuric acid.

In order, during saponification, to prevent the undesired secondary effect of the sulphuric acid released, the half-ester solution diluted with water was mixed, before treating with steam, with NH_3 water, ammonium bicarbonate, potassium acetate or potash lye, with efficient cooling, in such a way that the whole of the acid released was neutralised. However, all the alkaline additives resulted in a reduction of about 30% in the anol yield. On evaporating the solution swollen with steam, in addition to the sulphuric acid-alkali salt, the corresponding alkaline salt of the acid ester was always found; this is not volatile in steam and therefore brings about a reduction in the yield. The addition of neutralising substances was therefore abandoned.

Investigation of solvents in the saponification reaction.

In further saponification experiments the effect of adding solvents to the half-ester solution in the saponification reaction was examined.

The sulphuric acid-half-ester solution was poured into methyl alcohol, ethyl alcohol or normal butyl alcohol, with efficient cooling and stirring. Still with good cooling and stirring, these alcoholic solutions were diluted with iced water, slowly warmed and finally distilled in steam.

The results of the experiments shown in Table 6 show that in this way the retrograde splitting of the cyclohexene may be prevented, but on the other hand increased polymerisation takes place. It is therefore more advantageous to dilute the half-ester solution with water only at a lower temperature and to subject the approximately 65% hydrocarbon solution produced after saponification to further hydration in a second phase.

The following conversions and yields are obtained in the two-stage process:

	Stage 1.	Stage 2.	Stage 3.
Decomposition :	78%	76%	94.75 %
Anol yield :	75%	66.4%	89.6 %
Anol formation:	96.4 %	88 %	94.4 %
Polymerisation:	2.5 %	9.6%	5.1 %

Catalysts.

In view of the well-known good catalytic action of silver salts in normal esterification reactions, a few hydration experiments were carried out with the addition of CH_3COOAg or Ag_2SO_4. In these experiments, however, the addition of silver has no effect on the yield or on the speed of the reaction.

Determination of the sulphuric acid consumption.

After ascertaining the most favourable experimental conditions for preparing cyclohexyl sulphuric acid ester, the question remained open as to whether during the hydration process losses in sulphuric acid occurred and whether the resultant diluted acid could be evaporated without trouble to 80% and re-use for fresh reactions. For this purpose, in many experiments a sulphuric acid balance was established. After diluting the half-ester with the required quantity of water a titrimetric and a gravimetric determinated of H_2SO_4 was carried out. Steam distillation was then carried out and the H_2SO_4 content of the distillation residue determined at the same time. Finally the now roughly 27% H_2SO_4 residue, after separating the polymerisate, was concentrated at 50 mm Hg until the H_2SO_4 had risen to 80%. The evaporation temperatures required with 50 mm Hg were 40° to 135°C. The 80% H_2SO_4 was indeed rather dark in colour, but could be used without difficulty for a hydration reaction. It was found that during the preparation of the half-ester, about 3-4% of the sulphuric acid used was lost in the form of SO_2. The subsequent treatment of the H_2SO_4 proceeded without losses, so that 96% of the H_2SO_4 originally used were available again as 80% acid for a new experiment.

In the oxidation of the esters formed from cyclohexene and organic acids with nitric acid, it must be supposed that in the first reaction there occurs a saponification of the ester to form cyclohexanol and organic acid. In the second stage the cyclohexanol formed is oxidised by nitric acid to form adipic acid.

Direct oxidation of half-ester,

The next step was to apply this possibility of the direct oxidation of the ester, under the saponifying and oxidising action of nitric acid, to the cyclohexyl-sulphuric acid ester. All the experiments in this direction were, however, unsuccessful, as (1) the sulphuric acid released by the saponification of the ester caused the nitrifying action of the nitric acid to be eclipsed by the oxidising action, so that large quantities of nitrated secondary products were obtained and (2) the sulphuric acid released increases the solubility of the adipic acid, so that the isolation of the adipic acid formed is made difficult.

It was also found that in the interest of the yield and of the purity of the adipic acid to be made, the detour represented by steam distillation and separation of the pure anol had to be allowed for.

The yield of about 80% on an average of the converted cyclohexene, which must be regarded as very good compared with the results previously published, make it appear that the hydration process described is the best means for obtaining adipic acid on the basis of "benzol".

Summary.

In part A of the present article, there are described the gas-analytical investigation of the oxidation of cyclohexanol and experiments for obtaining and making alkyl adipic acids in the pure state.

Part B comprises the treatment of the question as to the possibility of obtaining adipic acid on the basis of "benzol".

Cyclohexane and its derivatives are examined in many laboratory experiments as regards their ability for oxidation with nitric acid.

The most suitable substance was finally found to be cyclohexene, for whose conversion into cyclohexanol a hydration process was evolved producing yields of 90% of the theoretical amount.

Typed/COB

2nd April 1946.

M.T.Z. Feb., 1943, pps. 41-46

ENGINE AND PHYSICAL INVESTIGATIONS INTO THE NATURE OF KNOCK

by Dr.Ing.F.A.F. Schmidt, Berlin-Adlershof

Opinions as to the cause of knock in the gasoline engine have for a long time been divided, but the view which is generally shared to-day, that knock is to be attributed to an approximately simultaneous ignition of the unburnt residue of the mixture, has been represented in many papers, some of which date back a considerable time. In this connection mention may be made of the research work of Ricardo(1), Schnauffer(2), Pye(3), Withrow and Boyd(4), Rothrock and Spencer (5), Egerton(6), Broeze (7), Lindner(8) and others. It has also been ascertained that with the knock process, a number of parallels to other ignition processes exist, e.g. to self-ignition with Diesel combustion, and of course ignition delay; for instance, Wilkie(9) has pointed out the regular relationship between cetane and octane number. The reproducible effects on the knocking tendency of the pressure and temperature of the induced mixture also point to a regular connection between the reaction processes and knock processes in engines.

In order to obtain a clear picture of the laws governing the ignition process and to ascertain the factors that determine knock, theoretical investigations and experiments with knock phenomena in the engine, and with ignition phenomena in bombs and other apparatus, were commenced some years ago; some of the results obtained have already been published (10), (11), (12), (13). Similar research work by the writer has shown that both the ignition process in the diesel engine and the knock process in the gasoline engine can be explained by reactions whose speed is proportional to a factor $\frac{e^{b/T}}{p^n}$. (For explanation of symbols, see below). Analysis of knock tests showed that the established laws governing the knock phenomena in an engine in relation to compression, initial temperature and pressure, and ignition timing, for a given fuel with a constant air excess can be expressed by a single equation for the speed of reaction, taken as proportional to a power of the pressure and the reciprocal of an e-function of the inverse value of the temperature, with the same constants for all experiments. For a comparison of the results obtained from measurements of the ignition delay with those from knock measurements, from the equation for the speed of the reaction:

$$\frac{d(B)}{dz} = \frac{p^n d}{e^{b/T}} \qquad (1)$$

was an expression derived for the ignition delay in the gaseious phase, so that it is possible to determine the constants in Equation (1) from the values measured for the ignition delay. The equation thus obtained(14) for the ignition delay z in the gaseous phase(14a) is:

$$z = \frac{e^{b/T_1}}{p^n} a \beta \qquad (2)$$

In Equations (1) and (2) the symbols have the following meanings:

(B) - the molecular concentration of the fuel.
z - time
T_1 - the absolute temperature at the commencement of the ignition delay
p - the pressure at the beginning of the ignition delay
a, b, d and n - values depending on the type of fuel, which in the temperature range under consideration may on the whole be regarded as constant
T - the variable temperature during the ignition delay
β - a correction factor, allowing for any temperature increase that occurs through the reaction during the delay period

In the event of the reaction proceeding with the same heat development in the whole temperature range under consideration for calculating the ignition delay, the value β can also be given a numerical value.

The constants b and n do not, in this case, represent any exactly defined values, but are mean values which can be evaluated as empirical quantities, and no special physical significance can be attached to them(15). In applying these equations, no assumptions can be made as to the course of the reaction in individual cases, especially with regard to time, but the equations characterise the total reaction process, in which it must be assumed that intermediate reactions occur and various reactions are superimposed on each other, i.e. in almost all cases that occur in practice they proceed as chain reactions. The calculation in accordance with this method does not therefore describe the processes during ignition individually. It only enables the result of the ignition process to be computed mathematically.

The application of the above-mentioned relationships presupposes that the velocity of the reactions in the unburnt part, which lead to knock, can be expressed in the entire temperature range under consideration by an equation with the unchanged constants. Actually, the character of the reaction may vary with the pressure and temperature to a very considerable degree, as has been frequently shown(16). In the course of previous evaluations, it has nevertheless been shown that uniform relationships may be assumed and that calculations can be made with a degree of accuracy generally adequate for technical purposes in the experimental range under consideration.

In the case of equation (2), a temperature increase, corresponding to the introduction of the value β is presupposed during the reaction. With the occurrence of chain reactions, however, the possibility exists of accelerating the reaction very considerably without appreciable temperature increase(17). Reactions without heat development must nevertheless be regarded as exceptional with fuels that burn on the whole with great heat development. The assumption that heat is also released as a result of the chain reaction is the more general one. More recent measurements concerning the processes during the ignition delay period have confirmed the correctness of this assumption.

In the interpretation of the knock experiments mentioned, a reaction equation was obtained, which indicated, at the moment when the commencement of knock was apparent from the indicator diagram, a rapid inflammation due to the increase in the speed of the reaction.

A comparison of the constants obtained from the analysis of knock tests in an engine by varying the operating conditions (see equation 1) showed good qualitative agreement with the values obtained from Equation (2) based on ignition delay measurements.

In the mathematical investigation of the knock process in the engine the reaction speeds, and therefore the constants, could naturally only be determined approximately owing to uncertainties in determining the temperatures in the engine and owing to the influence of "wall effect" and the other inaccuracies inherent in running engines. Estimates of the limits of error nevertheless showed that the values thus obtained must be of the correct order of magnitude.

As these errors in comparative engine tests with various types of fuel are always essentially the same, and act in a similar manner, the main interest centres round the relative variations of the constants in changing over to other types of fuel.

The influence of the fuel properties on the effects of pressure and temperature on the speed of reaction, obtained in ignition delay measurements in a compression apparatus was found to be of the same order as in the engine tests.

Particularly valuable were observations on the knock-limit using gasoline with and without the addition of lead tetraethyl. In analysing these tests, the knock-reducing action of the lead tetra ethyl could be allowed for as a first approximation, in accordance with the above theoretical considerations, by an alteration in the value of d in Equation (1).

These favourable results of the analysis methods described(18) gave reason to expect that further investigations would provide means of characterising the ignition behaviour generally, and especially the ignition process during knocking, within a definite range of pressure, temperature and air excess, by means of a few constants.

As the available experimental data were not adequate for this purpose, further and more accurate experiments were conducted. The new investigations aimed also at ascertaining the effect of temperature and pressure on the ignition process.

In order to obtain the constants determining the ignition process in accordance with Equations (1) and (2), ignition delay measurements were carried out both in a bomb with liquid fuel injection and in an apparatus with approximately adiabatically compressed fuel vapour - air mixtures, corresponding to the method first applied by Tizard and Pye(19). From a comparison of the results of these measurements, the effect of the process of mixture formation could be approximately ascertained. Parallel with these experiments, engine tests were conducted, in which the boost pressure and temperature were varied. The index figures obtained from these three series of experiments corresponding to Equations (1) and (2) were ascertained and compared on the most uniform basis possible.

In the adiabatic compression apparatus evolved by my collaborators, M. Scheuermeyer and H. Steigerwald(20), the mixture to be investigated is compressed with the help of a piston actuated by compressed air. With Tizard and Pye this piston was driven by a crank; in an apparatus developed by W. Jost and H. Teichmann, the piston movement is initiated by a falling weight(21). The new apparatus described under(20) produces, with relatively simple construction, particularly short compression times, and thus ensures a very much higher degree of accuracy than the other apparatus described. To reduce wall-effect, the cylinder diameter of 80 mm. was made as great as possible in comparison with the apparatus of Jost and Teichmann, which has a cylinder diameter of 30 to 53 mm.

Fig.1 shows a diagram of the experimental arrangement used. In its upper position the piston, at the end of compression, is braked in a very short distance (about 1/25 of the stroke by brake-rings) and thus arrested in its end position. The experimental arrangement, including the container for preparing the fuel-vapour and air mixture, can be pre-heated by circulating hot oil; furthermore an initial pressure, higher or lower than atmospheric, can be employed. This makes it possible to vary the pressure and temperature within wide limits during compression, and ignition delays may be measured over a large range of pressure and temperature, especially, however, in the range associated with knocking in an engine. It is impossible to vary the compression ratio by inserting different intermediate rings between the cylinder and the cylinder head. The ignition delay is then measured from the pressure diagram given by the quartz indicator, or else with the aid of a photo-cell.

The bomb for measuring the ignition delay, which was constructed by my former collaborator W. Franke and further developed by E. Lonn(22), is shown in Fig.2. As opposed to the hitherto familiar types of experimental apparatus, which work at low temperatures, it is possible to use temperatures up to 1000° abs, and thus to measure ignition delays of the same order of magnitude as in the compression apparatus. In order to get the most uniform possible temperature conditions in the bomb, it was placed in a large furnace. The fuel-injection, which may take place in the gaseous or liquid state, is controlled by mechanical release devices. The ignition process is observed with a photo-cell or by means of pressure measurements. All the processes are recorded by a cathode ray tube.

The following figures show some of the results of the measurements made recently with the experimental arrangements described.

Fig.3 shows three pressure-time diagrams with approximately adiabatic compression, with different compression pressures but at constant compression temperature; Fig.4 shows three diagrams with different compression temperatures and constant compression pressure. In the upper diagram in Fig.3 (compression pressure 10.8 ata), a slower rise of pressure with ignition will be noticed than at the higher compression pressures. This phenomenon is even more clearly apparent in Fig.5, at 7.1 ata compression pressure; this means to say that as the pressure falls the sudden ignition surge, which resembles knocking, gradually gives way to slow combustion.

As already mentioned, it is not certain whether the assumption that the speed of reaction is a definite function of pressure and temperature, is actually a correct one. According to the theory of the chain reaction, the chemical changes in the mixture which take place before the moment of observation, and depend on the pressures and temperatures before that time, may be of decisive influence on the speed of the reaction. The measured pressure change during the period of ignition delay, makes it possible to draw certain inferences with regard to the reaction process. Figs. 3 and 4 enable the conclusion to be formed that the rate of reaction does not in fact depend solely on pressure and temperature, since in this case a slight but gradual transition to combustion could be expected. Certain deviations may be explained by locally different reaction processes in the combustion chamber. According to Zeise(16), a distinction must, if possible, be made, in the engine ignition process, as with observations in tubes, between the slow pre-reaction, which paves the way for the actual spontaneous ignition, and the ignition reaction proper; during the pre-reaction the temperature rise is only slight.

In Fig. 6 the ignition delay values measured in the bomb and in the compression apparatus are compared for a fuel with the addition of lead tetraethyl. The ignition delay values in the bomb apparatus (with injection of liquid fuel) are naturally, owing to the process of mixture-formation preceding the ignition, considerably higher than the ignition delay values in the compression apparatus. Nevertheless, even a casual glance will show that the character of the ignition delay curve is the same in both cases. The magnitude of the effects of pressure and temperature corresponds fairly accurately to the values given in previously published estimations based on experiments with engines. Emphasis should however be laid on the result that, even with a fuel in the gaseous state, the ignition delay and ignition behaviour generally, are decisively influenced by the pressure, and that this is a definite pressure influence, and not the indirect influence of temperature. For investigating the knocking and ignition processes it is of great importance that the effect of pressure ascertained on the basis of these experiments should be obtained as an effect based on the reaction process of the fuel in question. The fuel would be quite differently assessed if it were to be assumed that an indirect temperature influence is chiefly responsible for the effect of pressure on the ignition process. In the experimental results shown, e.g. for the range associated with knock in an engine, a pressure variation of 1 : 2 corresponds to temperature variation of over 100°C. Thus the great effect of pressure on knock is explained mainly by the effect of pressure on the rate of reaction. These findings do not agree with some of the published results and conclusions of other writers in technical literature(23). From these latter investigations it was concluded that the speed of the reaction during knocking depended chiefly on temperature alone, and the effect of the boost pressure on knocking was largely a matter of indirect temperature influence. On the other hand, our investigations have shown that the relationship of the pressure influence to the temperature influence in the reaction process is of decisive importance.

The influencing of the speed of reaction by the addition of lead tetraethyl to the fuel will be seen from Fig. 7, which shows for various compression pressures the ignition delays of a fuel, with and without the addition of lead, as a function of the final compression temperature. These values, measured in the compression apparatus, show that by the addition of lead tetraethyl the ignition delay in this case is increased approximately proportionately. According to the decrease in reaction speed, in the unburnt part of the mixture by the addition of lead tetraethyl, a correspondingly higher boost pressure can be permitted in engine operation. Fig. 8 shows the permissible boost pressure at incipient knock against the boost air temperature, using fuel with and without the addition of lead tetra-ethyl. The dashed curves shown in Fig. 8 are the values (multiplied by a constant factor) for gasoline with lead tetraethyl, this factor being selected so that for one point (air excess ≈ 1.1 ; t_1 = 50°C) there is agreement with the measured value for unleaded gasoline. The dashed curves agree very well with the curves measured for gasoline without the addition of lead.

For combustion in an engine, besides the properties of the fuel, the composition of the gas, especially the effect of the residual gases on the composition, is of some importance in the reaction process occurring in the unburnt part of the mixture. From ignition delay measurements(23) in which the fuel was injected into air with admixtures of nitrogen, oxygen and carbon dioxide, the essential result was that, with mixtures of oxygen and nitrogen, in accordance with theoretical expectations, the ignition delay is not determined by the total pressure, but mainly by the partial pressure of the oxygen, and that with larger additions of carbon dioxide, the ignition delay becomes greater. This result may easily be reconciled with the ideas given above concerning the occurrence of the ignition process, since the rate of reaction depends mainly on the oxygen concentration. Moreover, the influence of the CO_2 admixture, which is relatively small, is comprehensible having regard to the part played by carbon dioxide in the reaction process as a speed-reducing final reaction product.

From the comparative investigations with different fuels, as described above, and the ignition behaviour of the fuels in various apparatus and in the engine, it is proved that with the aid of an index figure b, which is approximately valid for the temperature range in question and represents the effect of temperature on the reaction process at ignition, and an index figure n representing the effect of pressure, and approximately valid for the pressure range in question, and finally a third index figure (z_1), characterising the ignitability at a certain operating condition, the ignition properties of the fuel can be adequately described for all practical purposes. The third index figure mentioned would have to be adjusted to the relevant application of the fuel, e.g. in the case of engine experiments, it would be one referring to the main operating range of the engine, having regard to the temperature and pressure conditions. The tendency to knock can only be shown clearly by an operating factor if in the comparative experiments to be made this same factor is altered, e.g. the compression ratio or the boost air temperature (both of which chiefly influence the mixture temperature at the end of compression). If, however, the temperature, or alternatively, the pressure is very considerably changed, it is no longer possible to represent the results by a figure. In the aforementioned index figures, the dependence of the ignition process on the air excess, or on the oxygen concentration does not arise. The elucidation of the question of how far the influence of the excess air ratio on knock in an engine is due to a direct effect of the composition of the mixture on the speed of the reaction or indirectly to the temperature, is a task for further experiments, which are at present in progress. In the ignition process in the diesel engine, the effect of excess air is only of slight importance, as in ignition of the jet of fuel, the ignition commences mainly in those regions in which the most favourable mixture conditions are present.

SUMMARY

It has been shown how generally valid index figures can be ascertained for the ignition properties of fuels. These index figures were obtained on the basis of a theoretical relationship for the reaction process, from engine measurements, as well as from ignition measurements in apparatus for adiabatic compression, and in a bomb. The result of all these experiments was that the effect of temperature on the reaction process leading to ignition can, in the main, be characterised by an e-function ($e^{b/T}$), and the effect of pressure by a function of the pressure (p^n). Thus the reaction process depends chiefly on the relation between the effects of pressure and temperature. The third index figure is a constant which, according to the use to which the fuel is put, provides data relating to the ignitability of the fuel for a determined state of pressure and temperature, e.g., in engine tests for the main operating range of the engine. Actually the figures for b and n depend to a very large extent on the pressure and temperature range under consideration. Nevertheless, for practical purposes, a sufficient degree of accuracy will be attained using constant values for the range in question. The problem as to the most practical characterisation of the effect of the excess air ratio can only be decided when sufficient experimental results are available. It will also be seen from the experiments that - as may also have been concluded from other published research work - one constant only, such as the cetane or the octane number is not sufficient. A comparison of the very different engine and physical measurements shows good qualitative agreement between the index figures when different fuels are used. The constants obtained from engine tests, bomb tests and tests in the compression apparatus, were of the same order of magnitude, and their relative change when the fuel was altered was in all cases the same. For a good distinction to be made between properties of fuels, three, or to simplify matters, at least two index figures are recommended, one of which may be used for characterising the ratio of the effects of temperature and pressure on the reaction process (instead of the exact characterisation of both forms of effect).

A few comparative results that are so far available for fuels with and without lead tetraethyl in the engine and in the bomb give grounds for expecting that the influence of anti-knock agents can be shown in a very simple manner for estimating purposes by a constant factor in the reaction equation. The properties of the fuel will probably remain essentially the same as regards the dependence on temperature and pressure of the reaction process, but on the whole there will be a reduction in the speed of the reaction. A study of how far a constant value can as a rule be relied on will only be possible when further experiments are available.

References and Footnotes

(1) H. R. Ricardo, Schnelllaufende Verbrennungsmotoren, Springer, Berlin 1932.

(2) K. Schnauffer, Das Klopfen von Zündermotoren, Z. VDI, Vol.75 (1931) p.455, Dieselmaschinen-Sonderheft No.5, Vol.75, p.127, V.D.I.Verlag, Berlin.

(3) D. R. Pye, Die Brennkraftmaschinen. Translated and revised by Wettstädt, Springer, Berlin 1933.

(4) Lloyd Withrow and W. G. Boyd, Following combustion in the gasoline engine by chemical means. Ind. Engng. Chem., Vol.22 (1930), p.945.

(5) A. M. Rothrock and R. C. Spencer, A photographic study of combustion and knock in a spark-ignition engine. NACA-Rep.1938, No.622.

(6) A. C. Egerton, General statement as to existing knowledge on knocking and its prevention. Publ. by The Science of Petroleum (Oxford University Press).

(7) J. J. Broeze, H. van Driel and L. A. Peletier, Betrachtungen über den Klopfvorgang im Ottomotor. Schriften der deutschen Akademie der Luftfahrtforschung, part 9 (1939)

(8) W. Lindner, Die Entzündung und Verbrennung von Gas- und Brennstoff-Dampf-Gemischen. V.D.I.-Verlag, Berlin 1931.

(9) W. Wilke, Untersuchungen am Hesselman-Motor. Brennkrafttechn. Jahrb. Vol.18 (1937).

(10) F.A.F. Schmidt, Beitrag zur theoretischen und experimentellen Untersuchung von Verbrennungsvorgängen im Zünder- und Dieselmotor. Luftfahrtforschung 1937, Vol.14, No.12.

(11) F. A. F. Schmidt, Theoretische Untersuchungen und Versuche über den Zündverzug und den Klopfvorgang. VDI-Forschungsheft 392 (1938).

(12) F. A. F. Schmidt, Untersuchungen über den Zündverzug im Dieselmotor und den Klopfvorgang in Ottomotor. Berichtsheft "Motor und Kraftstoff" des VDI, Berlin, 1939, p.65.

(13) F. A. F. Schmidt, Gegenseitige Beinflussung von Gemischbildung und Zündungsvorgängen im Verbrennungsmotor. Paper read at the 5th public session of the German Academy for Aeronautical Research on 11.5.39 in Berlin: "Physikalische und chemische Vorgänge bei der Verbrennung im Motor", part 9 of the Schriften der deutschen Akademie der Luftfahrtforschung. 1939.

(14) In the paper mentioned under (11), the influence of temperature on the speed of reaction was given by the term $e^{b/T} . \sqrt{T}$. The influence of the e-function preponderates here to such an extent that the influence of $\sqrt{T}$ is of no consequence: the factor $\sqrt{T}$ has therefore been omitted subsequently.

This corresponds approximately to the chemical portion of the ignition delay, if an approximate division of the total ignition delay into a chemical and a physical part is taken into consideration. In this connection, reference should be made to Fig.8 from which the influence of the thermal processes will be seen.

(15) With simplified hypothesis, e.g. on the supposition, which of course does not apply to engine combustion, of a bimolecular reaction, the ignition delay can be calculated theoretically by using molecular data. The number of transformed molecules is proportional to the number of collisions between oxygen and fuel molecules, whose total energy exceeds a determined amount, the activating energy E. From the kinetic theory, we thus have fuel quantity decomposed per unit time and therefore the curve of the gas temperature during the ignition delay. The constants in the equation for the ignition delay are thus mainly given by the activating heat of the reaction and from the molecular data. The activating energy E appears (in the e-function ($e^{E/RT}$; R = gas constant).

(16) H. Zeise, Das physikalisch-chemische Problem der motorischen Zündung von Gasmischen,

II. Selbstzündung und Klopfen. Z. F. Elektrochem. 47 (1941), p. 779/800 and Forsch.-Ing.-Wes., Vol. 13, part 1, p. 43.

(17) O. M. Todes and collaborators, Die Theorie der Wärmeexplosion, Mitt. I: Acta Physicochimica URSS 6, 785 (1936), Mitt. II: Acta Physicochimica URSS, 11, 153 (1939). Mitt III: Acta Physicochimica URSS 14, 27/52 (1941) and Mitt. IV: Acta Physicochemica URSS 14, 53/70 (1941).

(18) Compare Forschungsheft 392, p. 7-13.

(19) H. T. Tizard and D. R. Pye, Phil. Mag. ~~(6)~~, Vol. 44 (1922), pp. 79-121 and (7) Vol. I (1926), p. 1094-1105.

(20) M. Scheuermeyer and H. Steigerwald, Die Messung des Zündverzuges verdichteter Kraftstoff-Luft-Gemische zur Untersuchung der Klopfneigung. To be published shortly in MTZ.

(21) W. Jost, Reaktionskinetische Untersuchungen zum Klopfvorgang I, Ztschr. Elektrochem. 47, 262 (1941); H. Teichmann, Reaktionskinetische Untersuchungen zum Klopfvorgang II, Ztschr. Elektrochem. 47, 297 (1941).

(22) E. Lonn, Zündverzugsmessungen an flüssigen Kraftstoffen für Ottomotoren. Luftfahrtforschung, Vol. 19 (1942) p. 344.

(23) W. Jost, Schriften dtsch. Akad. Luftf.-Forsch., Part 9, Berlin 1939, pp. 133-158; W. Jost. Z. Elektrochem., Vol. 47 (1941) pp. 262-234; W. Jost & H. Teichmann, Naturwiss. Vol. 27 (1939), pp. 318/319.

(24) This index figure may be replaced also by the octane number.

Diagrams

Fig. 1 - Diagram of the DVL apparatus for approximately adiabatic compression of gaseous fuel-air mixtures.

Fig. 2 - Bomb for measuring ignition delays for fuels injected in the liquid state.

Fig. 3 - Pressure-time diagrams for adiabatic compression of gaseous fuel-air mixtures at constant compression temperature and at different compression pressures.

Fig. 4 - Pressure-time diagrams for adiabatic compression of gaseous fuel-air mixtures at constant compression pressure and at different compression temperatures.

Fig. 5 - Pressure-time diagram for adiabatic compression at low compression pressure.

Fig. 6 - Ignition delay in terms of temperature at different pressures, for a leaded fuel.

Fig. 7 - Ignition delays of gasoline with and without lead, in terms of compression temperature at different compression pressures, from measurements in the compression apparatus.

Fig. 8 - Permissible boost pressure at the knock limit in terms of the boost air temperature, for gasoline with and without addition of lead and at different excess air ratios, from engine tests at 2600 r.p.m. and C.R. of 7 : 1.

20th February, 1946.

der sonstigen durch den Motorbetrieb bedingten Ungenauigkeiten nur näherungsweise bestimmt werden. Abschätzungen der Fehlergrenzen zeigten jedoch, daß die so ermittelten Werte in der Größenordnung richtig sein müssen.

Da diese Fehler bei vergleichenden Motorversuchen mit verschiedenen Kraftstoffen jeweils im wesentlichen dieselben sind und sich in ähnlicher Weise auswirken, sind vor allem die relativen Änderungen der Konstanten bei Übergang zu anderen Kraftstoffen von Interesse.

Der Einfluß der Kraftstoffeigenschaften auf die Druck- und Temperaturabhängigkeit der Reaktionsgeschwindigkeit wurde bei den Auswertungen der Zündverzugsmessungen in einer Verdichtungsapparatur in ähnlicher Größe wie bei den Auswertungen der Motorversuche ermittelt.

Sehr aufschlußreich waren Versuche über die Klopfgrenze bei Verwendung von Benzin mit und ohne Zusatz von Bleitetraäthyl. Bei der Auswertung dieser Versuche konnte die klopfmindernde Wirkung des Bleitetraäthyls entsprechend den obenstehenden theoretischen Betrachtungen in erster Näherung durch eine Änderung des Wertes *d* in Gleichung (1) berücksichtigt werden.

Diese günstigen Ergebnisse der beschriebenen Auswertungsmethoden [18]) ließen erwarten, daß durch weitere Untersuchungen die Möglichkeit geschaffen wird, mit wenigen Konstanten für einen bestimmten Bereich des Druckes, der Temperatur und des Luftüberschusses das Zündverhalten ganz allgemein, insbesondere aber den Zündvorgang beim Klopfen, zu kennzeichnen.

Da die vorliegenden Versuchsunterlagen hierfür nicht ausreichten, wurden weitere genauere Versuche durchgeführt. Die neu in Angriff genommenen Untersuchungen hatten auch die genaue Ermittlung des Temperatur- und Druckeinflusses beim Zündungsvorgang zum Ziel.

Zur Ermittlung der für den Zündungsvorgang maßgebenden Konstanten entsprechend Gleichung (1) und (2) wurden Zündverzugsmessungen sowohl in einer Bombe mit flüssig eingespritztem Kraftstoff als auch in einer Apparatur mit annähernd adiabatisch verdichteten Kraftstoffdampf-Luft-Gemischen — entsprechend dem von Tizard und Pye [19]) erstmals verwendeten Verfahren — durchgeführt. Aus dem Vergleich der Ergebnisse dieser Messungen konnte der Einfluß der Gemischbildungsvorgänge annähernd ermittelt werden. Parallel zu diesen Versuchen wurden Motorversuche bei Veränderung des Druckes und der Temperatur der Ladeluft vorgenommen. Die aus den genannten drei Versuchsreihen ermittelten Kennzahlen entsprechend Gleichung (1) und (2) wurden jeweils ermittelt und auf möglichst einheitlicher Basis verglichen.

In der von meinen Mitarbeitern M. Scheuermeyer und H. Steigerwald [20]) entwickelten Apparatur zur adiabatischen Verdichtung wird das zu untersuchende Gemisch mit Hilfe eines durch Druckluft bewegten Kolbens verdichtet. Bei Tizard und Pye wurde der Kolben mittels eines Kurbeltriebes betätigt; in einer von W. Jost und H. Teichmann entwickelten Apparatur wird die Kolbenbewegung durch ein Fallgewicht eingeleitet [21]). Die neue unter [20]) beschriebene Apparatur ergibt bei verhältnismäßig einfachem Aufbau vor allem sehr kurze Verdichtungszeiten und ermöglicht damit eine erheblich höhere Genauigkeit als die erwähnten anderen Apparaturen. Der Zylinderdurchmesser wurde zur Verminderung des Wandeinflusses mit 80 mm Durchmesser möglichst groß gegenüber der Apparatur von Jost und Teichmann, die einen Zylinderdurchmesser von 30 bis 53 mm aufweist, gewählt.

Bild 1 zeigt ein Schema der verwendeten Versuchseinrichtung. In seiner oberen Stellung wird der Kolben am Ende der Verdichtung auf sehr kurzem Weg (etwa $^1/_{50}$ des Hubes) durch Bremsringe abgebremst und sodann in seiner Endlage arretiert. Die Versuchseinrichtung einschließlich dem Behälter für die Aufbereitung des Kraftstoffdampf-Luft-Gemisches kann durch umlaufendes Heizöl vorgewärmt werden; ferner kann ein gegenüber dem atmosphärischen Zustand höherer oder geringerer Anfangsdruck eingestellt werden. Damit ist die Veränderung des Druckes und der Temperatur bei der Verdichtung in weiten Grenzen möglich, und die Zündverzüge können über einen großen Druck- und Temperaturbereich, insbesondere aber in dem Bereich, der für das Klopfen im Motor entscheidend ist, gemessen werden. Die Veränderung des Verdichtungsverhältnisses wird durch Einsetzen verschiedener Zwischenringe zwischen Zylinder und Zylinderkopf ermöglicht. Die Messung des Zündverzuges erfolgt aus dem mit Quarzgeber aufgenommenen Druckverlauf oder auch mit Hilfe einer Photozelle.

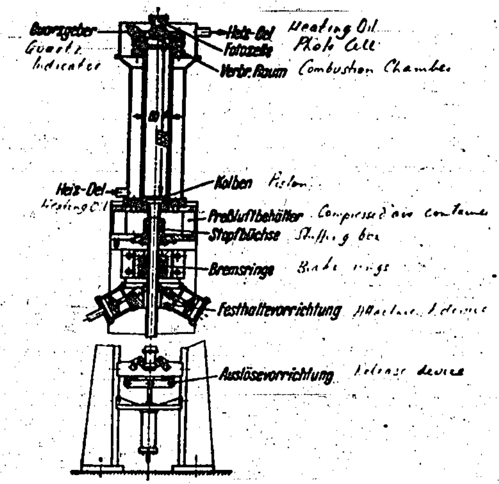


Bild 1. Schema der DVL-Apparatur zur annähernd adiabatischen Verdichtung gasförmiger Kraftstoff-Luft-Gemische

Fig 1 DIAGRAM OF DVL APPARATUS FOR THE APPROXIMATELY ADIABATIC COMPRESSION OF GASEOUS FUEL-AIR MIXTURES

Die Bombe zur Messung des Zündverzuges, die von meinem früheren Mitarbeiter W. Franke gebaut und von E. Lonn [22]) weiterentwickelt wurde, ist in Bild 2 dargestellt. Gegenüber den bisher bekannten Versuchsapparaturen, die mit geringeren Temperaturen arbeiteten, gestattet sie, Temperaturen bis zu 1000° abs. einzustellen und damit Zündverzüge in derselben Größenordnung

---

[18]) Vgl. Forschungsheft 392, S. 7—13.

[19]) *H. T. Tizard* u. *D. R. Pye*, Phil. Mag. (6), Bd. 44 (1922), S. 79—121, ebenda (7), Bd. 1 (1926), S. 1094—1105.

[20]) *M. Scheuermeyer* u. *H. Steigerwald*, Die Messung des Zündverzuges verdichteter Kraftstoff-Luft-Gemische zur Untersuchung der Klopfneigung. Erscheint demnächst in der MTZ.

[21]) *W. Jost*, Reaktionskinetische Untersuchungen zum Klopfvorgang I, Ztschr. Elektrochem. *47*, 262 (1941); *H. Teichmann*, Reaktionskinetische Untersuchungen zum Klopfvorgang II, Ztschr. Elektrochem. *47*, 297 (1941).

[22]) *E. Lonn*, Zündverzugsmessungen an flüssigen Kraftstoffen für Ottomotoren. Luftfahrtforschung, Bd. 19 (1942), S. 344.

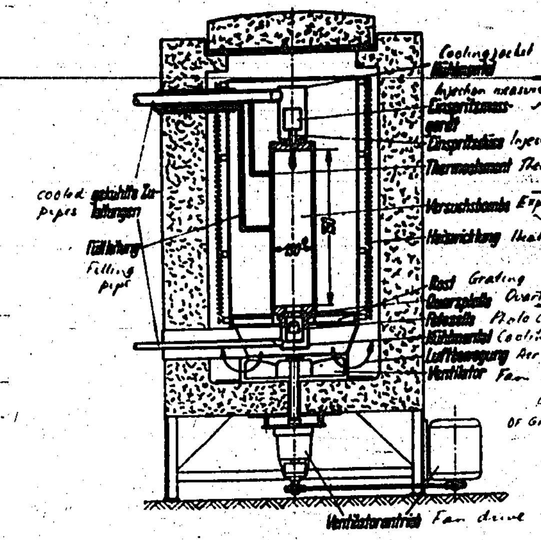


Bild 2. Bombe zur Messung von Zündverzügen flüssig eingespritzter Kraftstoffe

Fig 2 BOMB FOR MEASURING THE IGNITION DELAYS OF INJECTED FLUID FUELS

wie in der Verdichtungsapparatur zu messen. Um einen möglichst gleichmäßigen Temperaturzustand in der Bombe herzustellen, wurde sie in einem großen Heizofen untergebracht. Die Einspritzung des Kraftstoffes, die in gasförmigem oder flüssigem Zustand erfolgen kann, wird durch mechanische Auslösevorrichtungen gesteuert. Der Zündungsvorgang wird mit Photozelle oder Druckmessung verfolgt. Alle Vorgänge werden mit Braunscher Röhre aufgezeichnet.

Die folgenden Bilder zeigen einen Teil der Ergebnisse der in letzter Zeit mit den gezeigten Versuchseinrichtungen durchgeführten Messungen.

Constant final temperature of compression 745 °K

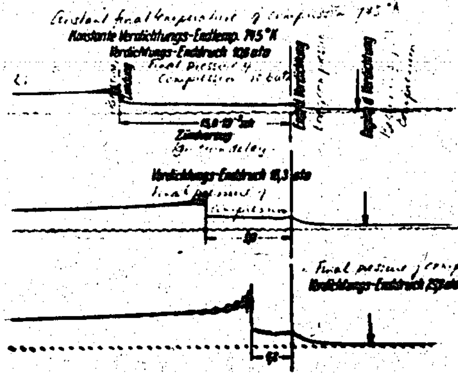


Bild 3. Druck-Zeit-Diagramm bei adiabatischer Verdichtung gasförmiger Kraftstoff-Luftgemische für verschiedenen Verdichtungsenddruck bei konstanter Verdichtungsendtemperatur

Fig 3 PRESSURE-TIME DIAGRAM WITH ADIABATIC COMPRESSION OF GASEOUS FUEL/AIR MIXTURES FOR VARIOUS COMPRESSION END PRESSURES AT CONSTANT COMPRESSION END TEMPERATURES

CONSTANT COMPRESSION END PRESSURE 22.4 ata

Konstanter Verdichtungs-Enddruck 22,4 ata

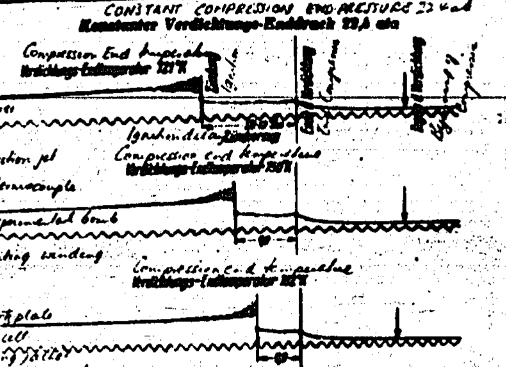


Bild 4. Druck-Zeit-Diagramm bei adiabatischer Verdichtung gasförmiger Kraftstoff-Luft-Gemische für verschiedene Verdichtungsendtemperaturen bei konstantem Verdichtungsenddruck

Fig 4 PRESSURE-TIME DIAGRAM WITH ADIABATIC COMPRESSION OF GASEOUS FUEL AIR MIXTURES FOR VARIOUS COMPRESSION END TEMP

In Bild 3 sind drei Druck-Zeit-Diagramme bei annähernd adiabatischer Verdichtung mit verschiedenem Verdichtungsenddruck bei unveränderter Verdichtungsendtemperatur, in Bild 4 drei Diagramme mit verschiedener Verdichtungsendtemperatur bei konstantem Verdichtungsenddruck wiedergegeben. Im oberen Diagramm in Bild 3 (Verdichtungsenddruck 10,6 ata) ist deutlich ein langsameres Ansteigen des Druckes bei der Zündung zu erkennen als bei den höheren Drücken. Noch deutlicher wird diese Erscheinung in Bild 5 bei 7,1 ata Verdichtungsenddruck, d. h. mit sinkendem Druck geht der plötzliche klopfähnliche Zündeinsatz allmählich in eine langsame Verbrennung über.

CONSTANT COMPRESSION END PRESSURE

Compression End Pressure

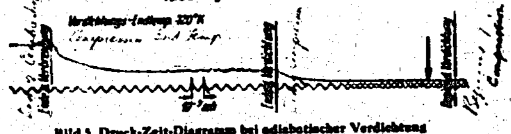


Bild 5. Druck-Zeit-Diagramm bei adiabatischer Verdichtung für geringen Verdichtungsenddruck

FIG 5 PRESSURE TIME DIAGRAM WITH ADIABATIC COMPRESSION FOR LOW COMPRESSION END PRESSURE

Wie schon oben erwähnt, ist es nicht sicher, ob die Annahme, daß die Reaktionsgeschwindigkeit eine eindeutige Funktion von Druck und Temperatur ist, auch tatsächlich zutrifft. Nach der Theorie der Kettenreaktion können die chemischen Umsetzungen im Gemisch, die bereits vor dem betrachteten Zeitpunkt stattfanden und von dem Verlauf von Druck und Temperatur vor dem betrachteten Zeitpunkt abhängen, von entscheidendem Einfluß auf die Reaktionsgeschwindigkeit sein. Der gemessene Verlauf des Druckes während der Zeit des Zündverzuges ermöglicht nun gewisse Rückschlüsse auf den Reaktionsverlauf. Bild 3 und 4 lassen darauf schließen, daß die Reaktionsgeschwindigkeit tatsächlich nicht allein von Druck und Temperatur abhängig ist, da in diesem Fall ein weicher allmählicher Übergang zur Verbrennung zu erwarten ist. Gewisse Abweichungen können allerdings auch mit einem örtlich verschiedenen Reaktionsverlauf im Verbrennungsraum erklärt werden. Nach Zeise [10]) muß möglicherweise beim motorischen Zündvorgang ähnlich wie bei Beobachtungen in Röhren

Fig. 6 Ignition delays of a fuel with the admixture lead tetraethyl, dependent on temperature for various pressures.
A – Ignition delays, measured in the bomb of injected fluid fuel.
B – compression apparatus of gaseous fuel-air mixture

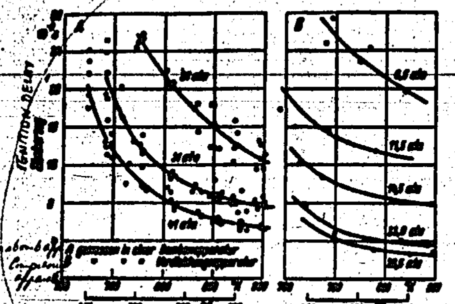


Bild 6. Zündverzüge eines Kraftstoffes mit Zusatz von Bleitetraäthyl, abhängig von der Temperatur für verschiedene Drücke
A in der Bombe gemessene Zündverzüge flüssig eingespritzter Kraftstoffe
B in der Verdichtungsapparatur gemessene Zündverzüge des gasförmigen Kraftstoff-Luft-Gemisches

zwischen der langsam verlaufenden Vorreaktion, die die eigentliche spontane Zündung vorbereitet, und der eigentlichen Zündreaktion unterschieden werden, wobei während der Vorreaktion die Temperatursteigerung nur gering ist.

Die in der Bombe und in der Verdichtungsapparatur gemessenen Zündverzugswerte sind für einen Kraftstoff mit Zusatz von Bleitetraäthyl in Bild 6 miteinander verglichen. Die Zündverzugswerte in der Bombenapparatur (bei Einspritzung von flüssigem Kraftstoff) sind naturgemäß wegen dem der Zündung vorangehenden Gemischbildungsvorgang erheblich höher als die Zündverzugswerte in der Verdichtungsapparatur. Jedoch zeigt schon eine oberflächliche Betrachtung, daß der Charakter der Zündverzugskurven in beiden Fällen derselbe ist. Die Größe der Druck- und Temperaturabhängigkeit entspricht ziemlich genau den Werten, die bei den schon früher veröffentlichten überschlägig ermittelten Berechnungen aus motorischen Untersuchungen gewonnen wurden. Als wesentliches Ergebnis ist hervorzuheben, daß auch beim Kraftstoff in gasförmigem Zustand der Zündverzug und überhaupt das Zündverhalten entscheidend vom Druck beeinflußt wird und daß es sich bei dem sehr starken Druckeinfluß nicht um einen indirekten Einfluß der Temperatur handelt. Für die Erforschung des Klopf- und Zündungsvorganges ist es von großer Bedeutung, daß die auf Grund dieser Untersuchungen festgestellte Druckabhängigkeit als ein Einfluß ermittelt ist, der im Reaktionsvorgang des betreffenden Kraftstoffes begründet ist. Die Beurteilung des Kraftstoffes würde sich ganz anders ergeben, wenn man annehmen würde, daß für die Druckabhängigkeit des Zündungsvorganges im wesentlichen ein indirekter Temperatureinfluß entscheidend ist. Bei den dargestellten Versuchsergebnissen entspricht z. B. für den Bereich, der beim Klopfen im Motor in Betracht kommt, einer Druckänderung von 1 : 2 eine Temperaturänderung von über 100 °C. Damit ist die starke Druckabhängigkeit des Klopfens im wesentlichen durch die Druckabhängigkeit der Reaktionsgeschwindigkeit erklärt. Die Feststellungen stimmen mit einigen in der Literatur bekanntgegebenen[23]) Ergebnissen und Schlußfolgerungen anderer Verfasser nicht überein. Aus diesen Untersuchungen wurde geschlossen, daß die Reaktionsgeschwindigkeit beim Klopfen empfindlich nur von der Temperatur abhänge und der Einfluß des Ladedruckes auf das Klopfen ein überwiegend indirekter Temperatureinfluß sei. Demgegenüber ergibt sich aus unseren Untersuchungen, daß das Verhältnis des Druckeinflusses gegenüber dem Temperatureinfluß beim Reaktionsvorgang von entscheidender Bedeutung ist.

Die Beeinflussung der Reaktionsgeschwindigkeit durch Zusatz von Bleitetraäthyl zum Kraftstoff ist aus Bild 7 ersichtlich, in dem für verschiedene Verdichtungsenddrücke die Zündverzüge eines Kraftstoffes mit und ohne Bleizusatz abhängig von der Verdichtungsendtemperatur dargestellt sind. Diese in der Verdichtungsapparatur gemessenen Werte zeigen, daß durch den Zusatz von Bleitetraäthyl der Zündverzug in diesem Falle jeweils annähernd proportional vergrößert wird. Entsprechend der Verringerung der Reaktionsgeschwindigkeit im unverbrannten Teil des Gemisches durch Zusatz von Bleitetraäthyl kann beim Motorbetrieb ein entsprechend höherer Ladedruck zugelassen werden. In Bild 8 ist der sich aus Motorversuchen ergebende zulässige Ladedruck an der Klopfgrenze über der Ladelufttemperatur bei Verwen-

---

[23]) *W. Jost*, Schriften dtsch. Akad. Luftf.-Forsch., Heft 9, Berlin 1939, S. 133—156; *W. Jost*, Z. Elektrochem., Bd. 47 (1941), S. 262—264; *W. Jost* u. *H. Teichmann*, Naturwiss., Bd. 27 (1939), S. 318/319.

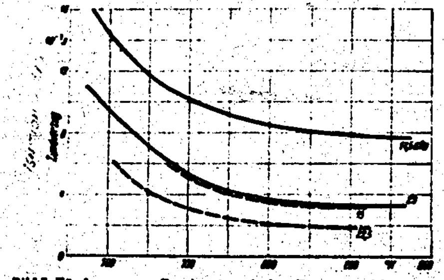


Bild 7. Zündverzug von Benzin mit und ohne Zusatz von Bleitetraäthyl abhängig von der Verdichtungsendtemperatur für verschiedene Verdichtungsenddrücke nach Messungen in einer Verdichtungsapparatur
——— Benzin mit Bleitetraäthyl
– – – Benzin ohne Bleitetraäthyl

Fig 7. IGNITION DELAY OF PETROL WITH AND WITHOUT ADMIXTURE OF LEAD TETRAETHYL, DEPENDENT ON COMPRESSION END TEMPERATURE FOR VARIOUS COMPRESSION END PRESSURES, FROM MEASUREMENTS IN A COMPRESSION APPARATUS
——— PETROL WITHOUT LEAD TETRAETHYL
– – – " WITH

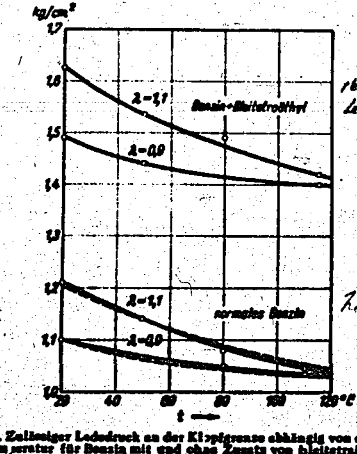


Bild 8. Zulässiger Ladedruck an der Klopfgrenze abhängig von der Ladelufttemperatur für Benzin mit und ohne Zusatz von Bleitetraäthyl und für verschiedene Luftüberschußzahlen nach Versuchen am Motor mit der Drehzahl n = 2600 U/min und einem Verdichtungsverhältnis ε = 7

Fig 8. ADMISSIBLE CHARGING PRESSURE AT THE KNOCK LIMIT DEPENDENT ON THE TEMPERATURE OF THE CHARGING AIR FOR PETROL WITH AND WITHOUT ADMIXTURE OF LEAD TETRAETHYL AND FOR VARIOUS AIR EXCESS FIGURES FROM EXPERIMENTS ON ENGINE WITH SPEED n = 2600 r.p.m. and a COMPRESSION RATIO ε : 7

German Organisation of Fuel Research and Development

A. von Philippovich

It is difficult to give an exact plan of the German organisation in this direction, as a completely comprehensive system was not achieved. In the attached diagram an attempt has been made to include all the different institutions dealing with fuels and lubricants, but it must be remembered that only those fully underlined were important. I am not competent to discuss all the different changes which occurred and the connections between the various institutions; I can only discuss the organisation as a whole, as I saw it.

Most effective was the planning by the Air Ministry in conjunction with the Supreme Command of the Army, as they co-operated to a certain extent in planning the supply and the qualities of fuel and lubricants. Research work was primarily conducted by the Forschungsabteilung of the Technisches Amt, but, at a later date, was given over to the Forschungsfuhrung, which was to have been the supreme authority on all research work done in connection with aircraft. As a matter of fact that was the case for aerodynamics and matters connected therewith, whereas work on lubricants and fuels was mostly done by the Reichamt fur Wirtschaftsausbau, which had close connections with the I.G., and also ran institutes of its own at the various T.H. and Universities.

The Technische Akademie der Luftfahrtforschung replaced a Luftkriegsakademie, for which there were too few participants in the courses; the work covered experiments with safety fuels as well as combustion with jets.

The Akademie der Luftfahrtforschung was a purely scientific corporation which was largely identical in personnel with the Lilienthalgesellschaft, which incorporated more members and had various Fachgruppen to discuss problems of the day, and to co-ordinate views on them.

The OKH developed through its Heereswaffenamt the supply and quality of its fuels and lubricants, working in co-operation with the firms in the same way as the Air Ministry.

The OKM was not very active in that direction.

Speer (Ruk) worked in co-operation with the Reichswirtschaftsamt, but had no general line of its own.

The Reichsverkehrsministerium was mostly interested in the Reichsbahn and in motor traffic, so that it was first connected with the Reichsforschungsrat, which was later taken over by the Kultusministerium, but played a subordinate part and was latterly, in fact, non-existent.

The Kultusministerium was important because of its direction of T.H.s and Universities and to a certain extent of the other associated institutes, e.g. the Bergakademie Freiburg.

The Kaiser Wilhelmgesellschaft owned the Institute in Muelheim/Ruhr and is interesting for this reason. The society obtained money from the Reich and from industry and had an institution of its own, in the same way as the PTR and the CTR, and had its own VDI activities which it continued independently of the State - at least to a certain extent.

The Innenministerium is only mentioned as the directive of the PTR and the CTR, though it did not influence the work much.

The Wirtschaftsministerium headed the Wirtschaftsgruppen who did no research work at all, but controlled only the qualities of their products, as e.g. the Gruppe Kraftstoff.

-o0o-

Changes of organisation were frequent and not always successful. The development was directed towards giving the Forschungsfuhrung and the Technisches Amt in conjunction with the Reichsamt fur Wirtschaftsausbau the major authority, and certainly with further development there would have been closer co-ordination. As it was, exchange of ideas took place at the different meetings of the Lilienthalgesellschaft, the Reichsamt fur Wirtschaftsausbau and the Air Ministry, and the general trend of research work was directed by the last two organisations.

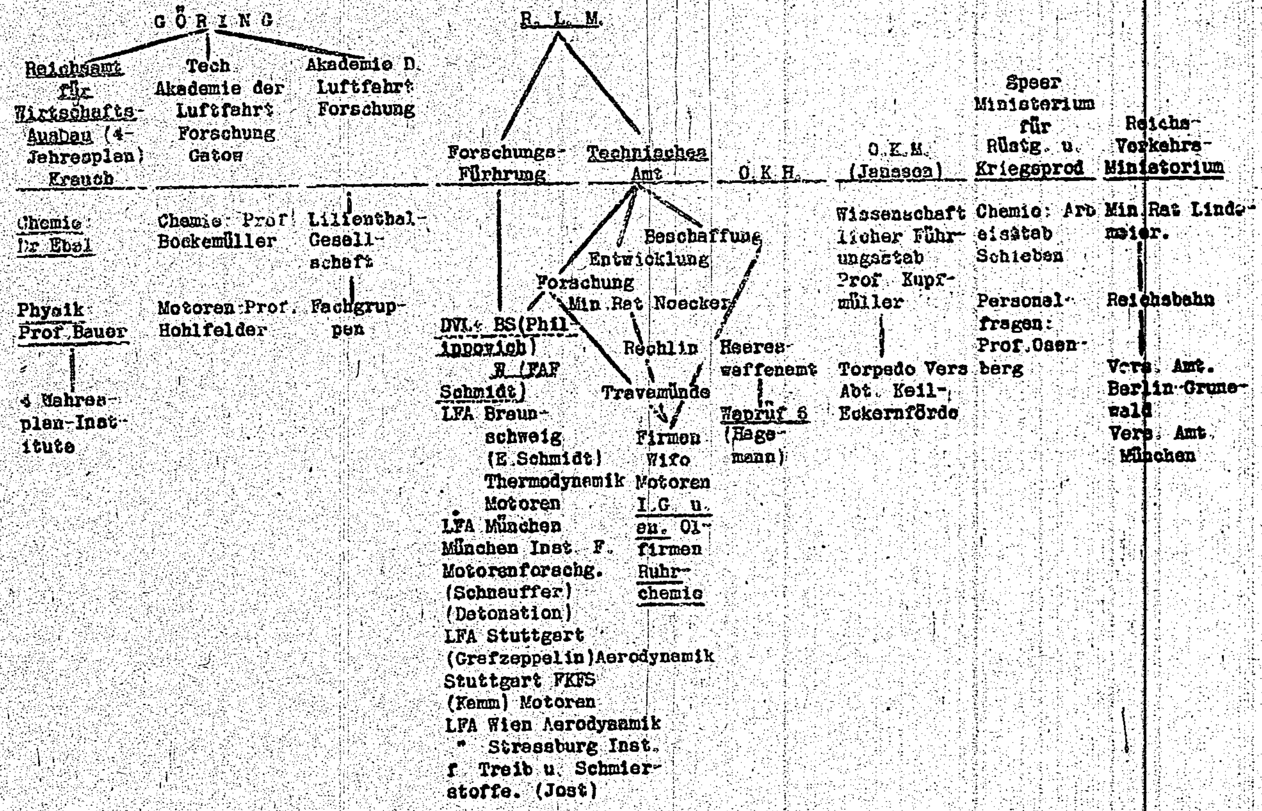
There may be some omissions in the picture given, but a more exact plan of the organisation of work on fuel and lubricants has been delivered by Ministerialrat Noecker to W/Cdr. Cunningham, AI.12, of the Air Ministry, to which reference may be made.

Philippovich.

Typed: JHM
1.3.46.

Kultusministerium (Menzel)	Kaiser Wilhelm Gesellschaft (Menzel)	Innen Ministerium	Wirtschafts Ministerium	V.D.I.
Technische Hochschulen	**K.W.I. Mühlheim**	P.T.R.	Industrierat	**Schmierausschuss**
Universitäten Reichs Inst. f. Erdölforschung	" Breslau	C.T.R	Wirtschaftsgruppe Kraftstoff	
Bergakademie: Freiberg Clausthal			Ges. f. Mineralölforschung	
Reischsforschungsrat				

ORGANISATION D. DEUTSCHEN BETRIEBSTOFFBEARBEITUNG



Copy UNCLASSIFIED

BRITISH INTELLIGENCE OBJECTIVES SUB-COMMITTEE.
32, BRYANSTON SQUARE,
LONDON, W. 1.

C.P.V.A. Report No.9. 25th February, 1946.

Summary of Report
on
The Development of a Method for the preparation of Polyxol Greases

prepared by the Chemical Research and Development Department, Ministry of Supply, Shell Mex House, Strand, W.C.2.

Coal and Mineral Oil Research Institute, Technical School, Berlin,
Eislinger-Fils 8.2.45

Requirements of Services stated to be as follows :-

Air Force - Lubricants for temperature range +50 to -60°C.

Army - Lubricants for optical instruments for temperature range +50 to -40°C as well as thick oil for Ocular-Optik with little change in thickness over same temperature range.

Navy - Specification of Grease containing 0.5% graphite given - Ubbelohde drop point 80°C. Consistency 0.4-0.6 (nach HWA). Torque test at +20°C and -20°C specified.

Greases were produced by oxidation of oil at high temperatures in presence of catalysts by blowing air through. Details of tests using Manganese stearate (0.2%) and resinate are given; other catalysts mentioned are 'Soligene of different types', naphthylamine, p- and o- nitrophenol, pyrogallol and aniline. Oils giving best results are paraffin base and solvent-refined raffinates. Optimum temperatures appear to vary from about 190°C to just over 300°C. Optimum conditions vary for each oil or mixtures of oils used as starting materials.

The chief interest lay in producing greases with good low temperature properties for aircraft instruments. It was found that the limit of low temperature workability of the grease was approximately the same as the setting point of the original oil; this temperature was judged by a practical test in a remote control mechanism. Change in neither rate of air flow nor reaction temperature produced any marked difference in this property. Experiments were therefore made with low viscosity, low setting point spindle oils instead of the motor oils hitherto used. Greases satisfactory down to -40°C were then obtained from Oil AB11 (Rhenania Ossag Mineralölwerke); a limit nearer -50°C was obtained by treating mixtures of this with 'Frischöl'.

Attempts were made to follow the course of the reaction by following the changes in specific gravity, acidity, viscosity, iodine No., mean mol. wt., setting point and carbon, hydrogen, oxygen content.

The greases are claimed to have the following properties: Water insolubility and repellancy. Stability above the drop point. Low vapour pressure even at high temperatures so that use in hot climates does not influence subsequent use at low temperatures. No corrosive ingredients so that they can be used with any metal. No water content and insignificant ash. The drop point and consistency can be controlled to any desired value.

SM(B)6310-(11/2/46)S.R.2.

Research Institute for Lignite and Mineral oil
of the Technical University, Berlin.
Department at Eislingen/Fils

The Development of a method for the manufacture of PX greases

During war-time it is necessary to employ weapons under the most varied conditions. This made it imperative to develop technical lubricants which are relatively unaffected by changed external conditions such as cold and heat.

The different parts of the German Army have stated their requirements somewhat as follows :-

1) The Air Force requires lubricants for the temperature range +50 to -60°C

2) The Army fixed the temperature limits for the greasing of optical instruments at +50 and -40°C; also the grease for ocular optics (Okular-Optik) is required to possess a good packing (calking) effect. This packing property should not be seriously affected within the temperature range +50 to -40°C.

3) The Navy makes the following demands :-

a. Specifications - The fire control grease must be made from a cold-resistant mineral oil. It must not corrode metals, must not contain any inorganic loading apart from 0.5% of graphite and must be resistant to sea and fresh water.

b. Technical data

Spec. Gr. @ 20°C	0.880 to 0.930
Colour	brown-black
Appearance	homogeneous
Drop point	= 100°C after kneading in the kneading machine HWA for 15 to 20 mins. after 200 strokes
Flow point	80°C (min.)
Neutralisation number	to be found
Proportion of graphite	0.5% (according to wick test)
Ash	= 1%
Behaviour in cold	can be stirred (Siemens method) down to -40°C
Stability	less than 2.5% oil separates at 60°C (25 g grease and suiter glass I/G3)
Consistency	0.4 to 0.6 according to HWA method)

c. Technical tests - The movement of friction in a ball bearing # 19 of the E-series according to DIN 615 must not exceed

30 cm gm at +20°C
90 cm gm at -20°C

when the conditions correspond to the Lubrication Directions for Fire Control Instruments (Schmierung et. Schmiervorschrift für Feuer-leitgeräte) at numbers of revolution from 60 to 5000 revs/min.

The Institute developed a process by means of which greases were produced from mineral oils with results that approximate more closely to the demands of the Wehrmacht authorities than those otherwise produced by industry.

The following idea is at the basis of the method of production. If mineral oil fractions are subjected to treatment by oxygen at elevated temperatures, complicated chemical reactions occur, which, depending on the type of the initial oil and on the conditions, lead either to the thickening or to the coking of the oil. If the treatment is sufficiently long, coking always eventually occurs: The oxygen attacks the hydrocarbon molecule at the point which has the lowest bonding strength. This point, according to Criegge, is the C-H bond. The energy of activation necessary to split up the C-C or the C=C bond is considerably higher than that necessary to sever the bond between C and H. According to the modern view the initial step is an addition of O_2 to the hydrocarbon molecule, which is then followed by a reaction chain. In the course of this reaction chain intermediate products such as peroxides, alcohols, ketones, aldehydes and acids are formed. The oxidation process is accompanied by decomposition reactions, the latter being responsible for the fact that the substance obtained at the end consists of oxidation products having molecules of very varied sizes. Depending on the conditions of the reaction the unsaturated fragments formed during the cracking will either tend to crack further or to polymerise. The molecular weight and the viscosity of the products of oxidation will rise or fall if the polymerisation or the cracking are the dominant reactions. If the former predominates one obtains a solid grease-like product, the properties of which are mainly determined by the chemical composition of the initial oil and by the conditions of manufacture.

The best prospects of obtaining good greases are offered by thermally stable oils, e.g. those based on paraffins or solvent raffinates. The type of grease produced - soft, vaseline-like, or hard, tough consistency is determined mainly by the temperature of the process, the quantity of oxygen admitted per unit time, and the added catalyst. The temperature range most favourable for the production of a soft paste-like grease depends on the type of oil and is confined to within narrow limits. The same applies to the quantity of oxygen per unit time. If the most favourable range is either not reached or exceeded, either cracking occurs or hard, asphalt-like substances are formed. The range within which one may vary temperature and oxygen supply are so narrow in some cases, that only tough and hard greases can be obtained from such oils.

The picture is completely changed again in the presence of catalysts. The limits of the most favourable temperature and oxygen supply are displaced. Under certain circumstances there may be a fundamental change in the character of the end-products. A large number of catalysts of the most varied kind have been found to be useful for accelerating or directing the reaction in the manufacture of greases. This is due to the fact that the transformation of oil into fat only occurs after a long chain of reactions. Numerous oxidation promoters and negative oxidation promoters as well as polymerisation catalysts are counted among these catalysts. It is not, however, possible, to say that substances of the type mentioned are favourable in grease production because unde the conditions of grease manufacture many oxidants, antioxidants and polymerisation accelerators also exhibit a strong tendency favouring decomposition.

The following characteristics are typical for the greases (Polyxol greases) produced under the conditions described above:

Drop and Flow-point	controllable within wide limits
Consistency	"
Behaviour against water	completely insoluble, very hydrophobic
Behaviour above the drop point	no decomposition when the drop point is exceeded
Behaviour on storage	stable
Corrosive properties	does not corrode any metal
Water content	nil
Ash content	low

The above-mentioned properties of low "Polyxol greases" are in many respects superior to those of the soap greases.

Greases for aircraft instruments have to be usable down to very low temperatures (ca -60°C) apart from other properties which Polyxol greases possess in any case. A systematic investigation was therefore instituted into the modification of the low temperature characteristics of the Polyxol greases by changing the initial oil or the conditions of manufacture.

The first experimental series was carried out with a large number of oils of various origins and different viscosity grades of at a reaction temperature of 190°C with a supply of air amounting to 8 litres/hour, 0.02% by wt. of manganese stearate being used as a catalyst. The greases produced under these conditions were tested at low temperatures, if their properties seemed at all promising. The low temperature test was carried out in adjustment screws of the ordinary field glasses of the Wehrmacht. The limiting temperature below which the grease became unusable was taken to be that temperature at which the screw could no longer be moved by hand.

The limiting temperature values measured in this way are reproducible to within ± 2%.

Experimental series I

Greases from mineral oils, temperature of production 190°

Origin of oil	Trade name	Consistency	limiting temp. for use
DAPG	SAE 50	moderately soft, shiny,	-15
DAPG	SAE 20	partially decomposed, unusable	---
Leuna	KF 9	clear, tough, sticky	+10
DVOAG	Rotring	soft, ropey	-20
DVOAG	Arctic	Medium hard	-22
Nerag	N 345	cloudy, hard	-14
Nerag	Zyl. I	tough, sticky	- 5
DAPG	SAE 40	clear, medium soft	-18
Ruhrbenzin	RB 42250	hard, tough, sticky	+20
Ruhrbenzin	RB 22460	Hard, tough, sticky	+12
Jedlicze	Einheitsöl	oily, partially decomposed	-16
Wintershall	Neutralöl	opaque, partially coked	---
Valvoline	XRM	soft, slightly clouded	-18
Valvoline	Magnet-A	soft, slightly clouded	-20
Schliemann	Merkur 65	decomposed	---

It has already been mentioned that the conditions of reaction as used, are not suitable for all oils under test, some of the oil decomposing. Under different conditions varying from oil to oil, these oils would also give useful greases of a hard or soft consistency.

In no case were the oils usable below -22°C. The observed limiting temperatures roughly correspond to the solidifying points of the initial oils (-15 to -25°). The only exceptions are the synthetic oils of the I.G. Farbenindustrie and the Ruhrbenzin. The greases produced from these oils have such a tough and sticky character that they can only be employed for protective coatings (Hemm-Mittel) but not as lubricants. The limiting low temperature at which they can be used therefore lies correspondingly far above the solidifying point of the initial oil.

In the course of further experimental series it was investigated whether by the use of different conditions of reaction greases could be obtained having more favourable characteristics at low temperatures. Some of the oils under test were treated at 220° (experimental series II) and also at 250° (experimental series III).

Experimental series II
Greases from mineral oils, production temp. 220°

Origin of oil	Trade name	Consistency of grease	limiting low temperature for use
DAPG	SAE 50	medium softness, shiny	-15
DAPG	SAE 20	slightly decomposed	-18
Leuna	KF 9	very tough, sticky	+30
DVOAG	Rotring	medium tough, ropey	-16
DVOAG	Arctic	medium hard	-20
DAPG	SAE 40	medium soft, shiny	-14
Jedlicze	Einheitsöl	soft, slightly decomposed	-18
Wintershall	Neutralöl	opaque, decomposed	---
Valvoline	Magnet A	medium soft, opaque	-16

Experimental series III
Greases from mineral oils, production temp. 250°

DAPG	SAE 50	medium hard, shiny	-12
DAPG	SAE 20	medium soft	-18
Leuna	KF 9	hard, sticky	---
DUUAG	Rotring	medium hard	-12
DVOAG	Arctic	medium hard	-15
DAPG	SAE 40	medium hard	-12
Jedlicze	Einheitsöl	soft	-17
Wintershall	Neutralöl	opaque, gravelly	-16
Valvoline	Magnet A	medium soft	-16

No improvement in the low temperature characteristics of the oil resulted when while keeping all other factors constant, the temperature of the reaction was raised. Most greases become somewhat harder and their usability at low temperatures decreased somewhat. Experiments carried out at low temperatures (150 to 17.) did not yield any better results. Almost all oils are considerably decomposed. No homogeneous grease was attained. In order to ascertain the influence of the quantity of injected air same oils were treated at 190° with varying quantities of air per unit time in the presence of 0.02% by wt. of manganese stearate.

Experimental series IV
Effect of the quantity of air on the consistency of the greases

Trade name of oil	Quantity of air l/hour	Consistency of grease	Limiting low temperature for use
SAE 50	4	slightly decomposed	-15°C
	8	medium soft, shiny	-15
	16	medium hard	-14
KF 9	4	clear tough sticky	+10
	8	clear tough sticky	+10
	16	hard tough sticky	+30
XRM	4	soft, sl. decomposed	-20
	8	soft, sl. cloudy	-18
	16	soft clear	-18

A change in the quantity of air supplied does not have an appreciable effect on the low temperature characteristics of polyxol greases.

Variation of the catalyst gives the same result. Oxidation catalysts, e.g. stearates, resinates, "soligens" of various kinds and autoxidation catalysts such as naphthylamine, p- and o-nitrophenol, pyrogalol, aniline and others all gave greases of somewhat the same low temperature characteristics.

The low temperature limit for use is generally identical with the solidifying point of the initial oil. At present therefore the only possibility of producing Polyxol greases with better low temperature characteristics is to use spindle oil having very low solidification points as initial materials for the production of Polyxol instead of the engine oils used in the experimental series I - IV where the solidifying points lay between -15° and -25°.

The observed results led to the introduction of low-solidifying spindle-oils as initial materials. It had been known from earlier investigations that the transformation of the spindle oils of low viscosity and rather low boiling point into greases occurs only at relatively high temperatures (250° and higher). At lower temperatures one always obtains decomposition with the formation of coke and sludge. The following theory while being in agreement with all other facts known so far was advance to explain this surprising phenomenon.

"Every oil has a so-called critical temperature of decomposition which depends on its chemical composition. Below this temperature it is decomposed by the oxidation treatment, above this temperature one observes, apart from the oxidation an increase in the viscosity, growing with length of treatment; this finally yields a solid grease-like product. The critical temperature of decomposition is that temperature at which there is a balance between the velocities of reaction of cracking, leading to decomposition, and of secondary polymerisation which increases the viscosity. At lower temperatures the velocity of the cracking reaction is the higher, at elevated temperatures the velocity of the polymerisation reactions are greater. One thus has to exceed the temperature of decomposition if one intends to produce lubricants".

The following experimental results obtained with two low solidifying spindle oils confirm the explanation given above of the process of oxidation and polymerisation.

Experimental series V
Experiments with spindle oils as a function of the temp. of reaction and the supply of air (catalyst: MN-stearate)

Temp. of reaction	Quantity of air 1/hour	Consistency of grease	Pour-point
1. AB 11 oil (Rhenania-Ossag, Mineralölwerke)			
130	240	Decomposition, formation of sludge and coke	--
160	240	"	--
190	4	"	--
190	16	"	--
220	15	slighter decompos'n	--
230	8	soft grease, clouded	170
230	15	"	156
240	16	" , clear	158
250	8	soft grease, clear	159
250	16	"	155
260	8	"	136
260	16	"	150
280	8	medium soft, clear	72
280	16	"	57
300	1	no thickening	--
300	8	tough, hard	70

Temp. of reaction	Quantity of air 1/hour	Consistency of grease	Pour point
2. Servo-oil (Deutsche Vacuum-Öl-AG)			
190	8	Decomp. formation of coke	--
190	16	"	--
190	32	"	--
200	16	"	--
220	16	"	--
240	16	"	--
260	16	"	--
280	16	clouded, paste-like	142
290	16	tough, hard-	88
300	16	"	79

In low-temperature tests those greases proved best which were produced at temperatures a little above the critical temperature of decomposition. The greases obtained from AB 11 oil between 240 and 260 may be used down to about -40°C. When the temperature of production is raised further the low temperature limit for use recedes again. Greases produced at 300° can only be used down to 0°C.

Servo-oil only gave solid products from 290° upwards. The consistency of these greases was in the main similar to the greases produced from AB 11 oil at 300°. A field-glass screw greased with servo-grease could no longer be turned even at +5°C.

The low temperature characteristics of the AB 11 greases may be improved by mixing a grease with a specially high drop point with fresh oil or with an initial material which has been slightly oxidised.

Grease from AB 11 oil
Conditions of manufacture: 250°, 16 litres/hour air

Addition of fresh oil % by wt.	Pour Point °C	Low temp. limit °C
0	176	-40
10	176	-40
20	175	-45
40	152	-46
60	135	-50
80	grease flows as paste at room temperature	

The low temperature limit at which Polyxol greases are usable is therefore at about -50°C.

Experiments for the elucidation of processes occurring during oxidation

The reactions occurring in the production of greases are still completely unexplained. Experiments were therefore carried out with the purpose of studying the physico-chemical properties of oils during the production process. Pure cetane was used as the starting out material for these experiments. The cetane was treated with 8 litres/hour of air at 200° in the presence of 0.2% by wt. of manganese stearate. Every 24 hours samples of the cetane were taken, these samples were then tested as to density at 20°C, the acid number, the viscosity at 20°C, the iodine number, the solidification point and the elementary composition.

The course taken by the reaction was thus:

Sample No.	time of reaction, hrs.	product of reaction
1	46	light brown
2	70	reddish
3	94	light red brown
4	118	red brown
5	142	dark red brown
6	166	brown
7	190	dark brown
8	214	dark brown
9	240	beginning decomposition
10	262	strong decomposition, coke formation.

The following physico-chemical data were determined for the samples:-

Sample No.	Cetane	1	2	3	4
Density @ 20°C	0.7731	0.7911	0.7970	0.8030	0.8089
Acid No. mg KOH/g	0.1	1.9	3.7	4.9	5.9
Viscosity @ 20°C, °E	1.29	1.43	1.46	1.54	1.59
Iodine No.	7.0	4.6	4.6	4.1	3.8
Solidification No.	+13.8	12.1	11.8	11.2	10.8
Elementary analysis:					
Carbon Wt. %	85.01	83.89	83.28	83.03	82.48
Hydrogen Wt. %	15.08	14.76	14.47	14.29	14.15
Oxygen Wt. %	0.00	1.35	2.25	2.68	3.37

Sample No.	5	6	7	8	9
Density @ 20°C	0.8158	0.8190	0.8241	0.8252	0.8295
Acid No. mg KOH/g	7.3	8.4	8.9	8.2	10.2
Viscosity @ 20°C, °E	1.64	1.70	1.79	1.97	3.85
Iodine No.	4.3	5.1	5.1	6.7	--
Solidification No.	+10.4	10.1	9.8	9.8	9.8
Elementary analysis:					
Carbon Wt. %	81.77	81.89	--	--	--
Hydrogen Wt. %	13.92	13.81	--	--	--
Oxygen Wt. %	4.31	4.30	--	--	--

Density, acid number and viscosity increase continuously within certain limits. The iodine number decreases at first but seems to increase again when the decomposition begins. The solidification point falls to a small extent. The elementary composition also changes uniformly. There seems to be a discontinuity however in the increase of the oxygen content, when decomposition starts. Perhaps one may draw the conclusion from this that the assimilation of oxygen is displaced in favour of the cracking reaction when the decomposition sets in.

As the cetane was decomposed in the course of the oxidation-polymerisation a further experiment was started up with Essolub 40 (German-American Petroleum Company). The oil was treated at 190° in the presence of manganese resinate as catalyst with 8 litres of air per hour and per litre of oil. The samples withdrawn at intervals of 24 hours showed the following properties:

Sample No.	Essolub 40	1	2	3	4
Density ~~20°C~~	~~0.8934~~	~~0.8954~~	~~0.9009~~	~~0.9060~~	~~0.9089~~
Acid No. mg KOH/g	0.2	0.4	0.9	1.6	2.2
Viscosity 50°C, °E	9.6	10.2	11.7	13.8	16.4
100°C, °E	2.08	2.10	2.29	2.44	2.70
Mean mol. weight	445	478	488	495	518
Elementary analysis:					
Carbon Wt. %	86.39	86.29	86.14	85.61	85.41
Hydrogen Wt. %	13.14	12.99	12.97	12.68	12.70
Sulphur Wt. %	0.61	--	--	--	--
Oxygen Wt. %	0.00	0.11	0.28	1.10	1.28

Sample No.	5	6	7	8	9	10
Density 20°C	0.9130	0.9169	0.9239	0.9321	0.9348	0.9380
Acid No. mg KOH/g	2.6	2.9	3.3	4.7	5.8	6.4
Viscosity 50°C, °E	20.4	25.9	63.8			
100°C, °E	2.98	3.34	4.35	---- solid grease ------		
Mean mol. weight	527	534	544	570	620	613
Elementary analyses:						
Carbon Wt. %	85.24	85.08	84.96	84.96	84.45	84.43
Hydrogen Wt. %	12.65	12.35	12.31	12.27	12.12	12.12
Sulphur Wt. %	--	--	--	--	--	0.61
Oxygen Wt. %	1.50	1.96	2.12	2.16	2.82	2.81

Fundamentally the same continuous change in the physico-chemical properties has occurred in both oils in the course of the reaction. All the same one observes remarkable differences in the behaviour of the decomposing cetane and the Oil Essolut 40 when changing into a grease.

The increase in the acid number and in the oxygen content and also the decrease in the content of carbon and hydrogen is considerably greater for cetane than for Essolut 40. The increase in the viscosity is more rapid in the latter.

It is striking that the finished grease which is produced from Essolut 40 does not even contain 3% oxygen. This fact demonstrates that the main process is not the oxidation but the polymerisation even if the hydrocarbons which are completely stable at the temperatures employed are first attacked by oxygen.

Description of the method

The low temperature properties of the greases produced according to the method of the Institute is generally the same as the low temperature stability of the lubricating oils used as starting material. Oils of low viscosity with particularly low solidifying points form an exception. The lubricating greases produced from such oils always have worse low temperature characteristics than the starting materials. All the same, this method made it possible to produce greases which are still usable at -40°C. The consistency as well as the structure of the greases may be changed by the way the ageing is carried out.

The oxidation greases have the following advantages as compared to the soap greases which have generally been employed so far:

1. They are completely insoluble in water and they are hydrophobic
2. There is no separation or decomposition either at high or at low temperatures. It is quite permissible to exceed the flow point.
3. Consistency and flow point of the greases may be adjusted as desired.

4. They have low vapour pressures even at high temperatures so that the low temperature properties are unaffected or very slightly affected even if the oils are used in hot regions over long periods.
5. They have no corrosive properties; for this reason they are already being used as anti-corrosion greases.
6. They do not contain water or any appreciable amounts of ash.

Chemical reactions during the oxidation of the oil produce oxidized, cracked, and polymerized substances. Apart from the lubricating grease as main product, one obtains water and low-boiling oils as by-products.

The grease sample 1 No. J 7 which is sent with the report has been produced under the following conditions.

Quantity of oil	1025 cc (mixture of 1000 cc. AB 11 and 25 cc Ruhrchemie synthetic oil R 200)
Quantity of air supplied for oxidation	10 litres/hour and per litre oil
Working temperature	250°C
Catalyst	none used
Duration of experiment	91 hours
Yields	grease 920 gm. water 34 gm. oil (Kondensöl) 119 cc.
Ubbelohde Drop point	125°C

Added to the report are:

1 sketch "Apparatus for the manufacture of PX grease",
grease samples, marked

J 2	manufactured from ZdM 9 oil
J 3	" " a mixture of AB 11 with 5% vol. Ruhrchemie oil R 2000
J5	" " a mixture of AB 11 with 5% vol. Ruhrchemie oil R 2000 Consistency somehwat more solid than J 3.

These three samples were taken from earlier experiments carried out at the end of 1944.

J 7 was manufactured within the scope of the present assignment.

Further 3 samples: oil AB 11, oil ZdM 9 and oil Ruhrchemie R 2000 from which the greases were produced.

DESCRIPTION AND WORKING INSTRUCTIONS FOR THE RUHRCHEMIE VAPOUR LOCK APPARATUS.

(A) Description of Apparatus.

Fig. 1 shows how this apparatus is constructed. On the suction side of the delivery pump G, the fuel flows from the container A through the heating coil B, and enters the delivery pump directly from the latter. The temperature in the delivery numb is measured (F). The delivery pump forces the fuel - as in the engine - into the float chamber of a carburettor M. From here the fuel flows through an adjustable throttle P and a flow meter Q via an overflow R into a collecting tank below. The container C is normally filled with water, while at "break-off" temperatures above 90°C glycol must be used.

(B) Calibration of the flow meter

The figures recorded by the flow meter are only relative values, so that the true values for the flow must be obtained by calibration. The specific gravity of the fuel must be taken into account, since this influences the value recorded. A calibration curve is attached, from which the true flow can be read off for densities from 0.660 to 0.900 g/cm^3. It is advisable to check a point on the curve from time to time, using gasoline of a known density.

The flow meter is checked in the following manner:-

The overflow R is removed from the overflow container from below, and a measuring vessel (1000 cc. measuring cylinder) placed beneath. Then a gasoline of known density is poured into A, and the pump is set working without heating. By adjustments at P various flow volumes are set and the time in which a certain volume flows into the measuring cylinder is recorded.

(C) Test Method

To assess the behaviour of a gasoline as regards the formation of vapour lock, the "break-off" temperature at various flow volumes must be measured, and a "break-off" temperature curve plotted *). In general, it is only necessary to measure consumption at 4 points, as long as they are distributed evenly over the whole range. An example of such a "break-off" temperature curve is given in Fig. 3. In our measurements, the settings 2,4,6 and 10 on the flow meter appeared to be suitable.

The gasoline under test is fed into A. Care must be taken that the temperature of the gasoline is not above + 15°C. If the gasoline is not known, the "break-off" temperature is first determined at a lower flow value (e.g. flow meter setting 2.), so as to avoid too high consumption during the measurement. Since this would generally be above 70°C with ordinary engine gasolines, the heating vessel is heated at heat setting 3 to about 60°C. The delivery pump is not set working until the temperature is about 10°C below the "break-off" temperature expected. The heater is then switched back to setting 2, and heating continued. The rise in heat should not be too rapid during the tests, so that the "break-off" can be more easily followed, although this has no effect worth mentioning on the "break-off" temperatures measured.

---

*) see publication by Dr. Schaub u. Dr. Velde ATZ 44 (1941) pp. 549-556.

In our measurements so far it was 1.2°C per minute. After connecting up the pump the required level is set in the flow meter Q by regulating the cock P. There is then a certain level of liquid in L. The original setting of the flow meter Q (e.g.2) falls somewhat at first, and is re-set once. It then generally remains unchanged, and does not fall until near the "break-down" point. As the temperature rises, the level of L is observed and recorded, as is also the temperature at which the liquid first falls below this level. From here onwards the level in the float chamber falls, slowly at first, and then with increasing speed, and the temperatures are noted at which the level of the liquid passes certain marks, e.g. 30, 20, 10, 0. The break-down temperature is the temperature at which the liquid in the level glass L is no longer visible (level 0). At this moment the setting of Q also falls. Fig. 2 shows as an example the level in the float chamber and the flow volume. One observes that in both cases the fall was very rapid, so that the break-down temperature can be determined exactly. At low consumption one observes the first signs of a fall at about 4-5°C below the break-down temperature, and at higher consumption at about 2-3°C. The break-down temperature is related to the flow volume which was originally set, and was then re-set.

Having found such a point for the break-down temperature curve, one can then after some practice predict more or less what the break-down temperatures will be at the other consumption rates, for the gradients of the curves do not vary greatly. We then heat or cool without using the pump until the temperature is a few degrees below the value which is expected, and then proceed in the manner described above.

When the position of the break-down temperature curve is more or less known, the measurements can be begun with maximum consumption, after which it is no longer necessary to cool in order to carry out further measurements at low consumptions, so that the measuring process is completed fairly rapidly. In appendix 1 is a test result which proved to be the best obtained, and is recommended as a model.

When the individual break-down temperatures have been measured, the control cock on the flow meter should be closed immediately, so that a certain amount of fluid remains in the float chamber, and no air gets into the pipe leading to the control valve. But if in spite of everything this should happen, any air bubbles should be removed from the pump. One of the two openings in the cover of the float chamber is covered with the hand, and pressure is applied to the pipe line through the other by means of bellows and the air is then blown out.

When first starting the air which is in this pipe is removed in the same way. For this purpose the pump is set working until a certain level is reached in the float chamber, when it is disconnected, and gasoline is then forced into the pipe with the bellows until the air bubbles have passed out through the flow meter and the overflow vessel.

D) Sources of error

The following sources of error occur:-

1. Apparatus leaking: The apparatus should be tested thoroughly and often, since even small leaks on the suction side can affect the break-down temperature considerably. Leaks occur less often in the pipe system than in the pump itself. They can be detected here by pouring liquid (gasoline or soap solution) onto the cover of the pump, and creating a slight excess pressure in the pump by blowing in air. Any leaks are observed as small bubbles, especially at the thermometer screws or the securing screw of the cover.

Leaks are also revealed by the rate of delivery of the pump, as will be described below.

2. Pipes fouled or blocked by foreign bodies: Foreign bodies must be removed, and pollution got rid of. The question of expelling air bubbles from the pipe between the float chamber and the flow meter was discussed in Section C.

3. The membrane is not working efficiently, or is leaking: In this case, it should be replaced. This very seldom occurs. Replacements can be drawn from the firm of W. Feddeler in Essen; state purpose for which required. It is not advisable to install other membranes, because these vary very much in quality, and can cause faults.

4. Flow meter faulty: This may be caused by slight pollution. The flow meter can be cleaned by flushing and blowing out with air.

(E) Testing the Apparatus.

The following are the possible methods of checking faults:-

1. Testing the delivery of the pump currently with gasoline and air. The above faults, such as leaks, obstructions, or faulty membranes, are indicated by reductions in delivery. This could also be caused by the membrane having too small a thrust, just as too high a delivery would indicate that the thrust was too large. When the apparatus is delivered, the air delivery is fixed at 420 ± 5 litres per hour, and that of gasoline at 90 ± 10 litres/hour by a suitable arrangement of the pump and the eccentric drive, resulting in a certain membrane lift (about 6.4 mm). If these values alter, the membrane lift should not be altered if it can be avoided, for the reason that the alteration in delivery is seldom found here. It is particularly important to maintain the air delivery laid down above from the point of view of reproducibility of the results. Leaks on the suction side of the apparatus manifest themselves generally in a comparatively sharp fall in the gasoline delivery, whereas the air delivery is less sensitive in this respect.

   To measure the air delivery, the tube connecting A and B is detached, and replaced by a hose with a nozzle, which connects by means of a rubber hose with a normal liquid gas meter of 3-5 litres volume. The flow is then timed by the gas meter. The gasoline delivery is measured by detaching the tube K from the pump and replacing it by the nozzle which is supplied, attached to which is a Buna hose. The gasoline flow without heating is measured again with a measuring cylinder.

2. Establishing the "break-off" temperature for a certain reference gasoline.

   Such a gasoline can be drawn from Ruhrchemie A.G. Oberhausen Holten. It should be stored in a cool place. If the results are too high, this is generally due to an alteration in the gasoline. The reason might also be too large a delivery stroke. In this case the air delivery will also be above normal. If the break-off temperatures are too low, then it is a question of one of the above errors.

Remarks

It has frequently been observed that leaks occurred at the lower end of the flow meter. These are nothing to do with the material of which the packing is made, butare generally due to the screw-caps not being tight. The Klingerit packings have proved to be gasoline-tight.

Setting the flow volume by means of the slide cock is somewhat difficult at first, and requires practice. Therefore in many quarters the slide cock was replaced by a turn-cock. But it is very difficult to keep this tight, especially with hot gasoline, so that we recommend that the slide cock be left in the apparatus until such time as finely adjustable cocks which are satisfactory in every respect are available.

APPENDIX I

EXAMPLE OF A MEASUREMENT OF THE "BREAK-OFF" TEMPERATURE

Apparatus No. 1	Flow setting True volume of flow l/h	2 3.2	4 6.0	6 8.7	10 14.1	Remarks
Gasoline F.213	Level glass	Temperature at the pump °C				
Delivery	45	76	66	63	60	
Gaso.90 l/h Air 425 l/h	40	76.5	66.5	63.5	60.5	
Date 26.8.43	30	77	67	64	61.5	
Tester pfs.	20	77.5	67.8	64.5	62	
	10	78	68.5	65	62.3	
Break-down temperature	0	78.5	69.3	65.5	62.5	

TRANSLATION OF F.I.A.T. REPORT No. 873.

THE SELF-IGNITION REACTION OF HYDROCARBONS WITH BRIEF INDUCTION TIMES.

By W. Jost

In an apparatus in which gaseous mixtures could be rapidly compressed adiabatically from various initial pressures and temperatures, and in whose development Messrs. v. Müffling, Rögener, Rohrmann, Teichmann and v. Weber were particularly concerned, Messrs. Rögener and Braesch investigated the self-ignition reaction of mixtures of n-heptane and air, by recording the pressure-time curve with the aid of piezo quartz and the electron ray oscillagraph.1)

The research conducted by my former colleagues reveal a characteristic two-stage course of the ignition such as is well known at low pressures and long induction periods, and such as was recently disclosed for brief induction times for the first time by Rögener and v. Weber, by means of ionisation measurements.2)

Use was made of the photographs A to I of Rögener-Braesch of January 1944.

Photographs A to E show a typical pressure curve, as reproduced in Fig. 1 from photograph C 1 to the scale of 10 : 1 for the latter portion (the first part is rectilinear). Two induction periods follow one another, the pressure-time curve exhibits two points of inflection, which indicates that speed of the reaction obtained from this as dp/dt would exhibit two extrêmes, first a maximum and then a minimum.

The second induction period, from the first point of inflection to the end (i.e. the moment of instantaneous pressure rise), forms about 1/6 (C 1), 1/8 (A 2) 1/4 (B 1) up to almost $\frac{1}{2}$ (E 1) of the total induction period, which gives in all cases for the second induction period values of $\tau_2 = 0.0004$ sec.

In experiments F - H, the second induction period is probably likewise indicated, but not with any certainty, and it is in all cases very much shorter than in the first experiments (Experiment I 2 shows only the first induction period and no ignition). Besides log τ log τ_1 ($\tau_1 + \tau_2 = \tau$) is also plotted (in a figure which is no longer in my possession) for experiments A-E; on an average τ_2 amounts to about $3.9 \cdot 10^{-4}$ sec., with maximum fluctuations 4.55 and 3.55, but definite relationship with temperature cannot be detected. For τ_1 there is approximately obtained:

$$(A - E)\ \tau_1 \approx 5.37 \cdot 10^{-13} \exp (33\,600/RT);$$

---

1) The apparatus, in which it was mainly a question of reaching high speeds of compression and of avoiding undesirable vibrations, will be described elsewhere.

2) e.g. E.A. Andreew, Acta Physicochimica USSR 6 (1937) 57; B.V. Aivazow and M.B. Neumann, Acta Physicochimica USSR 6 (1937) 278.

the deviations in the experiments are not inconsiderable. For the induction period of experiments F - I (which are carried out at a lower initial temperature and consequently higher pressure), there are obtained:

$$(F - I) \quad \tau \approx 4 \cdot 10^{-17} \exp (45\,700/RT)$$

In order to ascertain whether the first induction period can be assigned to a heat explosion (which is unlikely from the figures of the interpolation formula), the following method was adopted. Up to the maximum of the reaction velocity, the temperature rises by less than 100° (altogether, the temperature rise during the first induction period is comparable with that of cold flames, where it is 100 to 200°); with a temperature rise of about 2000° for complete conversion, the conversion would therefore only be in the region of 10% (of course under certain circumstances more as in the case of a reaction leading to an aldehyde or similar stage). One will therefore, as a rough approximation, attempt to reckon with a reaction in the region of zero. For the rate of heating with adiabatic reaction, it may therefore be asserted that

$$dT/dt \approx c \exp (-E/RT)$$

where E is the apparent activation energy of the reaction. It is now possible to take the rise dT/dt at various moments from the recorded curve, and compare this with the values obtained with a reasonable value for E, e.g. about 30,000. The following, for example, is then obtained, Tab. 1.

Table 1

Interpretation of Experiment A 2

t = time from the end of compression. Abscissa 1 mm = 2.82 . 10^{-4} sec. Ordinate 1 mm = 0.90 atm.

t (sec)	p (atm)	Rise α (Degrees)	tg α	T (° abs. calculated from pressure rise)
0	15.8	<2	<0.035	759° abs.
$2.54 \cdot 10^{-3}$	15.8	<2	<0.035	759
$2.82 \cdot 10^{-3}$	15.8 ÷	7	0.123	759 (÷)
$3.1 \cdot 10^{-3}$	16.3	18	0.325	783
$3.3 \cdot 10^{-3}$	17.8	85	11.4	855

In a purely thermal reaction, the tangent values should behave as the corresponding exponential functions of the temperature, i.e.

ascertained: <1 : <1 : 3.5 : 9.3 : 326
calculated 1 : 1 : 1 : 1.77 : 9.15

calculated values 0 exp. (15000/T)

The ascertained values cannot be reproduced with any reasonable choice of activation energy, even assuming considerable uncertainty in reading off the angles. If, for instance, it is assumed that at the third measurement point the temperature is 10°

above that of the first, an activation energy of 144 kcal would be needed in order to explain the observed temperature increase of 3.5 times. Moreover, the subsequent points would not tally.

Experiment A 1 is qualitatively analogous.

Experiment B 1 produced the following result (Table 2).

Table 2.

Interpretation of experiment B 1

Absciss a 1 mm = $2.5 \, . \, 10^{-4}$ sec.
Ordinate 1 mm = 0.9 atm.

t (sec)	p (atm)	α (degrees)	tg α	T
0	20.2	<2	0.035	788° abs
$1.36 . 10^{-3}$	21.7	85	11.4	848

Speed ratio - ascertained 1 : >326
calculated 1 : 3.78 for E = 30.000

Experiment B 2 analogous, likewise Experiment C

Experiment D produced Table 3.

Table 3

Interpretation of experiment D

Abscissa 1 mm = $1.64 \, . \, 10^{-4}$ sec., ordinate 1 mm = 0.9 atm.

t (sec)	p (atm)	α (degrees)	tg α	T
0	17.5	<2	0.035	754° abs
$2.6 . 10^{-3}$	19	80	5.7	819

Speed ratio - ascertained 1 : >163
calculated 1 : 4.93 for E = 30,000

Table 4

Interpretation of Experiment E

Abscissa 1 mm = $5.27 \, . \, 10^{-4}$ sec. Ordinate 1 mm = 0.9 atm.

t (sec)	p (atm)	α (degrees)	tg α	T
0	23	<2	0.035	802° abs
$7 . 10^{-4}$	25.3	88	28	882

Speed ratio - ascertained 1 : >800
calculated 1 : 5.75 for E = 30.000

In experiments F to I, as mentioned above, the pressure curve is different. For instance, the interpretation of experiment G gave Table 5:

Table 5.

Interpretation of experiment G 3

Abscissa 1 mm = $1.89 \cdot 10^{-4}$ sec. Ordinate 1 mm = 0.9 atm.

t (sec)	p (atm)	α (degrees)	tg α	T
0	20.6	mean < 2	<0.035	704° abs
$4.7 \cdot 10^{-3}$	20.6			
$5.31 \cdot 10^{-3}$	21.8	74	3.5	745

Speed ratio - ascertained 1 : >100
calculated 1: 3.2 for E = 30,000

Experiment I 2 did not reach complete ignition.

Interpretation of the second induction period.

For investigating the second induction period, the following method was adopted. In Fig. 2 the recorded curve of photograph C 1 is plotted, magnified 10 times.

For mm 14 (1), 14.5 (2), 15 (3) and 15.3 (4), the increases were gauged, then from the recorded pressures the temperatures were obtained, after which log tg α was plotted against 1/T; within the limits of experimental errors, a straight line could be drawn through the measurement points with the equation

$$\text{tg}\ \alpha = 10^{5.4} \exp(-23{,}000/RT)$$

Thus there is extrapolated for (5) 13 mm, tg α = 0.33, α = 18° with T = 864° abs. Thus the curve 4321 was graphically extended backwards (corresponding to an integration), whereby a hypothetical starting level was obtained, from which this second explosion probably started. On the other hand, the actual increase in (5) is 75°, tg α = 3.73; for the speed of reaction actually observed, on the assumption of the above analysis, there must remain over from the primary reaction an amount of tg α = 3.40 corresponding to α = 73.5°. Using this figure and the hypothetical end level for the primary reaction, the dashed curve was traced for the second part of the primary reaction. Although the analysis is somewhat arbitrary, it should be remembered that for any curve for the secondary reaction which does not exhibit an inflection point in the pressure increase at an early stage, the qualitative analysis does not deviate appreciably from that of the drawing.

Thus only two possibilities remain:

1 - The analysis given (or a similar one) is accepted. There then follows for the primary reaction a non-symmetrical S-shaped pressure rise, corresponding to a time-asymmetric velocity curve, which, according to v. Müffling 3) is to be expected in the case

---

3) L. v. Müffling, Z. Physik 122 (1944) 787 et seq.

of a chain break in the second order. This primary chain reaction is followed, and partly overlapped, by a secondary reaction, for which the mechanism of a heat explosion cannot be disregarded, but yet cannot be proved. The curve thus constructed for the primary reaction would appear to favour the likelihood of a chain explosion.

2 - The pressure rise with a point of inflection corresponds ~~formally to a rate of reaction with negative temperature co-~~ efficient, with the temperature coefficient 0 at the point of inflection. This reaction must follow the primary reaction immediately after the maximum velocity (first point of inflection in the pressure rise curve). This curve cannot, of course, be disregarded, but a reaction with true negative temperature coefficient is comparatively improbable. From the diagrams was determined the temperature of the second point of inflection, but this is only possible with a low degree of accuracy.

Table 6.

Temperature of the second point of inflection T_W0 abs

Experiment	A1	A2	B1	B2	C1	C2	D	E
T_W	995	977	987	962	939	954	954	1040

The lack of certainty in reading off is too great to permit of drawing reliable conclusions.

ATTACHMENT II.

ON THE PRINCIPLE OF LUBRICATING OIL MIXED POLYMERISATION.

I.G. Leuna Memo of 12th January, 1942.

The principle of the mixed polymerisation method consists of the mutual reaction of natural and synthetic lubricating oil hydrocarbons. As starting materials the lubricating oil fractions of petroleum are used on one hand and the lubricating oil fractions of the synthetic ethylene polymers or of paraffin crack-products on the other. There are two conditions for the success of the reaction: firstly, asphalts, resins and paraffins have to be practically completely removed; secondly, the synthetic polymers have to be employed in the immediate condition in which they are formed, i.e. containing aluminium chloride. Under normal conditions, the lubricating oil fraction of the petroleum, having been cut out by means of vacuum distillation, is then subjected to the following working process:

1.) The crude lubricating oil fraction is freed from asphalt and resin by means of liquid propane.

2.) The pretreated lubricating oil fraction is dewaxed by means of the well-known solvent method: propane, benzene-acetone or ethylene chloride.

3.) The lubricating oil fraction which has been freed from asphalts, resins and paraffins is extracted by means of a selective solvent such as phenol or furfural. Olefinic and aromatic hydrocarbons should be extracted. As these hydrocarbons, however, in their turn dissolve naphthenic-and-paraffinic hydrocarbons, the resulting extract actually contains all four types of hydrocarbons. The quantity of the extract is regulated with regard to the required quality of the end product and the chemical composition of the petroleum used. For German paraffinic crude the quantity extracted is about 10 - 20% when automobile oils are wanted; 30- 40% of the lubricating oil fraction pretreated according to 1.) and 2.) are extracted when aero-engine oils are wanted.

In the mixed polymerisation method process 3.) is left out. To produce an aero-engine oil according to this method the 30 - 40% of the lubricating fraction, pretreated according to 1.), and 2.) are kept in this fraction. The fraction is heated to about 100 - 120°C. It is then transferred to a stirrer vessel at atmospheric pressure where it is brought into contact with crude ethylene polymers; these polymers come directly from the reaction autoclave, and thus contain aluminium chloride and they are at the same temperature as the petroleum lubricating oil fraction. The two substances are then stirred together for about 3 - 4 hours at the temperature indicated above. During that period the olefinic and aromatic hydrocarbons of the natural lubricating oil fraction react with the ethylene polymers under the influence of the aluminium chloride. The resulting mixed polymerisation product is then refined in the same way as the pure ethylene polymers.
In the production of aero-engine oils one has to use a ratio by weight of natural lubricating oil hydrocarbon to ethylene polymerisation product of 1 : 1; in the production of automobile oils this ratio has to be 2 : 1 or 3 : 1.
A comparison may be made between the behaviour in the engine of a mixed polymerisation product aero-engine oil and a physical mixture of the same parts of finished ethylene polymer SS906 and a mineral lubricating oil refined by extraction in the usual way.

The mixed polymerisation product then has the better properties. Thus:

SS 906 + refined lubricating oil 1 : 1   13 hours running time.
Mixed polymerisation oil   1 : 1   18·5 "   "   "

This shows that the method of mixed polymerisation does not only open the way for a fuller utilisation of the natural lubricating oil basis but that it also yields an end product of higher quality.

ZORN (Signed).

ATTACHMENT III.

MIXED POLYMERISATION OF SS OIL WITH MINERAL OIL.

I.G. Leuna - 1st February, 1943.

Amononiakwerke
Merseburg
Dr. Metzger
Me 127.

Leuna Werke
1.2.43.

This paper concerns the mixed polymerisation of crude ethylene polymers with mineral oil. The conditions obtaining in this reaction had to be examined mainly with respect to the quantitative aspect. The quality of the oils produced and their value as aero-engine oils is the subject of investigations which are now in progress. The mineral oil component made available for this work was a distillate (lubricating oil distillates 1-3) from a well at Hauskirchen. It had been dewaxed without a sulphuric acid pre-treatment; the asphalt had been removed with propane but it had not been refined by extraction. The oil had the following constants:

$d_{20} = 0{\cdot}915$
$V_{20} = 53{\cdot}3^{\circ}E$
$V_{38} = 15{\cdot}46^{\circ}E$
$V_{50} = 7{\cdot}93^{\circ}E$
$V_{99} - 1.862^{\circ}E$
V.I.= 54.5.

Flash point = 220°
Setting point= -18°
Acid number - 0·28
Saponification number = 1·23
Conradson Carbon = 1·09%

In close analogy to previous experiments by Dr. Zorn and Dr. Haag at Oppau the reaction was carried out as follows:

Ethylene was polymerised in an autoclave in the usual manner. After the polymerisation had been completed the whole of the crude polymerisation product which was still at a temperature of 110°C. was stirred into the mineral oil which had been heated to between 90° and 150°. The mixture was maintained at the temperature of the reaction for 3 hours under stirring. A small sample of the pure ethylene polymers had to be secured before the mixing in order to determine its constants (after refining). This had to be taken into account when calculating the yield.

A number of feeds are quoted below; the significance and the methods of computing the figures in the various columns are explained subsequently.

Charge in kg.		Yield	—	Charge for mixed polymer, kg.		Yield, kg.		
1. First runnings	2. $AlCl_3$	3. SS Polymer	4. SS analysis sample	5. Crude ethylene polymer	6. Min. Oil	7 Total	8. Crude Oil	9. Sludge
8	1.4	35.4	1.1	34.3	21.0	55.3	49.3	6.0
8	1.4	34.7	1.1	33.6	21.0	54.6	49.2	5.4
8	1.4	33.5	0.9	32.6	20.0	52.6	47.2	5.4
8	1.4	35.8	0.8	35.0	20.0	55.0	49.0	6.0
32	5.6	139.4	3.9	135.5	82.0	217.5	194.7	22.8

The figures in columns 1,2,4,6,7,8,9 are determined by weighing.

The values in the other columns are calculated thus:

Column 5 from Total yield 7 - mineral oil charge 6.

Column 3 from column 5 + analysis sample 4.

The total quantity of ethylene used works out to 101.8 kg. from column 3 - (1+2).

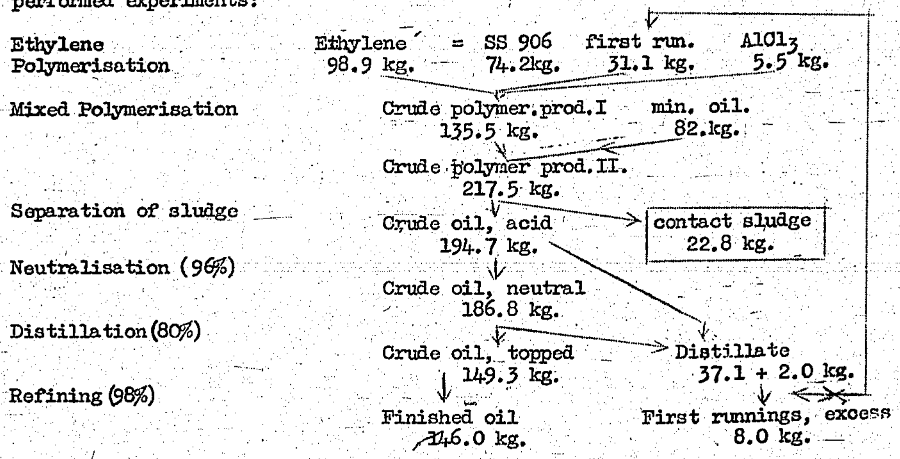
The ethylene present in the mixed polymerisation charge is then computed from total ethylene x $\frac{\text{column 5}}{\text{column 3}}$ to be 98.9 kg.

Similarly the first runnings $= 32 \times \frac{135.5}{139.4} = 31.1$ kg.

$AlCl_3 = 5.6 \times \frac{13.5}{139.4} = 5.45$ kg.

For further treatment the hot reaction product was run off and allowed to settle for twelve hours. By this means the contact sludge is deposited as an asphaltic mass and may then be removed completely. The remaining acid crude oil was stirred with 0.5% methanol and neutralised with 2% of slaked lime. It was then pressed through a filter press. The yield was the same for a number of feeds on the laboratory scale and a 100 kg. feed, amounting to 96% of neutral crude oil. After a subsequent vacuum distillation the average residue was 80% of the feed. The loss due to refining is to be estimated at not more than 2%. The yield of SS 906 from ethylene may be taken to be 75% according to the works experience of the SS oil plant at Leuna. 74.2 kg. of SS oil could thus have been produced from 98.9 kg. ethylene.

The following flow diagram may be drawn up on the basis of the performed experiments:



The end product consists of 74.2 kg SS Oil = 50.8%
71.8 kg Min.Oil = 49.2%

In this case the components were present practically in the ratio 1 : 1.

The following point has to be borne in mind when ethylene is used for mixed polymerisation. In place of the R - oil of which quantities of 7% of the finished SS oil are obtained, an asphalt is now left which has to be worked up. (e.g. by coking) and which does not yield any additional lubricants.

The observed yield data still have to be checked by means of large scale tests.

The testing of the oils with respect to their use in engines is still in progress. The following table gives the constants of the mixed polymerisation product side by side with those of the pure SS oil, measured on the above-mentioned analysis samples.

	SS 906	Feed N 865,866	Mixed polymer (M P 10-12)
V_{38}	86.7	85.0	34.85
V_{99}	5.69	5.68	3.11
V.I.	109.5	109.3	108
Flow point	224°	206°	221°
Sett. point	- 34°	- 30°	- 30°
Density	0.855		0.870

The Conradson coke value is still erratic; when the working up has however been finally fixed it will not exceed 0.15.

METZGER (Signed).

ATTACHMENT VI.

DESCRIPTION OF THE LUBRICATING OIL PLANT RHEINPREUSSEN.

Lurgi Gesellschaft - 31st May, 1945.

Drawing AS 1263 is a flow sheet of the lubrciating oil synthesis plant.

The first stage in the process is the chlorination of the crude distillate from the Fischer Tropsch synthesis boiling between 200° and 350°C. This stage is worked discontinuously. A quantity of about 1 m^3 of crude distillate is pumped through the chlorine-tower for several hours. A temperature of between about 80° and 100°C is obtained by means of a heat exchanger. This temperature is maintained later when the heat of reaction is conducted away by cooling. Chlorine is drawn as a liquid from the stock tank which is under the vapour pressure of the liquid chlorine - about 10 - 15 atm. The chlorine expands and vapourises at the throttle valve and is then led into the bottom of the chlorine tower. HCl gases escape at the top of the tower; they are cooled in a cooling tower and then led out of the process into a gasometer. The cooling tower is cooled indirectly by means of gasoline as cooling liquid. This is kept in circulation and maintained at a low temperature by means of a cooler. The chlorinated intermediate product is stored in a storage tank and thence led into the second stage.

The second stage consists of the synthesis. The chlorinated crude distillate is mixed with gasolene and naphthalene in stirrer vessels, this being done discontinuously. The quantities are measured out in measuring vessels before they are mixed. The measuring vessel for the crude distillate holds 600 litres, those for gasolene and naphthalene hold 1400 litres. Each of the six stirrer vessels has a capacity of 3 m^3. To start up the synthesis the mixture is raised to about 120°C. by means of the heating jacket around the stirrer vessels and aluminium-filings are added. The reaction takes place under atmospheric pressure: the escaping HCl gases are cooled in the same cooling tower as the HCl gases which, as mentioned above, escape during chlorination. The undesirable tar products which are formed during the synthesis are allowed to settle in 4" settling vessels". The deposit is again mixed with gasoline in a stirrer vessel, the tar being extracted in this way. The remaining tar residue is removed. The stirrer vessel for the mixing of tar and gasoline has a capacity of 4 m^3.

The intermediate product produced during the synthesis is led from the settling vessels into two parallel stirrer vessels; there it is treated with fuller's earth and lime at a temperature of 150°. The lime treatment serves the purpose of neutralisation. The used fuller's earth and lime are removed by means of a filter press.

The third stage in the plant consists of distillation. In this stage the intermediate products formed during synthesis are fractionated. Using a distillation tower the low boiling fractions(gasoline and naphthalene) are removed first. The distillation is carried out under an absolute pressure of 200 - 300 mm Hg. The distillation vessel is heated with steam under 100 - 150 atm. pressure. This is heated in an oven and circulates through the oven and the distillation vessel. The fractionating column works continuously and has been constructed for a maximum influx of 1800 kg/h and a maximum quantity of distillate of 1100 kg/h. A low temperature cooling plant separates the distillate from the fractionating column into naphthalene and gasoline. This low temperature cooling plant consists of two chillers which are cooled to about - 20°C by the evaporation of ammonia; the naphthalene is then separated by means of a centrifuge.

The bottoms in the fractionating tower contain the oils produced by the synthesis. They are cut into four fractions, distillates I, II, III, IV, in a high vacuum distillation apparatus. Distillate IV is the required lubricating oil, whereas distillates I, II and III have lower boiling ranges.

The last stage of the plant consists of the dewaxing and fuller's earth treatment of distillates I, II and III. These two parts of the plant have not been used and are therefore not in action. It had been planned to use acetone as a dewaxing solvent. The mixture of distillate and acetone is cooled to a low temperature in chillers and conveyed on to a down filter of about 1.5 m^2 area and a maximum capacity of 500 kg liquid, acetone and oil. The filtrate is sucked off by means of a vacuum pump. The acetone is distilled off from the dewaxed oil in a stripper. In order to ward off the danger of explosion, the apparatus is filled with an inert gas. The dewaxed oil is finally treated with fuller's earth in a stirrer vessel with a capacity 5 m^3. The used fuller's earth is removed in a filter press.

LURGI,
Company for Heat Technology, Ltd.

ATTACHMENT VIII

The scientific principles of the synthesis of lubricants.

(I.G. Leuna, Dr. H. Zorn report

14th May, 1943)

Leuna Works
15.5.43

"Verily, chemistry does resemble the changeable Proteus, often 'she' seems a goddess, often a fickle woman. Yet we like her for behind her deceptive moods, in arch play, she holds out the promise of eternal laws yet to be discovered".

These words were addressed by the great experimentalist Ludwig Claissen to his friend Anwers on New Year's day, 1927. I became acquainted with the subject of lubricants in that same year. Very soon I had come to know the "deceptive moods" of these substances which at this time did indeed make an arch play of chemists. In the tables and graphs attached I shall paint a picture of those laws that are hidden behind the arch game and of the way we have succeeded in transforming the play into serious action, i.e. a synthesis.

The first attempts at the production of lubricants by synthesis were made during the first world war. At that time Dr. Schneider tried to produce lubricating oils by polymerising the unsaturated constituents obtained from brown coal generators. We followed up this work in the year 1926 by passing gaseous olefins into tar oils and hydrogenation oils in the presence of aluminium chloride. This working method was tried out in a pilot plant at Leuna in the year 1930/31. No high-grade engine oils were obtained in this way, but only machine oils. The tests did however provide the impetus for a more thorough investigation of the polymerisation of chemically pure olefins of known constitutions.

Fig. 1. This figure represents a partial result of these investigations. It is seen that only straight-chain olefins with terminal bonds give a good yield of polymerisation products of good viscosity - temperature characteristics. Both yield and V.I. are bad if the double bond is situated in the middle of the molecule or if one hydrogen atom in the terminal double bond atoms is substituted by an alkyl group. Dimethyl octylene deserves attention because it gives a good yield of polymerisation products with a very high viscosity. The results of this scientific investigation were applied technically in the Paraffin - crack-product-polymerisation method.

When Paraffins in the gaseous state are cracked, the product consists of straight chain olefins with a terminal double bond. The polymerisation of these olefins may be pictured as shown in fig. 2. We wanted to find out whether this diagrammatic representation is correct and therefore tried to synthesize hydrocarbons of the type shown. Dr. Metzger and Dr. Nieuburg developed and carried out the synthesis indicated in fig. 3. We started with octyl aldehyde. This we transformed to hexyl-heptyl-acrolein by means of the aldol condensation. The product was reduced to the corresponding alcohol with the aid of a nickel-kieselgulor-contact. The alcohol was transformed into the corresponding 2 - hexyl- 1-iodine-detane by reaction with iodine and red phosphorus. This product was now combined with the sodium salt of hexyl-malonic acid - ethyl ester. The resulting ester was saponified, decarboxilised and the resulting acid again reduced to the alcohol. This alcohol was again transformed to the iodide with phosphorus and iodine. The iodide was either reduced to the hydrocarbon or again combined with the sodium salt of the ethyl ester of hexyl malonic acid for the synthesis of the next higher homologue. The hydrocarbons quoted in the table below were obtained in this way which is, it is true, somewhat laborious but also very exact.

Fig. 4 (after page 3 on reel)

In the homologuous series 1 - 5 it is seen that the viscosity rises with increasing molecular weight but that the viscosity temperature characteristics improve continuously. The same applies to the homologues 6, 7 and 8. These hydrocarbons are obtained from the iodides by means of Wurtz's reaction. In this way we succeeded in synthesising a hydrocarbon $C_{64}H_{130}$ with a mol.wt. of 899. This corresponds to the average size of the molecule in superheated steam cylinder oils i.e. in high-molecular mineral oils. This was the first time that an exact synthesis of a high molecular lubricating oil hydrocarbon had been achieved. All these compounds have a remarkably low melting point, in particular the last named hydrocarbon which still has a melting point of - 39.

The next

fig. 5 (after page 3 on reel)

shows how the viscosity-temperature characteristics change, at constant molecular size. (Trans.) when variations occur in the intramolecular branching of the C-chains. It is seen that the viscosity-temperature characteristics improve as the number of side chains decreases.

The next

fig. 6 (after page 3 on reel)

also shows the effect of the type of branching on the viscosity-temperature characteristics at constant molecular size. With increased branching the viscosity-temperature-characteristics become worse and the viscosity increases. The nearer the molecule approaches spherical shape the more unfavourable becomes the effect of temperature on the viscosity. The following

fig. 7 (after page 4 on reel)

exhibits the same phenomena for the hydrocarbons C_{16} and C_{24}. Short or branched side chains are very unfavourable as is shown by the hydrocarbons 10 or 9. The effect of short side chains on the melting point is very remarkable. Hydrocarbons 1 - 5 may serve as an illustration. Here, the introduction of one methyl group into the hexadecane lowers the melting point by 57°. A second methyl group causes a further lowering by 40°. This distinguishes aliphatic from aromatic hydrocarbons as is shown by the following

fig. 8 (after page 4 on reel)

A comparison of benzene, toluene and the xylenes illustrates the point. The viscosity temperature characteristics are very unfavourable when a straight chain of C-atoms partly or completely closes to form a ring. This is proved by the table below.

fig. 9 (after page 4 on reel)

Here you can see that with increasing cyclisation a large rise in the viscosity occurs simultaneously with a considerable worsening of the viscosity temperature characteristics. Hydrocarbon No.7 deserves attention. One consequence of these generalisations to which we came as a result of tedious and protracted synthesis was that it stimulated us to thinking about the application of these generalisations in large-scale practice. The paraffin-crack-product-polymerisation method always leaves us with a mixture of olefins the composition of which we cannot control. Our deliberations led us on to ethylene. Dr. Otto had shown at the time that it is possible to polymerise ethylene to n-butylene in the presence of small quantities of boron fluorides. We believed that by using a more active catalyst it should also be possible to polymerise ethylene to a greater extent giving longer chains with long side chains. By using chemically pure ethylene and aluminium chloride as catalyst polymers could be obtained which combined good viscosity-temperature characteristics with good behaviour at low temperatures. Thus originated the ethylene lubricating oil synthesis.

When ethylene lubricating oils were tested in practice it appeared that under extreme conditions of lubrication the lubricating quality was not always adequate. Now, it is known in the mineral oil industry that the lubricating quality of mineral hydrocarbon lubricating oils may be improved by the addition of fatty oils. Fatty oils, i.e. esters of glycerol with high molecular fatty acids, have the disadvantage of being extremely sensitive to temperature. It was presumed that this thermal instability is due to the sensitivity of the secondary hydroxyl-group of the glycerol. Trimethylol-ethane was placed at my disposal by arrangements made by Director Dr. Giesen. The esters produced therefrom with Leuna carboxylic acid showed a very good thermal stability. This opened a way of producing esters which would stand up to the high thermal demands of aero-engines. This success contributed to my transfer to Leuna. In collaboration with Dr. Löwenberg, Dr. Metzger, Dr. Gänicke, Dr. Heidinger and Dr. Rössig an investigation into the connection between the chemical constitution and the properties of the esters was carried out there on a very broad basis.

The next

fig. 10, 57089 (after page 5 on reel)

shows esters of tri-and tetrahydric alcohols with various acids. Let us compare first the esters of normal octyl-acid. There are no differences in the magnitude of the viscosity or the viscosity-temperature characteristics between trimethylol-ethane and trimethylol-propane; but there are differences in the low temperature properties. In this respect the trimethylol-propane is superior to trimethylol-ethane by 61°. The viscosity-temperature characterists of glycerol are equivalent to those of the two alcohols. The viscosity itself however is lower and the setting point is considerable higher than that of trimethylol-propane but lower than that of trimethylol-ethane. Pentaerythritol gives an ester of considerably higher viscosity, an even higher setting point and somewhat better viscosity temperature characteristics. It is very interesting to compare the esters formed by these four alcohols with a branched acid: 2-ethyl-hexyl-acid. All these esters have very low setting points. There is no difference, in this case, between trimethylol-ethane and trimethylol-propane. The glycerol ester has the lowest viscosity, the pentaerythritol ester again has the highest viscosity and also the best viscosity-temperature characteristics. If 1 in place of the 2 -ethyl -hexyl acid one uses the mixture of carboxylic acids obtained from those alcohols of the isobutyl-oil which boil between 200-250° one obtains an ester the viscosity properties of which are equivalent to those of the esters mentioned previously but which have not quite so favourable a setting point. The setting point of the glycerol ester of this acid is remarkable. Esters of this kind could be used as softeners in the lacquer industry and as switch oils in the electrical industry. The effect of incomplete esterification of these polyalcohols on the viscosity-temperature characteristics is very interesting. These relations are shown up in the next

fig. 11, 57082 (after page 6 on reel)

In the case of both trimethylol-ethane and of pentaerythritol it is seen that the viscosity becomes higher and the viscosity-temperature characteristics worse as the number of free hydroxyl groups in the ester increases. This is quite plausible because free hydroxyl groups have the effect of associating the ester molecules. It is known that all alcohols are strongly associated. Experiments which Prof. Dr. Wolff and his collaborators have carried out at Halle on my suggestion have revealed the interesting fact that the formation of these super-molecules is perfectly uniform. In the whole mass there is an equal number of double, treble, quadruple molecules up to aggregates of 12 molecules.

In the next

fig. 12, 57083

the investigation into the esters of the dihydric glycols has been represented. The dihydric glycols investigated were ethylene glycol, 1,4 Butylene glycol, 1,6 hexylene glycol, 1,6 methyl-hexylene glycol and dimethylol-propane. In the esters of straight-chain glycols with n-octylic acid an increase of the viscosity and a decrease i.e. an improvement of the x - value are observed when the molecular weight increases. The lowering of the setting point in methyl-hexylene-glycol and dimethylol-propane is of interest. This is another instance of the effect of the methyl group which we have already met in the case of hydrocarbon hexadecane. The setting point becomes very favourable if instead of the n-octylic acid one uses iso-octylic acid or the Lenna-carboxylic acid. The viscosity temperature characteristics however become a little less favourable when those branched acids are used.

In the next

fig. 13, 57098

the esters of adipic and methyladipic acid have been used. A comparison of the n-octanol and iso-octanol esters gives remarkable results. The latter has excellent low temperature properties which are due to the ethyl side chain. This is analoguous to the effect of the methyl group in the cases of cyclohexanol and methyl-cyclohexanol. In comparison with the octanol ester these two esters show a high viscosity and less favourable viscosity-temperature characteristics. This is in complete agreement with the hydrocarbon investigations. In this connection the table on the cyclisation of the c-atom-chain of the hydrocarbon C_{28} (fig.9) should be recalled. With respect to the viscosity-temperature characteristics there are only slight differences between the esters of methyladipic acid and adipic acid, the low temperature properties of the former, however, are appreciably better in some points. The cyclo-hexanol ester of methyladipic acid is of particular technical interest. It is used as a lubricant for clocks because it has the property of not spreading on metal surfaces but of remaining stable as drops. It is also used as an additive to our "aviation pressure oil".

The following

fig. 14, 57092

gives more detailed information about the effect of the methyl group in dicarboxylic acid. Compare the n-octanol and n-dodecanol esters of α and β methyladipic acids on the one hand and the corresponding esters of adipic acid on the other. Note that the viscosity-temperature characteristics of α -methyl-adipic acid are always somewhat less favourable than those of the β methyladipic acid. This is a beautiful illustration of the importance of the position of a side chain in the molecule. If the acids are esterified with branched alcohols, such as for example our Lenna alcohols or the oxy-alcohols obtained by oxidation of di-iso-butylene, esters are produced which have excellent low temperature properties. The esters of sebacic acid are particularly remarkable in this connection; they combine a good setting point with excellent viscosity-temperature characteristics, and thus are superior to adipic acid. The ester of β -methyl-adipic acid with Lenna alcohol is used in the production of low-temperature-resistant engine and axle oils. Some have also been found to be suitable as softeners for Igelit.

The following

fig. 15, 57096

represents the effect of an increase in the size of the molecule on the viscosity-temperature charactersitics. Polyhydric alcohols have been esterified with normal octylic acid on the one hand and on the other with a long chain semi-ester of adipic acid and the Lenna alcohol fraction from 140 - 180, i.e. mainly C_6- and C_7- alcohols. It is seen that the viscosity of the latter esters is considerably higher than that of the ester of n-octylic acid. As the branched Lenna alcohols have been used to make up the semi-ester it goes without saying that the low temperature properties of this ester are excellent; this is shown by the setting points. The lubricating quality of esters of this type is also very good. They have been put to practical use as cutting oils. The straight chain in a molecule may also be enlarged by ethoxylising an alcohol.

The result of the investigation of this question has been represented in the following

fig. 16, 57095

The iso-C_9-alcohol mixture obtained by oxidation of di-isobutylene was taken first. The ethoxylation was performed by passing ethylene oxide into the anhydrous alcohols. Here it is important that all alcohol-molecules should take up equal amounts of ethylene oxide. Such uniform distribution of the ethylene oxide was achieved only when boron fluoride was used as a catalyst. From the above fig. 16 it is seen that the viscosity rises and that the viscosity-temperature characteristics improve with increasing content of ethylene oxide. The low temperature properties on the other hand deteriorate with further additions of ethylene oxide. It is very interesting to make a comparison between the esters of Leuna alcohol (treated with ethylene oxide) and adipic, methyl adipic and sebacic acids. The low temperature properties of these three esters are identical; the viscosity rises and the viscosity-temperature-characteristics improve in the order adipic, methyladipic and sebacic acid. Here again the sebacic acid ester is the more favourable one. Unfortunately these esters have the disadvantage of being less miscible or losing their miscibility with special hydrocarbon oils when they contain much ethylene oxide. One must not add more than one molecule of ethylene oxide; if two molecules of oxide are added the miscibility of the esters with hydrocarbon oils has already disappeared at room temperature. At higher temperatures, however, e.g. 80°, this ester becomes completely miscible. With still more molecules of oxide the miscibility disappears even at higher temperatures.

In this way we had to some extent become acquainted with the relations existing between the constitution and the viscosity properties of an ester. We now started to investigate the connection between constitution and lubricating quality. In this work we employed an apparatus developed at the Technical Test stand Oppau, the so-called chain apparatus as shown in

fig. 17, 1105

this consists of a chain loaded by weights and pressed against the drum from below along half the latter's circumference. Chain and drum are immersed in the oil under test; the oil may be heated by an electric heater. When the drum is rotated the chain is carried with it, to a greater or smaller extent depending on the lubricating quality of the oil, and thus produces a corresponding deflection of the balance. As the contact between chain and drum is confined to the single points of the members of the chain and as the peripheral velocity is kept very low the instrument works in the region of boundary lubrication.

The next

fig 18, 57134

shows some results of the measurements made with this apparatus. The curves 1, 2 and 3 give data measured for esters of adipic acid and the straight chain alcohols Butanol, octanol and Dodecanol. It is seen that as the molecular weight rises the coefficients of friction fall and the dependence of the coefficients of friction on the temperature becomes more and more favourable. If, in these esters, the adipic acid is replaced by methyladipic acid, thus giving esters 4 and 5, it will be seen that the coefficient of friction of the methyladipic acid ester is always higher than that of the corresponding adipic acid ester. This effect of the methyl group is found to be confirmed in the next figure 19, 57133

by comparing the esters 2 and 6 as well as 6 and 7. The right half of the figure is of interest; here the wear given by the esters has been measured on a hard metal plate which was pressed against a steel plate. It is seen here that the ester with the highest coefficient of friction gives the smallest wear.

The same result is exhibited by the following

fig. 20, 57131

where the esters of dihydric glycols have been compared. The ester with the longest chain of C atoms has the lowest coefficient of friction. This ester on the other hand produces the greatest wear.

The following

fig. 21, 57132

once again shows the considerable fall in the coefficient of friction with constant (sic.? transl.) molecular weight of the ester. No.25 should be compared with 11, 12, 13 and 16. The temperature dependence improves similarly. For ester 16 one can even observe a small decrease in the coefficient of friction with rising temperature. A comparison of 11 and 12 is also remarkable. The branched acid again has the higher coefficient of friction and its coefficient of friction is more dependent on temperature. Furthermore it is interesting that incomplete esterification causes only little deterioration in the coefficient of friction and has no effect on the temperature dependence; thus compare 17 and 13. The order of the esters in wear tests is again the inverse of the order in friction measurements. For esters of even higher mol. wt. as shown in

fig. 22, 57130

it is again confirmed that the coefficient of friction decreases and that the μ - temperature curve flattens out as the molecular weight rises.

This interesting inversion of the grading with respect to lubricating quality, as given by the coefficient of friction, and the wear is explained by the force with which the molecules are bound to the surface. The work which must be expended in order to tear off from the boundary face a liquid of 1 cm^2 cross sectional area is called the work of adhesion. It can be determined by measuring the boundary face tension and the surface tension of the boundary face partners. In this case one can apply Duprée's equation: $H = b_1+b_2 - 12$.

Following my suggestion, Prof. Wolff at Halle has examined many substances with respect to the work of adhesion. Some results of this investigation are shown in the following

fig. 23, 57101

Of the behaviour of hydrocarbons that of benzene is interesting; benzene is bound more strongly to mercury than its product of hydrogenation, cyclohexane. In the series of alcohols one observes an increase in the work of adhesion with increasing length of the carbon chain. It is remarkable that branching of the C chain produces a fall in the work of adhesion.

For acids the work of adhesion is quite independent of the size of the molecule. This is probably due to the dimeric molecular association which is present in all acids. Only formic acid forms association molecules of order higher than 2. For esters, just as for alcohols, one observes an increase of the work of adhesion with rising molecular weight of the alcohol. Here it is remarkable that when branching occurs in the C chain of the alcohol this causes an increase in the work of adhesion. This difference in the behaviour as compared to pure alcohols is probably due to the arrangement of the molecules on the boundary face. There are two possibilities: either the C - chains are arranged at right angles to the boundary face or they are tangential to it. The question of which arrangement is preferred by the various materials depends on the one hand on the steric position of the dipole group (polar group ?trans.) in the molecule and on the other on the position and magnitude of the permanent dipole within the group.

Naturally, the work of adhesion is dependent not only on the lubricant but also on the partner making up the interface. In the next

fig. 24 (57087)

the differences in the work of adhesion for an aqueous and a metallic boundary face have been tabulated. The large differences existing between water and mercury are shown. On the average substances adhere to mercury two to three times as strongly as to water. From the work of adhesion one may then calculate the adhesive strength. The next

fig.25, 57085

shows the corresponding values for hydrocarbons, alcohols and acids. Again one can observe an increase in the adhesive strength; with an increase in the unsaturated character, for hydrocarbons; with an increase in the length of the C-chain, for alcohols; and in the case of acids an adhesion strength independent of the size of the molecule. These adhesive strengths which give a measure of the force necessary to tear off from the boundary face a cross-sectional area of 1 cm^2 correspond to the tensile strength obtaining in the bulk of the metal or liquid. The tensile strengths are calculated from the values of the boundary face tensions. The tensile strength $H_z = 20$. The magnitude of these values in the case of liquids is striking. To tear a liquid organic acid requires the same force, sometimes even a greater force as tearing a metal such as brass or iron. This fact immediately explains the inversion of the friction and wear characteristics. The larger the adhesive strength of a lubricant the greater is the carrying capacity of the lubricating layer and the smaller therefore is the coefficient of friction; the larger however should be the force with which a lubricant molecule can tear out a metal atom from its boundary face. When we want to minimise the wear in the development of lubricants we must not strive to obtain substances of very high (?) adhesive strengths but must try to obtain a certain optimum. In order to approach the latter we must not pay too much attention to the dipole forces of the molecule but rather to the dispersive forces of the molecule which depend on the specific quantum bonding in the C-atom chain.

Not only the lubricant is, however, responsible for the wear. The other boundary face partner also affects this value. The next

fig. 26, 1412

shows the difference in the wear properties of various metals lubricated with the same substances. A certain substance such as for instance the polyether alcohol LK 2200 may cause very little wear on red brass; on soft metals it may produce so much wear that one could almost speak of the alcohol dissolving the soft metal. A pure mineral oil, such as e.g. K 7, also produces very different effects on different metals.

These differences in the behaviour of oils with different metals, are of course also observed in lubrication proper.

~~If in the next~~

fig. 27 (1180)

one regards the various states of lubrication of a plain bearing, one again notices the effect of the chemical constitution of the lubricant in that region in which the totational speed is low and where the load is correspondingly high. This is the region of partial and boundary lubrication.

The following

figs. 28 (57156), 29 (57157), 30 (57158)

represent the differences in the behaviour of various bearing metals in contact with the same oil in the state of boundary lubrication. The experiments were carried out by Prof. Heidebroek at Dresden. You will see how, depending on the nature of the bearing substance, the position of the point of transition from full (hydrodynamic) to boundary lubrication at constant load is a function of the nature of the material. One is dealing here with the activity of the forces at the boundary face extending over thicker layers of the liquid. The presumption that the boundary must have an orientative effect on deeper layers gains further likelihood from the comparison made in the next

fig. 31 (57159)

between the effects of two different bearing bushes for the same oil. It is seen that for a given bearing play, different oil pressures have to be applied, depending on the nature of the bearing material, for a flow of a given quantity of oil in unit time.

Apart from the forces originating at the surface the state of lubrication is affected by other factors which are due to the structure of the liquid.

The next

fig. 32 (57097)

shows some data obtained by Prof. Heidebroek on a gear wheel test instrument. This test instrument consists of two carefully mounted gear wheels; a piezo-quartz is built into the bearings of these wheels; by this means the slightest vibrations originating in the non-uniformities of the tooth-flanks may be registered on an oscillograph. In this instrument the tooth-flanks are lubricated with exactly 1 cc of lubricant. The time is now measured which elapses before the lubricating layer fails; this point is characterised by the occurrence of marks of oxidative corrosion (so-called frictional oxidation) on the tooth-flanks. The vibrations of the gear wheel are also registered and the amplitude of these vibrations is measured. In the figure seven oils have been investigated which differ in viscosity and chemical constitution. It is seen that the life, i.e. the time which elapses before frictional oxidation occurs, differs widely and that it is unrelated to the value of the viscosity. The same applies to the amplitude of vibration of the oils 13, 14 and 15. These three are esters: 13 is a poly-butylene glycol; 14 is a polyester of 2 mols. trimethylolethane and 1 mol. adipic acid esterified with Lenna-carboxylic acid; 15 is the same polyester in which the Lenna-carboxylic acid has been substituted by the soap acids (Seifenfettsäure) from the paraffin oxidation at Oppau. It is seen that 1 cc of ester 14 has an extremely long lubrication life whereas ester 15 is distinguished by a very small amplitude in its vibration oscillogram. This ester therefore ensures very quiet run of the gears. Oils 5, 6 and 7 are high-molecular ethylene polymers having a considerably higher viscosity than ester 15; all the same its vibrational amplitudes are twice as large as those of the ester 15 which is considerably more fluid. The value of the viscosity, i.e. the size of the molecule has thus no effect on the quiet running of gears. It is the structure of the molecule that matters. Oil 15 is a voltolized, compounded oil whose lubricating properties in the plain bearings are much praised. It does not offer any advantage for roller bearings.

The following

fig. 33 (57094)

shows the oscillograms of the oils mentioned above. One can very clearly recognise the nice quiet run of ester No.15 as compared to the irregular run of the voltolized compounded oil No.12 which has a viscosity seven times greater than No.15. We have succeeded in regulating the polymerisation of ethylene in such a way that one obtains polymers which have the same properties as the ester No.15 viz. they damp the vibrations and therefore reduce noise.

In the following

fig. 34 (57161)

we show you some results of sound measurements which were undertaken by Krupp with an oil of the above type. The effect of a damping oil of this type on the friction behaviour of a plain bearing is very interesting. The same oil which had been examined by Krupp was now studied in a plain bearing by Prof. Heidebroek. The following

fig. 35 (57154)

represents the result of this investigation. Oil K I is our damping oil. Oil K II is also an ethylene polymer of low viscosity. The completely different behaviour of oil K I is very well exhibited; it maintains the state of full (hydrodynamic) lubrication even at the smallest velocities. In the lower half of the figure it is shown that mixtures of oils K I and K II may be prepared which avoid the state of boundary lubrication even at small velocities. The next

fig. 36 (57155)

shows the effect of temperature on the friction behaviour of a plain bearing. The friction falls as the temperature rises because the viscosity is lowered. It is important that oil K I does not lead to boundary lubrication even at very small velocities, as shown by the lower figure.

The effect of temperature on the friction behaviour, as on lubrication generally, has confronted us in the last two years of war with a multitude of technical problems. The first of these problems was the lubrication of weapons at the very low temperatures which occur at the very great altitudes of the Air Force. In the next

fig. 37 (51026)

I show you the effect of the value of viscosity on the locking of an air force machine gun at very low temperatures. The task which we had been set here, was the production of thin oils which would make it possible to start a machine gun at -60° at its full firing rate. We achieved this, as shown in figure, with oils 494 and 495. For this purpose we had to look for substances which, while having a very low viscosity, would take up the high pressures of the various bearing points. In the following

fig. 38 (51027)

I show you the connection between the chemical constitution of various substances and their viscosities as well as their lubricating efficiency in machine guns. This efficiency is characterised firstly by the time taken to fire 50 shots and secondly by the number of shots that may be fired for a single lubrication of the gun. It will be seen that velocity of firing and total number of shots differ widely, depending on the structure of the various substances. The last substance No.442 provided the solution of the problem. This substance is obtained if one allows sulphur monochloride to react with the xanthate of amyl alcohol. The product is a golden-yellow oil which contains about 50% sulphur; it is, so to speak, liquified sulphur. It has not only done valuable service in the field of lubrication but it has also been applied in the field of lacquers. For caoutchouc lacquers, so-called "Pervinan"-lacquers there existed the problem of producing vulcanisable, liquid and easily applied lacquers. As the above product, called Nesulfol, is soluble in all lacquer solvents and as it decomposes when the lacquers are burnt in, with the liberation of highly reactive sulphur the latter is then available to vulcanise the Pervinan. At this point it should be remarked that it was a very happy idea of Dir. Dr. Giesen's to join a lacquer laboratory on to the lubricant laboratory. Both fields belong to the range of application of boundary face - research and of the investigation of the structure and properties of liquids.

The action of the Nesulfol in the lubrication of machine guns is shown in the next

fig. 39 (51025)

The difference in the effects of Nesulfol in esters and hydrocarbon oils is remarkable. 463 and 469 should be compared. In order to attain an equally good shot efficiency the hydrocarbon oil requires a larger addition of sulphur, as shown by comparing 469 and 495. For the purpose of its technical application we consequently had to choose a 1 : 1 mixture of hydrocarbon and ester. This product has been increasingly used by the Air Force since January 1941. We started with a monthly output of 5 tons and are today producing 50 tons per month.

We found a second field of application for our esters in the Reichsbahn. Here it was a question of developing axle oils for the east which would resist low temperatures i.e. developing axle oils which would possess a good absorbability in the lubrication pad (Polstor) of goods waggons at -40°C. Free lubrication of the axle bush bearing and with it the downward velocity of the waggons from the shunting incline of goods stations depend on a good suction efficiency of the lubrication pads of the waggons which are made from artificial silk fibres. If in winter the goods waggon does not cover the required rail distance the marshalling of goods waggons would require a large locomotive park which cannot be provided for this purpose. The axle oils which had so far been used by the Reichsbahn had been made from the by-products of petroleum refining. The next

fig. 40 (50764)

shows the composition of mineral axle oils. It is seen that they contain only 50 - 60% of proper lubricating oil hydrocarbons. The rest is made up of undesirable foreign bodies of varying composition.

Fig. 41 (50765)

shows the viscosity temperature characteristics of those oils. One can see the large differences in the value of the viscosities at -20 and -30°. By comparing the mixtures of oils amongst each other, e.g. 6 and 7 or 8, 9 and 10, one can also see that they have a very strong mutual influence on each other. First we tried to make the oils thinner by adding an ester and thus improving their low temperature properties. In this way it was indeed possible to reduce the low temperature viscosity very strongly but the suction into the lubrication pad could not be improved sufficiently by this means as is shown by the

fig. 42 (54694)

Addition of gas oil is better in this respect. This is especially shown by the suction at -10°. The effect of the gas oil is based on its good solvent power for paraffins and the other foreign bodies such as resins and asphalts, a property which the esters do not possess. In the temperature range, however, in which esters are miscible with hydrocarbons and the other substances, their high capillary forces become noticeable, as is particularly shown by the high absorbability at +50°. We have now solved the problem by blending 40 parts of an adipic acid ester with about 60 parts of a synthetic hydrocarbon oil. This mixture was quite homogeneous even at low temperatures. This is demonstrated by the linear course of the viscosity-temperature curve of our Y axle oil in the next

fig. 43 (57100)

as opposed to that of the natural axle oil. The necessary hydrocarbon components are produced by us by a second polymerisation of those hydrocarbons which are formed when the aluminium chloride sludge of the SS 906 production is decomposed. According to a decision of last March by Reichsminister Dr. Dorpmüller the whole rolling stock of the German Reichsbahn has to change over to this oil by 1945. This change-over will mean that about 50,000 tons/year of petroleum products of the German petroleum industry will be available for other uses.

I come finally to the most important field of application of synthesis viz. engine lubrication which has been the starting point of all our researches. The following

fig. 44 (46841)

shows the effect of a 25% addition of ester to a hydrocarbon aero engine oil. First one can observe the increase in the running time due to the addition of ester, secondly one observes the strong fall in piston ring wear.

Fig. 45 (45115)

shows that in the case of the synthetic oil No. SS 904 also a considerable improvement in the running time of the engine may be achieved by the addition of ester.

It is important however that even in the ester tests an inhibitor be present. This is made plain by comparing tests 475 and 580. We found the importance of the addition of inhibitors from engine tests alone about 8 years ago. It is only recently that we have succeeded in getting some more detailed information on their action.

The following

fig. 46 (57099)

shows the effect of oxygen on our synthetic oil SS 906. These experiments, begun by Dr. Fiedler and now being continued by Dr. Raichle, demonstrate that the oil SS 906 takes up oxygen with formation of peroxides. Simultaneously the iodine number falls as the content of peroxide rises, the acid number rises and the viscosity rises very strongly. The latter phenomenon in particular is very unwelcome when one has the task of developing a low temperature resistant oil which must not change its viscosity during use. For if such an increase in the viscosity occurs during use i.e. through oxidation, the low temperature resistance is thereby lost. We thus had to look for substances which avoid or diminish the cause of this thickening i.e. the formation of peroxides. In silver we found a substance which, though it does not prevent it completely, yet it very much diminishes the assimilation of oxygen and therefore the formation of peroxides. This is shown in

fig. 47 (57093)

We use silver in the form of a salt of D: Isobutylene-phenol-sulphide. The investigation showed that not all organic silver compounds are equally effective.

Fig. 48 (57091)

represents the increase in the viscosity due to oxidation as a function of the inhibitor content. It is seen that an addition of 0.2% of inhibitor roughly halves the viscosity increase. In the engine test carried out with this inhibitor the running time was improved by 100% and the formation of lacquer on the surface of the piston was also considerably reduced. The increase in the viscosity of the oil during use was also strongly lowered. In the results of the engine test the lowering of the lacquer formation is particular importance. We know that these lacquers contain a high proportion of oxygen. Now we can presume that their formation is primarily due to the peroxide effect. The end effect of this reduction of the lacquer formation is that the overhaul period of engines may be lengthened which amounts to a saving of ground personnel.

One aim of lubrication research must be to develop oils which cause no impurities to be deposited anywhere in the mechanism. Such oils would then be regarded as constructional elements of the engine. Research on inhibitors, which is part of the field of organic catalysis, may here have results of decisive military importance.

The next

fig. 49 (52270)

shows the present position in the development of a low-temperature aero-engine oil. It must be the aim of this development to produce an oil with no more than 2000°E at -40°. The next fig. 50 (57162)

represents the present position in the development of automobile oils. The problem set to us by the automobile industry, a solution to which we must strive to attain, is the production of an oil with a maximum viscosity of 1000°E at -40°. The following

fig. 51

represents the connection between the viscosity-temperature characteristics and the adhesive strength. The adhesive strength is a measure of the force required to set in motion a shaft resting in oil at low temperatures. It is measured in an apparatus developed by the Technical Test Stand Oppau and generally introduced by the Air Force. In the figure one can observe that the adhesive strength increases strongly with increase in the viscosity. If it is desired to reach the low values of the adhesive strength which are found for more fluid oils even for oils of higher viscosity then a great improvement in the viscosity-temperature characteristics, expressed in terms of the direction factor m, becomes necessary. Values of m of 3 and less must be obtained. At the present time they lie about 3.2. In the following

fig. 52 (57160)

I show you the corresponding values of the adhesive strength of our present automobile oils. One can see that at -35° this has the same adhesive strength as the best mineral Winter oil of the Wehrmacht. Thus we have already come very near to our appointed aim. All these problems of development are made more difficult in time of war because the quantity of raw materials necessary for the solution of the problems is getting more and more scarce. Thus we had to devote some of our synthesis work to the solution of raw material problems. Recently this has resulted in our taking up the work which we began in 1930 on mixed polymerisation . At that time we were able to show that the lubricating oil fraction of a petroleum freed from paraffin, asphalt and resin may be refined by bringing into contact with the crude polymers with aluminium chloride content from the paraffin -crack -product polymers(isation ?). The reactive hydrocarbons present in the mineral oil then react with the paraffin -crack -product polymers. Under these conditions the mineral oil hydrocarbons are alkylated, polymerised and isomerised. A mixed polymer product is obtained. It is shown in the following

fig. 53 (45174)

that this has better properties in the engine than the purely physical mixture of the synthetic product and the refined mineral oil. During the last year we have applied the same method to the polymerisation of ethylene and we have had the same success. We are now planning the construction of a refinery at Moosbierbaum where the combination of the refining of natural products with that of synthetic products is to be put into practice on a large scale. In this way the method discovered and patented in 1930 is finally being applied in practice. In connection with the construction of the Donau refinery we also have the hope that this unification of nature and synthesis should not remain confined to the field of lubrication but that the two will there join hands also in the field of fuels thus more and more perfecting the utilisation of natural products. In the following final figure, I should like to show up the influence lubrication research has so far had on the shape of the production of our organic division. In this

fig. 54 (57173)

you can see that for all but two products of our department an application has been found in the field of lubrication.

The "arch play" is ended. Systematic purposeful research work has weaned the lubricants off their deceitful moods. For the future, let us hope that it may be possible to continue the research and development work as before: it has contributed to the welfare of the Fatherland; many military problems have found their solutions only through this work.

Fig. 1

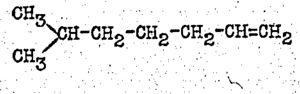
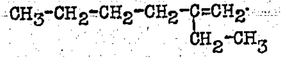
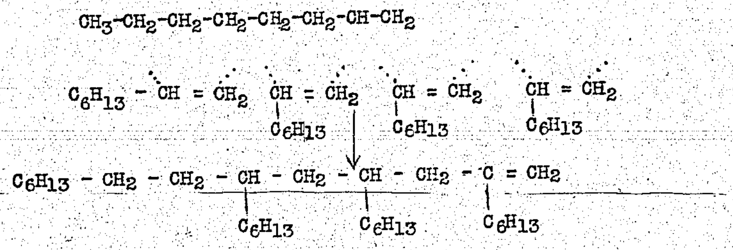
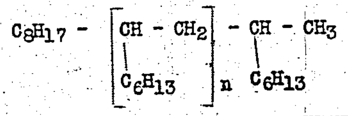
	Olefin	Yield	Viscosity 38°	99°	V.I.
C_7	$CH_3-CH_2-CH_2-CH_2-CH_2-CH=CH_2$	85%	34.4	2.91	99
	$CH_3-CH_2-CH_2-CH=CH-CH_2-CH_3$	45%	5.60	1.42	24
	$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH=CH_2$	70%	38.7	3.56	114
C_8	 $(CH_3)_2CH-CH_2-CH_2-CH_2-CH=CH_2$	85%	387	13.20	98
	 $CH_3-CH_2-CH_2-CH_2-\underset{CH_2-CH_3}{\underset{\mid}{C}}=CH_2$	58%	6.16	1.42	14

Fig.2

Polymerisation diagram of n-octylene

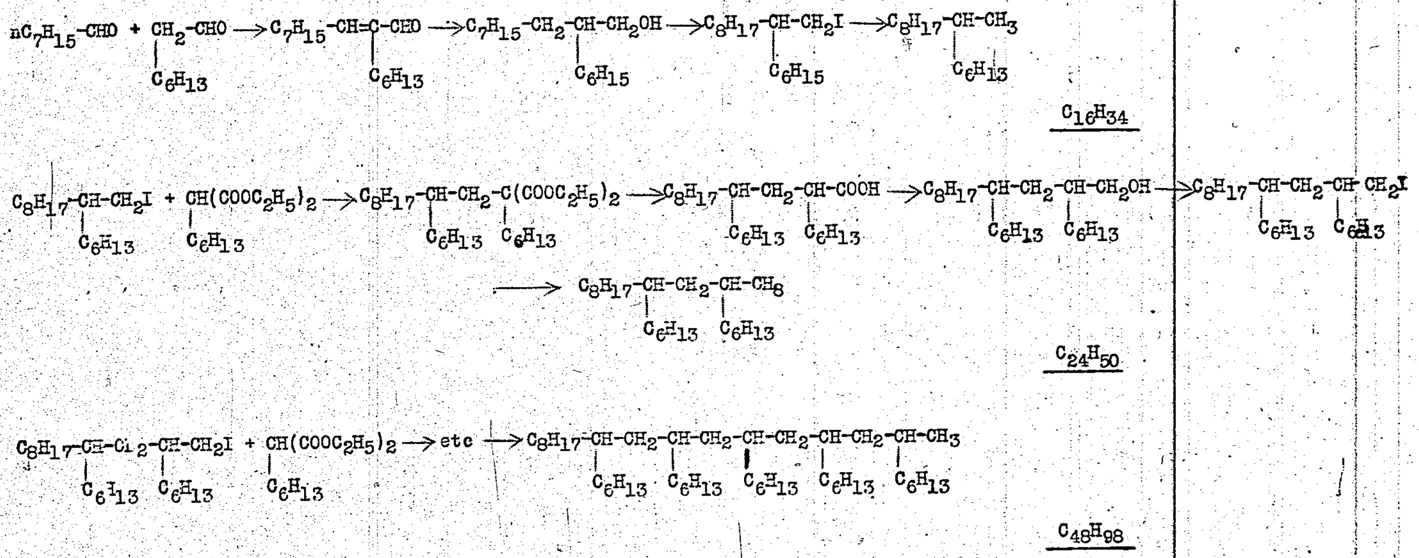


Reaction diagram of the synthesis of hydrocarbons of the general formula:



$$C_8H_{17}-\left[\underset{C_6H_{13}}{\underset{|}{CH}}-CH_2\right]_n-\underset{C_6H_{13}}{\underset{|}{CH}}-CH_3$$

Fig.3



$$nC_7H_{15}-CHO+\underset{C_6H_{13}}{\underset{|}{CH_2}}-CHO\longrightarrow C_7H_{15}-CH=\underset{C_6H_{13}}{\underset{|}{C}}-CHO\longrightarrow C_7H_{15}-CH_2-\underset{C_6H_{15}}{\underset{|}{CH}}-CH_2OH\longrightarrow C_8H_{17}-\underset{C_6H_{15}}{\underset{|}{CH}}-CH_2I\longrightarrow C_8H_{17}-\underset{C_6H_{13}}{\underset{|}{CH}}-CH_3$$

$C_{16}H_{34}$

$$C_8H_{17}-\underset{C_6H_{13}}{\underset{|}{CH}}-CH_2I+\underset{C_6H_{13}}{\underset{|}{CH}}(COOC_2H_5)_2\longrightarrow C_8H_{17}-\underset{C_6H_{13}}{\underset{|}{CH}}-CH_2-\underset{C_6H_{13}}{\underset{|}{C}}(COOC_2H_5)_2\longrightarrow C_8H_{17}-\underset{C_6H_{13}}{\underset{|}{CH}}-CH_2-\underset{C_6H_{13}}{\underset{|}{CH}}-COOH\longrightarrow C_8H_{17}-\underset{C_6H_{13}}{\underset{|}{CH}}-CH_2-\underset{C_6H_{13}}{\underset{|}{CH}}-CH_2OH\longrightarrow C_8H_{17}-\underset{C_6H_{13}}{\underset{|}{CH}}-CH_2-\underset{C_6H_{13}}{\underset{|}{CH}}\ CH_2I$$

$$\longrightarrow C_8H_{17}-\underset{C_6H_{13}}{\underset{|}{CH}}-CH_2-\underset{C_6H_{13}}{\underset{|}{CH}}-CH_3$$

$C_{24}H_{50}$

$$C_8H_{17}-\underset{C_6H_{13}}{\underset{|}{CH}}-CH_2-\underset{C_6H_{13}}{\underset{|}{CH}}-CH_2I+\underset{C_6H_{13}}{\underset{|}{CH}}(COOC_2H_5)_2\longrightarrow etc\longrightarrow C_8H_{17}-\underset{C_6H_{13}}{\underset{|}{CH}}-CH_2-\underset{C_6H_{13}}{\underset{|}{CH}}-CH_2-\underset{C_6H_{13}}{\underset{|}{CH}}-CH_2-\underset{C_6H_{13}}{\underset{|}{CH}}-CH_2-\underset{C_6H_{13}}{\underset{|}{CH}}-CH_3$$

$C_{48}H_{98}$

Fig.4

57088

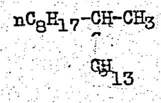
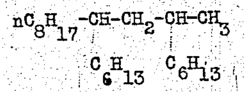
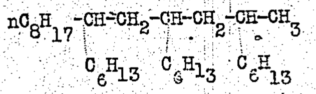
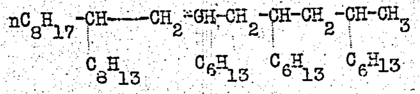
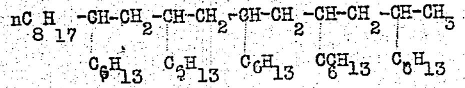
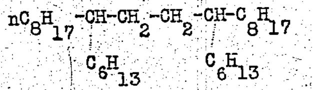
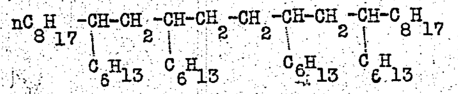
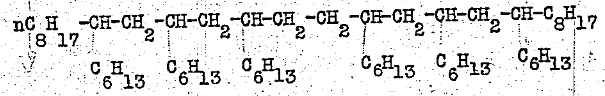
Nr	Formula	Mol Wt		Spec Wt. 20°C	Viscosity in c.St at 20	38	0	99	m.	Pole ht.	V.I	MPT .C
1.	$C_{16}H_{34}$	226	 $nC_8H_{17}-\underset{C_6H_{13}}{CH}-CH_3$	0.7738	4.20	2.92	2.30	1.28	3.32	0.1	–	. .
2.	$C_{24}H_{50}$	33	 $nC_8H_{17}-\underset{C_6H_{13}}{CH}-CH_2-\underset{C_6H_{13}}{CH}-CH_3$	0.8000	15.8	8.60	6.14	2.31	3.79	1.14	123	c.a.?
3.	$C_{32}H_{66}$	252	 $nC_8H_{17}-\underset{C_6H_{13}}{CH}-CH_2-\underset{C_6H_{13}}{CH}-CH_2-\underset{C_6H_{13}}{CH}-CH_3$	0.8115	38,56	18.50	12.1	3.74	3.71	1.22	118	c.a.?
4.	$C_{48}H_{82}$?	562	 $nC_8H_{17}-\underset{C_8H_{13}}{CH}-CH_2-\underset{C_6H_{13}}{CH}-CH_2-\underset{C_6H_{13}}{CH}-CH_2-\underset{C_6H_{13}}{CH}-CH_3$	0.8195	72.43	31.9	20.8	5.80	3.44	1.40	136	c.a. ?
5.	$C_{48}H_{98}$	674	 $nC_8H_{17}-\underset{C_6H_{13}}{CH}-CH_2-\underset{C_6H_{13}}{CH}-CH_2-\underset{C_6H_{13}}{CH}-CH_2-\underset{C_6H_{13}}{CH}-CH_2-\underset{C_6H_{13}}{CH}-CH_3$	0.8225	114.4	49.14	29.3	7.49	3.39	1.48	124	c.a. ?
6.	$C_{32}H_{66}$	450	 $nC_8H_{17}-\underset{C_6H_{13}}{CH}-CH_2-CH_2-\underset{C_6H_{13}}{CH}-C_8H_{17}$	0.8133	36.12	17.40	11.8	3.74	3.64	1.36	134	c.a. ?
7.	$C_{48}H_{98}$	674	 $nC_8H_{17}-\underset{C_6H_{13}}{CH}-CH_2-\underset{C_6H_{13}}{CH}-CH_2-CH_2-\underset{C_6H_{13}}{CH}-CH_2-\underset{C_6H_{13}}{CH}-C_8H_{17}$	0.8261	121.2	50.8	32	8.10	3.33	1.44	133	c.a. ?
8.	C_6H_{13}	899	 $nC_8H_{17}-\underset{C_6H_{13}}{CH}-CH_2-\underset{C_6H_{13}}{CH}-CH_2-\underset{C_6H_{13}}{CH}-CH_2-CH_2-\underset{C_6H_{13}}{CH}-CH_2-\underset{C_6H_{13}}{CH}-CH_2-\underset{C_6H_{13}}{CH}-C_8H_{17}$	0.8329	253.9	101	60	13.14	3.11	1.41	127	c.a. ?

Fig.5 57080

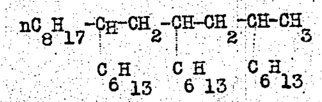
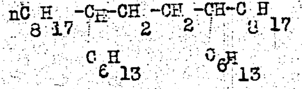
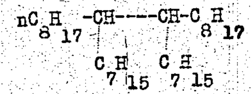
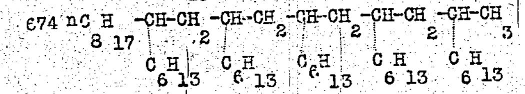
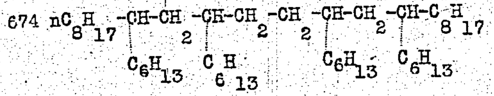
Nr	Formula	Mol. Wt.		Spec Wt.	Viscosity in c.St. at °C					Pole ht.	V.I.	M.Pt. °C
				20°C	20	38	50	99	m.			
1.	$C_{32}H_{66}$	450	 $nC_8H_{17}-\underset{C_6H_{13}}{CH}-CH_2-\underset{C_6H_{13}}{CH}-CH_2-\underset{C_6H_{13}}{CH}-CH_3$	0.8115	38.56	18.50	12.1	3.74	3.71	1.42	118	ca-80
2.	$C_{32}H_{66}$	450	 $nC_8H_{17}-\underset{C_6H_{13}}{CH}-CH_2-CH_2-\underset{C_6H_{13}}{CH}-C_8H_{17}$	0.8113	36.12	17.46	11.8	3.74	3.64	1.36	134	ca-20
3.	$C_{32}H_{66}$	450	 $nC_8H_{17}-\underset{C_7H_{15}}{CH}----\underset{C_7H_{15}}{CH}-C_8H_{17}$	0.8140	35.77	17.55	12.3	3.89	3.51	1.26	149	ca-80
4.	$C_{48}H_{98}$	674	 $nC_8H_{17}-\underset{C_6H_{13}}{CH}-CH_2-\underset{C_6H_{13}}{CH}-CH_2-\underset{C_6H_{13}}{CH}-CH_2-\underset{C_6H_{13}}{CH}-CH_2-\underset{C_6H_{13}}{CH}-CH_3$	0.8225	114.4	49.14	29.3	7.49	3.39	1.48	124	ca-60
5.	$C_{48}H_{98}$	674	 $nC_8H_{17}-\underset{C_6H_{13}}{CH}-CH_2-\underset{C_6H_{13}}{CH}-CH_2-CH_2-\underset{C_6H_{13}}{CH}-CH_2-\underset{C_6H_{13}}{CH}-C_8H_{17}$	0.8261	121.2	50.8	32	8.10	3.33	1.44	133	ca-50
6.	$C_{48}H_{98}$	674	$nC_{12}H_{25}-CH-CH_2-CH_2-CH-C_{12}H_{25}$	0.8032_{50}/	(94)	(42.5)	27.66	7.68	3.17	1.23	147	solid

Figure ~~23~~ 6

57101

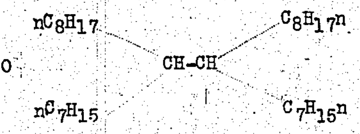
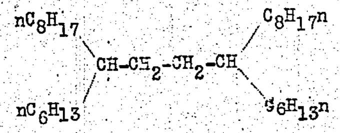
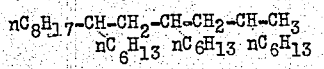
Nr	Formula	Mol Wt.		Spec Wt	Viscosity in c.St at °C					Pole		Molt Point.
				20° c	20	38	50	99	m.	ht.	VI.	°C
1.	$C_{32}H_{66}$	450	$CH_3-(CH_2)_{30}-CH_3$	0.776/75(37)		(20.3)	(14.4)	5.20	2.96	0.86	187	-70.5
2.	$C_{32}H_{66}$	450		0.8140	35.77	17.55	12.2	3.89	3.54	1.26	149	ca-80
3.	$C_{32}H_{66}$	450		0.8133	36.12	17.46	11.8	3.74	5.64	1.37	134	ca-20
4.	$C_{32}H_{66}$	450	 $nC_8H_{17}-\underset{nC_6H_{13}}{CH}-CH_2-\underset{nC_6H_{13}}{CH}-CH_2-\underset{nC_6H_{13}}{CH}-CH_3$	0.8115	38.56	18.50	12.1	3.74	3.71	1.42	118	ca-80
5.	$C_{32}H_{66}$	450	$(nC_5H_{11})_3\equiv C-C\equiv(nC_5H_{11})_3$	0.8204	78.96	31.6	19.5	4.90	3.85	1.96	86	ca-^{5}0

Fig. ~~8~~ 7 57084

	Formula	Mol wt.		Spec. wt. 20°C	Viscosity in cSt at °C 20	38	50	99	m	Pole ht.	V.I.	Melt. point
1	$C_{16}H_{34}$	226	$CH_3-(CH_2)_{14}-CH_3$	0.7733	4.39	2.94	2.42	1.30	3.34	0.1	-	18
2	$C_{16}H_{34}$	226	n $C_8H_{17}-\underset{CH_3}{CH}-C_6H_{13}$	0.7738	4.20	2.92	2.30	1.28	3.32	0.1	-	-36.8
3	$C_{16}H_{34}$	226	n $C_6H_{13}-\underset{CH_3}{CH}-\underset{CH_3}{CH}-C_6H_{13}$	0.7811	4.22	2.78	2.21	1.23	3.45	0.1	-	ca-80
4	$C_{16}H_{34}$	226	n $C_4H_9-\underset{C_2H_5}{CH}-CH_2-CH_2-\underset{C_2H_5}{CH}-C_4H_9$	0.7823	3.70	2.55	2.09	1.10	3.58	0.06	-	ca-80
5	$C_{16}H_{34}$	226	n $C_4H_9-\underset{C_2H_5}{CH}-CH_2-\underset{C_2H_5}{CH}-CH_2-\underset{C_2H_5}{CH}-CH_3$	0.7791	3.58	2.46	2.02	1.07	3.62	0.04	-	ca-88
6	$C_{24}H_{50}$	338	$CH_3-(CH_2)_{22}-CH_3$	0.7746 60	(14.9)	(8.98)	(6.63)	2.81	(3.2)	(0.7)	224	51
7	$C_{24}H_{50}$	338	n $C_6H_{13}-\underset{C_4H_9}{CH}-CH_2-CH_2-\underset{C_4H_9}{CH}-C_6H_{13}$	0.8020	16.96	9.05	6.28	2.32	3.89	1.3	117	ca-66
8	$C_{24}H_{50}$	338	n $C_5H_{11}-\underset{nC_5H_{11}}{CH}-CH_2-CH_2-\underset{nC_5H_{11}}{CH}-C_5H_{11}$a	0.8114	18.09	9.4	6.50	2.34	3.95	1.42	88	-
9	$C_{24}H_{50}$	338	n $C_5H_{11}-\underset{iC_5H_{11}}{CH}-CH_2-CH_2-\underset{iC_5H_{11}}{CH}-C_5H_{11}$a	-	23.2	10.85	7.43	2.41	4.20	2.05	26	-
10	$C_{24}H_{50}$	338	n $C_4H_9-\underset{C_2H_5}{CH}-CH_2-\underset{C_2H_5}{CH}-CH_2-CH_2-\underset{C_2H_5}{CH}-CH_2-\underset{C_2H_5}{CH}-C_4H_9$	0.8119	18.27	9.1	6.28	2.27	4.04	1.58	39	ca-66

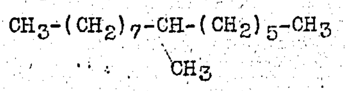
Fig.8 51105.

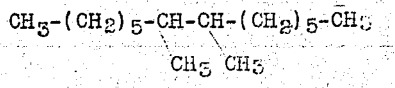
Constitution and Melting Point

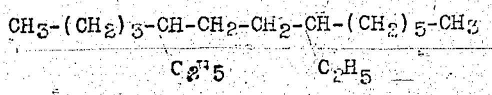
Benzene	+5.5°
Toluene	-95°
Ethylbenzol	-94°
m-Xylol	-54°
o-Xylol	-29°
p-Xylol	+13°

Contane:

$CH_3-(CH_2)_{14}-CH_3$ +18°


$CH_3-(CH_2)_7-\underset{CH_3}{CH}-(CH_2)_5-CH_3$ -39°


$CH_3-(CH_2)_5-\underset{CH_3}{CH}-\underset{CH_3}{CH}-(CH_2)_5-CH_3$ -80°


$CH_3-(CH_2)_3-\underset{C_2H_5}{CH}-CH_2-CH_2-\underset{C_2H_5}{CH}-(CH_2)_5-CH_3$ -80°

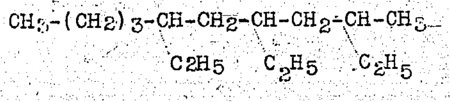

$CH_3-(CH_2)_3-\underset{C_2H_5}{CH}-CH_2-\underset{C_2H_5}{CH}-CH_2-\underset{C_2H_5}{CH}-CH_3$ -88°

Fig.~~7~~ 9

57081

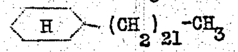
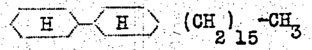
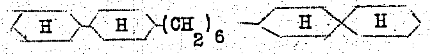
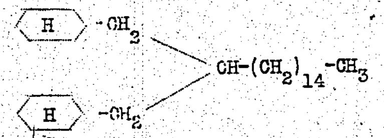
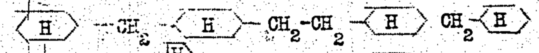
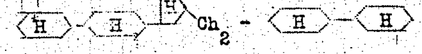
	Formula	Mol Wt		Spec	Viscosity in c.St. at °C				Pole		
				°C	20	38	50	99	m.	Ht.	V.I.
1.	$C_{28}H_{58}$	394	$CH_3(CH2)_{26}-CH_3$	0.9205/20	(22.2)	(12.8)	(9.3)	3.63	3.12	0.8	200
2.	$C_{28}H_{56}$	392		-	(37.3)	19.8	13.6	4.70	3.18	1.0	174
3.	$C_{28}H_{54}$	390		0.8617/40	(97)	(41.4)	26.06	6.65	3.46	1.51	124
4.	$C_{30}H_{54}$	414		0.9929/20	1050	282	140	20.7	3.43	2.01	94
5.	$C_{30}H_{58}$	418		—	68	30.2	18.7	5.16	3.62	1.59	116
6.	$C_{28}H_{50}$	86		0.9187/40	(4700)	(785)	276	21.8	4.18	4.27	-46
7.	$C_{30}H_{52}$	412		0.9448/60	(2.000.000)	(50.000)	(7000)	78	5.03	45.0	—

Figure 10

57089

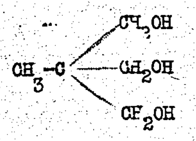
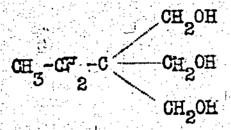
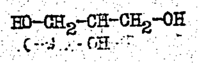
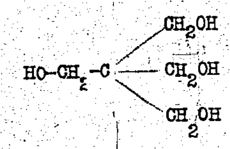
Ester from three and four valent Alcohols		Spec Wt 20°C	Viscosity in c.St. 20	38	50	99	m 20.99	Set Point
	+n-Octylic Acid	0.944	36.20	17.75	11.96	3.86	3.58	-8
	+ " "	0.948	37.00	18.00	12.20	3.86	3.57	-60
 $HO{-}CH_2{-}\underset{OH}{CH}{-}CH_2{-}OH$	" "	0.940	25.34	12.97	8.98	3.20	3.57	-24
	" "	0.959	50.79	23.80	15.69	4.73	3.50	+7
Trimethylolethane	+ i- Octylic Acid 2- Ethyl-hexyl Acid	0.948	49.30	20.90	13.5	3.84	3.88	-63
Trimethylolpropane	+ " " " "	0.948	64.82	26.28	16.09	4.17	4.02	-58
Glycerine	+ " " " "	0.952	40.27	17.39	11.10	3.21	4.11	-66
Pentaerythritol	+ " " " "	0.966	143.7	52.01	29.94	6.37	3.91	-45
Trimethylolethane	+ Leuna- Carboxylic Acid mixture 200/250	0.494	123.0	42.50	24.75	5.57	3.96	-48
Trimethylolpropane	+ " " "	0.958	144.7	50.20	28.60	6.30	3.97	-49
Glycerine	+ " " "	0.954	94.4	34.0	20.7	4.93	3.96	-60

Figure 10

continuation 57080.

Ester from three and four valent Alcohols		Spec Wt.	Viscosity in c.St				m.	Set Point
		20°C	20	36	50	99	20.99	
Pentaerythritol	+ Leuna- Carboxylic Acid mixture 200/250	0.961	453.0	117.2	66 5	10.46	3.88	-31