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2. Supply and Composition of Aviation Gasolines (a)(Cont'd.)

TABLE I (Continued)

Company and Location	Total Aviation Components	Base Stocks & Aromatics	Synthetic Isoparaffins
I.G. - Oppau	1,200	1,100	100
I.G. - Heydebrek	600	300	300
I.G. - Moosbierbaum	2,000	2,000	—
I.G. - Hüls	200	200	—
I.G. - Schopau	200	200	—
Total from above-listed Plants.	55,000	50,300	4,700
Aromatic Oils from Coal Tar	1,100	1,100	—
Grand Total	56,100	51,400	4,700

The volume figures given in Table I represent the highest production level in 1943 before bomb damage interfered greatly with production. (The highest production for an entire month was in 1943, and the average daily volume during that month was 52,200 barrels.) At that time, when the maximum daily production of total aviation gasoline was about 56,000 barrels, there was under construction, or being developed, extensions to increase that figure to nearly 100,000 barrels. (It is interesting to note that at the time the aviation gasoline production reached the figure of 56,000 barrels per day, the total German motor gasoline production was 55,000 barrels per day.)

(b) Composition and Specifications.

There were two (2) grades of aviation gasoline produced in volume in Germany, one the B-4 or blue grade, and the other the C-3 or green grade. Both grades were leaded with the equivalent of 4.35 cubic centimeters tetraethyl lead per gallon. The B-4 grade was simply a fraction of the gasoline product from coal and coal tar hydrogenation. It contained normally 10 to 15 percent volume aromatics, 45 percent volume naphthenes, and the remainder paraffins. The octane number was 89 by a measurement corresponding to the C.F.R.

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2. Supply and Composition of Aviation Gasolines (b)(Cont'd.)

motor method. The C-3 grade was a mixture of 10 to 15 percent volume of synthetic isoparaffins (alkylates and isooctanes) and 85 percent of an aromatized base stock produced by hydroforming types of operation on coal and coal tar hydrogenation gasolines. The C-3 grade was permitted to contain not more than 45 percent volume aromatics. This aromatic limitation sometimes required that the base stock component include some diluent other than the aromatic fraction, which could then be balanced if necessary by the inclusion of slightly more isoparaffin. (The C-3 grade corresponded roughly to the U. S. grade 130 gasoline, although the octane number of C-3 was specified to be only 95 and its lean mixture performance was somewhat poorer.)

The components of the two grades were therefore simple and few in number. The isoparaffins were produced by standard, well known methods and there was nothing abnormal found in their compositions. The base stocks were fractionated to end points of 300 to 320 degrees fahrenheit. No normal isopentane separation was carried out, and the pentane and butane contents were adjusted simply for vapor pressure control. Small amounts of specially synthesized aromatic compounds were included from time to time, but no regular large scale use of such materials was practiced. No aromatic amines or other special additives were used.

Oxidation inhibitors were not used in the regular blended aviation gasolines. It will be seen that the components were in general of such nature that oxidation inhibition should not have been necessary. Lead deposition from fuels was an operating problem, however, but no inhibitors were used for its prevention. This "lead instability" was believed to be related to aromatic content, and fear of lead deposits was a reason for the limitation of the aromatic contents of the two grades.

The relative volumes of production of the two grades cannot be accurately given, but in the last war years the major volume, perhaps two-thirds (2/3) of the total, was the C-3 grade. Every effort was being made toward the end of the war to increase isoparaffin production so that C-3 volume could be increased for fighter plane use. The isoparaffin usage in that grade had already been cut to a minimum.

In Table II are given the important RLM (Reichs Luftfahrtministerium) specifications for aviation gasolines supplied to the Air

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2. Supply and Composition of Aviation Gasolines (b)(Cont'd.)

Ministry. The complete specification sheet is appended. On that RLM sheet are also given specifications for aircraft diesel fuel. (The subject of diesel fuel manufacture in Germany is being covered by a U. S. Naval Technical Mission in Europe Report entitled, "German Diesel Fuel".)

TABLE II.

RLM Specifications for B-4 and C-3 Gasolines.

		Blue Grade B-4	Green Grade C-3
Density at 59°F.		0.710 - 0.760	0.760 - 0.795
Distillation °F.,	IBP	104 min.	104 min.
	10 percent	167 max.	176 max.
	50 percent	221 max.	230 max.
	90 percent	320 max.	320 max.
	E.P.	338 max.	356 max.
Recovery, percent volume		98 min.	98 min.
Reid Vapor Pressure lbs.		7.0 max.	6.3 max.
Aromatic Content, percent volume		25 max.	45 max.
Tetraethyl Lead Content,	percent volume	0.115 - 0.120	0.115 - 0.120
Ethylene Dibromide Content,	percent volume	0.050 - 0.053	0.050 - 0.053
Melting Point, °F		-76 max.	-76 max.
Leaded Octane Number (Motor Method)		89 min.	95 min.

Note—The mixture response curve for each gasoline shall at least equal that of a standard reference fuel, supplied by the R.L.M., at all air-fuel ratios between 0.75 and 1.3/ The following document transmitted to the Bureau of Ships relates to specifications:

I. Technische Lieferbedingungen für die Flugmotoren-Frontkraftstoffe. (RLM specifications for aviation gasolines).

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2. Supply and Composition of Aviation Gasolines (Cont'd.)

(c) Engine Testing.

The anti-knock performance of aircraft fuels was evaluated in two (2) different manners: by the octane number, using a test very similar to the C.F.R. Motor Method, and by a mixture response curve. The specifications of B-4 and C-3 fuels include both octane number and the mixture response curves.

Octane number was measured on the one-cylinder "I.G. Prüfmotor". The technical data for this engine are as follows:

Bore	65 mm.
Stroke	100 mm.
Volume	332 cc.
Power Output at 900 rpm.	0.7 kw.
Consumption at 900 rpm.	600 cc. per hour
Compression Ratio	4.0 to 15.0
Inlet valve clearance (cold)	0.20
Inlet valve opens	11° after top center
Inlet valve closes	173° " " "
Outlet valve clearance (cold)	0.25
Outlet valve opens	173° after top center
Outlet valve closes	3° before top center

The values obtained with this I.G. test engine agree quite closely with those obtained on the C.F.R. engine. All values given herein for octane numbers, motor method, were determined on I.G. engines. The test conditions for measurement of aviation fuels were as follows:

Speed	900 rpm.
Cooling Medium	Glycol and Water
Cooling Medium Temperature	300°F.
Inlet Temperature of Fuel-air mixture	300°F.
Ignition	22° before top center
Compression Ratio	Start of "medium heavy" knocking

The mixture-response curves of aircraft fuels were measured on a B.M.W. (Bayerische Motorenwerke) 132-F single cylinder engine. Liquid injection was employed and the following test conditions were used:

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2. Supply and Composition of Aviation Gasolines (c)(Cont'd.)

Speed	1600 rpm.
Compression Ratio	6.5
Cooling air temperature	77°F.
Cooling air pressure	200 mm H_2O
Begin Liquid Injection	26° to 30° after top center
Injection Pressure	60 atmospheres
Inlet air temperature	175° and 265°F.
Ignition	Highest power output at air to fuel ratios of 0.7, 0.9, 1.3 without knocking.
Air to Fuel Ratio	0.7 to 1.3
Measurement of knock	Audible

There are attached on the following pages two (2) small photographs which give several comparable mixture response values and plots for different components and fuels.

The first is a plot of air-fuel ratio (abscissa) against "useful" pressure in atmospheres. The B-4 and C-3 fuels are shown thereon (MOZ is motor method octane number).

The second is a table with a title meaning "Mixture-Response Power Outputs for Aromatic Fuels" showing relative power outputs of several components at air-fuel ratios of 0.9 and 1.1, and also their motor method and research method octane numbers. The top group is for mixtures of 50 percent volume of 73 octane number (unleaded) coal hydrogenation gasoline, leaded with 4.35 cc. tetraethyl lead per gallon, and 50 percent volume of each of the components listed, also leaded. The lower group is of well known materials for comparison. (Fliegerbenzol is aircraft fuel; Dehydrier means "from dehydrogenation process"; Aromatisierungs means "produced by a process yielding high aromatic contents.")

The composition of C-3, with a high aromatic content, resulted in that gasoline having a good rich mixture (less than 1.0) performance. Its performance, i.e., allowable power output, at lean mixture was not entirely satisfactory, however. If more isoparaffin had been included, the lean mixture performance would have been

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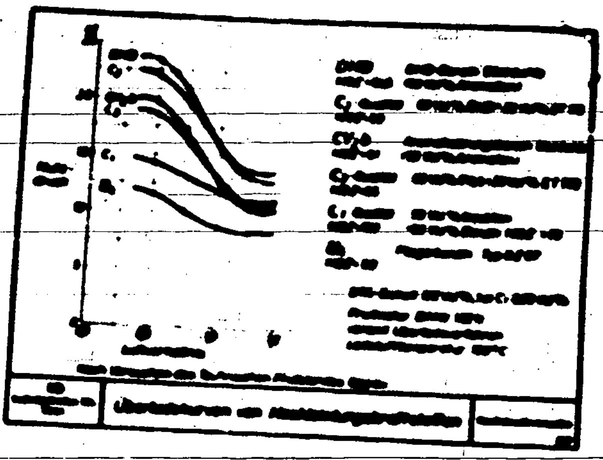

Durch Überladung erzielbare Leistung bei Aromaten-Kraftstoffen.

Leistung mit Äthyl-propylbenzol bei λ = 0,9 gleich 100 % gesetzt

20 Vol.-%iges Gemisch von Hydrierbenzin aus Steinkohle O.Z. 73 + 0,12 Vol % Pb mit:	% Leistung bei Luftüberschußzahl		Oktanzahl	
	λ = 0,9	λ = 1,1	Motor-methode	Research-methode
Äthyl-propylbenzol	100	71	99	110
Diäthylbenzol	95	67	97	107
[illegible]	81	6[illegible]	96	104
Dehydrier-Aromaten 150–175° C	80	39	93	103
Dehydrier-Aromaten 175–200° C	77	35	92	101
[illegible]	60	52	100	101
Zum Vergleich, bekannte Hochleistungskraftstoffe				
O.Z. 87 Fliegerbenzin aus Steinkohle (0,09 Vol % Pb)	44	33	88	91
O.Z. 100 Kraftstoff mit ca. 20 Vol % Isoparaffinen (0,09 Vol % Pb)	35	49	101	104
Aromatisierungsbenzin aus Steinkohle (300 at) (0,12 Vol % Pb)	64	30	90	110
Aromatisierungsbenzin aus Pech 700 at (0,12 Vol % Pb)	80	39	93	103
Isooktan rein 0,09 Vol % Pb	72	67	114	115

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2. Supply and Composition of Aviation Gasolines (c)(Cont'd.)

improved. This was recognized as the outstanding shortcoming in the German aviation fuel quality position. Had raw materials and equipment been available, more isoparaffins would have been included in the C-3 blend. As isoparaffin content increased, the aromatic content could simultaneously have been decreased (by use of base stocks with octane numbers equal to those of the aromatic base stocks) and a gasoline with increased heat content would have resulted. However, because of the relatively greater ease of manufacturing aromatics, they were used in large quantity to help gain a satisfactory lean mixture performance, with the result that rich mixture performance was not limiting.

(d) Safety Aviation Fuels.

A note should be made regarding the development of safety aviation fuels. The Germans were quite aware of the desirability of safety fuels. Tests had been made with 390 to 660 degrees fahrenheit fractions of coal and coal tar hydrogenation products, but no full scale use of such materials was being made.

Some tests had been made to relate flash point and boiling range of a safety fuel to its resistance to ignition by incendiary bullets. It was concluded from this work that for a safety fuel to be effective, the flash point must exceed 200 degrees fahrenheit and should be in the region of 300 degrees fahrenheit.

3. Specifications and Supply of Jet Fuels.

The requirements for jet fuels in Germany were increasing rapidly at the end of the war. The 1944 consumption was 650 barrels per day, and it was planned to increase that figure to 3,250 barrels per day in 1945. While that consumption apparently never was reached, the demands had become appreciable in terms of Germany's available supply of liquid fuels.

Mixtures of gasoline and diesel oil fractions were used as fuel in 1944, but with increasing requirements efforts were being made to use higher boiling fractions only in order to release all gasoline for other critical uses. Tests were in progress using materials from the sump phase and pre-hydrogenation steps in coal hydrogenation.

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3. Specifications and Supply of Jet Fuels (Cont'd.)

The tests had shown that only a low aromatic content could be tolerated if clean burning was to be obtained, and it was also concluded that some gasoline was necessary in order to obtain satisfactory ignition.

The status toward the end of the war was that gasoline-rich mixtures were still being used with the higher boiling diluents being any available material such that the blend met the following specifications:

(1) Viscosity maximum 12 centistokes at -31 degrees fahrenheit (or maximum 22 centistokes at -4 degrees fahrenheit). The viscosity specification was to insure flow through the fuel pump and good distribution in the fuel jets.

(2) Pour point maximum -31 degrees fahrenheit. (It was stated in another instance that in practice the maximum pour point was -40 degrees fahrenheit and that no crystal appearance could occur above -13 degrees fahrenheit). In a flight of one (1) to one and one-half (1½) hours, such as is experienced with jet fighters, the contents of the fuel tank can reach a temperature as low as -31 degrees fahrenheit. For long distance flights it was believed that the pour point specification would have to be lowered to -56 degrees fahrenheit.

(3) The fuel shall burn without carbon formation. Aromatic oils deposit carbon in the combustion chamber and the turbine. Paraffinic oils are clean burning and therefore desired for jet fuels. It was the opinion in Germany that the chemical character (and hence burning quality) of the fuel was of more importance than such properties as boiling range.

(4) Heating value minimum 18,000 BTU per pound.

(5) Sulfur content maximum 1.0 percent weight.

4. Synthesis of Isoparaffins.

Isoparaffins were synthesized commercially in Germany by two (2) processes; isobutylene polymerization followed by hydrogenation of the polymer, and by alkylation of butylenes and isobutane. Of the two processes, alkylation was much the more important from the stand-

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point of volume produced. Both of the above processes have been highly developed in America, and the German applications were not more highly developed than present practice elsewhere. They are described below, however, together with the methods by which their raw materials are produced.

The production of isoparaffins other than those obtained from the two commercial processes was given extensive study. The synthesis of triptane was studied and a process was designed from this work, although triptane itself is not the end product. This development is described below.

The isomerization of normal butane was being carried out commercially to supply isobutane to alkylation. The commercial process used is described in this section together with some new research on the isomerization of normal C_6 and C_7 paraffins.

(a) Isobutylene Polymerization and Polymer Hydrogenation.

This process for isooctane manufacture was employed at Leuna, Ludwigshafen-Oppau, and Heydebrek.

Isobutyl alcohol was synthesized directly from CO and H_2 by the "Isobutyl Synthese" (described in U. S. Naval Technical Mission in Europe Report titled "Synthesis of Hydrocarbons and Chemicals from Mixtures of CO and H_2"). The alcohol was dehydrated to isobutylene over precipitated alumina at 630 to 680 degrees fahrenheit and normal pressure. In this temperature interval a 95 percent conversion of alcohol to olefin was obtained, with a small accompanying yield of isobutyraldehyde. A one pass operation was therefore employed. Isobutyraldehyde and water were separated from the isobutylene by simple distillation. The aldehyde was hydrogenated to alcohol and recycled back to dehydration feed.

Isobutylene from the alcohol dehydration was compressed to 20 atmospheres, heated to 300 to 350 degrees fahrenheit and polymerized over a catalyst of 25 percent phosphoric acid on activated carbon. Unpolymerized isobutylene was separated and recycled, and combined dimers and trimers were taken overhead in a second column, leaving only a small amount of high boiling polymers as bottoms. The dimer-trimer mixture was then hydrogenated under 200 atmospheres of

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4. Synthesis of Isoparaffins (a)(Cont'd.)

hydrogen pressure at 660 degrees fahrenheit, using a tungsten nickel-sulfide catalyst. A hydrogen recycle of four (4) to one (1) based on fresh hydrogen was employed.

The hydrogenated fraction, known as ET 110 or Di 1000, had the following properties:

Density at 59° F.		0.710
Distillation, ° F, IBP		176
Distillation	10 percent	214
Distillation	50 percent	217
Distillation	90 percent	230
Distillation	EP	385
Octane Number (Motor Method) Unleaded		98
Octane Number with 4.35 cc. Tetraethyl Lead/gallon		115.

Before the advent of the alkylation process, isobutylene was being produced by isobutane dehydrogenation at Leuna, Pölitz, and Scholven. Polymerization and polymer hydrogenation systems were used to convert this isobutylene to T-52, a product nearly identical to ET 110. The processing of the isobutylene to T-52 differed from the ET 110 system only in that, due to slightly different feed composition, the polymerization catalyst in the T 52 process was 50 percent phosphoric acid on asbestos instead of the 25 percent phosphoric acid on active carbon catalyst in the ET 110 system.

The following document, transmitted to the Bureau of Ships, relates to this process:

II. Herstellung von Di. 1000.
(Flow diagram of the Di 1000
or ET 110 process)

(b) Alkylation.

Although research and development work on alkylation was started in Germany prior to 1940, the commercial production of alkylate did not begin until 1943. Prior to that time, Leuna, Pölitz, and Scholven had

4. Synthesis of Isoparaffins (b)(Cont'd.)

been producing isobutylene by isobutane dehydrogenation, and those dehydrogenation plants were then shifted to normal butane feed.

In early 1944, these three plants were still the only operating alkylation units, but plants were being constructed in Wesseling, Brüx, Böhlen, and Blechhammer. Had these plants all been completed and put into operation, Germany's alkylate outturn would have risen about 50 percent above her actual attained production.

Normal butane dehydrogenation and isomerisation processes were both in use in Germany. Appendix I to this report describes dehydrogenation, and the general subject of isomerisation is discussed later.

Only butylene alkylation was practiced in Germany. By the application of the processes of dehydrogenation, isomerization, and alkylation, C_4 components from the large coal and coal tar hydrogenation plants could be totally converted to butylene alkylate. (Some C_4 fraction was still being used as liquefied gas, but nearly all of the large hydrogenation plant C_4 outturn was to have gone ultimately into alkylates).

No propylene or amylene alkylation was carried out commercially. While these operations had been completely explored in the laboratory, it was not considered worthwhile to dehydrogenate propane, for example, to supply an additional olefin to alkylation and thereby increase the volume of alkylate at a sacrifice in quality. In calculating the optimum position on isoparaffin production, the most stress was placed on lean mixture performance rating. Rich mixture performance was at a lower premium apparently because of the relatively greater availability of aromatics and aromatizing capacity.

The alkylation plants varied in a few respects only from those in common use in America. (Complete plant descriptions are attached). Refrigeration of the reactor was accomplished by evaporating C_4 from the surface, compressing and liquefying, and returning the liquid to feed. The reactor itself was sometimes a stirred antoclave with no external recycle of reactor hydrocarbon phase being practiced. Only pure isobutane, prepared from reactor product through a series of columns, was then used for recycle to build up the isobutane to olefin ratio.

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4. Synthesis of Isoparaffins (b)(Cont'd.)

In other plants, however, a reactor system was used which consisted of a mixing and cooling vessel, where vapor was withdrawn to the refrigerating cycle, a circulating pump, and a time tank. Emulsion was recycled, and a portion of the emulsion was withdrawn to a settling vessel, from which acid was recycled back to the mixing vessel.

The important operating variables and yield figures for a butylene plant employing the last described reactor system are summarised in Table III. Triisobutylene from ET 110 plants was used for alkylation feed when available, and the alkylate yield and quality were about equal to those obtained when using the equivalent amount of isobutylene.

Regeneration of spent sulfuric acid from alkylation was practiced in at least one location (Leuna). In that plant, alkylation acid was diluted to ca. 50 percent concentration, the liberated oil (tar) layer was separated off, and the acid was reconcentrated in a "Pauling Kessel" to 93 or 94 percent acid. It was then fortified with SO_3 to 98 percent concentration.

The following documents, transmitted to the Bureau of Ships, relate to alkylation:

III. Herstellung hochklopffester isoparaffinischer Treibstoffe durch Alkylierung aliphatischer Kohlenwasserstoffe.

(I.G. Leuna - Dr. Pohl II report of 6 Jan. 1943)

IV. Alkylierung - Anlage-Leuna

(I.G. Leuna - flow diagram of Alkylation Plant)

V. Alkylierung und Destillation

(I.G. Leuna - report by Dr. Sträts of about April 1944)

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TABLE III

Characteristic Operating and Yield Data for Butylene Alkylation Plants

Reactor Feed Composition	
Isobutane, percent wt.	54.8
n-Butane, percent wt.	34.0
n-Butylene, percent wt. *	4.3
Propane, percent wt.	6.9
Ratio Isobutane to Olefin in Feed	13
Reactor Operating Variables	
Pressure, atms.	1.5
Temperature, °F	32
Fresh H_2SO_4 Feed, percent wt. acid	98
H_2SO_4 in Reactor Acid Phase, percent wt.	90-92
Acid to Hydrocarbon Volume Ratio	0.8 to 1.1
Acid Consumption, lbs. H_2SO_4/gallon of Aviation Alkylate	0.80
Ratio Isobutane to Olefin in Reactor	ca. 95
Yields and Product Quality	
Volumes Isobutane consumed per volume Olefin Feed	1.32
Volumes Aviation Alkylate produced per volume Olefin Feed	1.75
Octane Number (Motor Method) of Aviation Alkylate, Unleaded	94
Octane Number, Leaded with 4.35 cc Tetraethyl Lead/gallon	110
Aviation Alkylate, percent volume of total Debutanized Alkylate	93.5
Composition of Aviation Alkylate, percent volume	
2,3 Dimethyl Butane	6
2,4 Dimethyl Pentane	6
2,2,4 Trimethyl Pentane	21
2,3,4 " "	29
2,3,3 " "	28
Nonanes	10

*Of which alpha butylene is 43 percent and beta butylene is 57 percent.

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4. Synthesis of Isoparaffins (Cont'd.)

(c) The Peroptan Synthesis.

The premium value of triptane as an aviation gasoline component was recognized in Germany and much effort was put forth to develop a method for its synthesis. The most extensive study was made by a research group from I.G. - Ludwigshafen-Oppau.

Some triptane was first made by a Grignard reaction for testing to establish its anti-knock properties. In contemplating then what reaction could be used for its commercial production, the combination of isopropyl chloride (chlorpropane-2) with isobutane was considered. Also, by the use of the same type of reaction, it was considered that tertiary butyl chloride and isobutane might yield 2,2,3,3 tetramethyl butane, another octane with outstanding anti-knock properties.

In 1943 a program of study of the above type of reaction was undertaken. Propyl chloride was first made by direct reaction of propane and chlorine, using ultraviolet light as a catalyst. An 8:1 mol ratio of propane to chlorine was fed into a vertical iron tube, down the center of which was a mercury arc tube. The feed inlet temperature was 70 degrees fahrenheit and the heat of reaction was adequate to raise the temperature of the system to 140 degrees fahrenheit. A pressure of 20 atmospheres was maintained to keep the system totally liquid. Under these conditions complete reaction of the chlorine was obtained. The product was fractionated, removing first hydrogen chloride, then propane, and then separating the two monochlor isomers. A very small yield of residue remained.

The isopropyl chloride was reacted with isobutane at 32 degrees fahrenheit, using both ultraviolet light and a slurry of aluminum chloride as catalysts. One part of isopropyl chloride, five parts of isobutane, and one part of $AlCl_3$ were agitated under ultraviolet light until HCl liberation subsided. The HCl was removed, then isobutane was separated, and the higher boiling materials were examined. No triptane was ever found in the product, but essentially the entire yield was a mixture of isoparaffins boiling in the 190 to 370 degrees fahrenheit range. About 50 percent of the yield was 2,2,3 trimethyl pentane, and most of the product boiled between 210 and 230 degrees fahrenheit. The octane number of the total mixture was 96 to 98 and the rich mixture rating exceeded that of 2,2,4 trimethyl pentane.

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4. Synthesis of Isoparaffins (c)(Cont'd.)

It was found that chlorpropane-1 was equally as effective as isopropyl chloride for this reaction and the separation of the two isomers was discontinued. It was found also that all material boiling below 190 degrees fahrenheit formed in the reaction could be recycled back into the system without build-up. Based on propane and isobutane feeds, an 80 percent weight yield of product could be obtained.

The above operation was proposed as a process and the product was named "Peroptan". A plant to produce about 100 barrels per day was being designed for construction at Ludwigshafen-Oppau, but by early 1945 it had not progressed beyond the design stage. The plant was to take propyl chloride available at Oppau from the synthetic glycerin plant. The reactor for propyl chloride - isobutane was to be a 40 barrel autoclave. The 190 to 370 degrees fahrenheit fraction was to be separated and given a purifying hydrogenation over Raney nickel catalyst to remove about one percent weight of chlorine that remained combined in that fraction.

Isobutyl chloride and tertiary butyl chloride were also reacted with isobutane, following the same general procedure as given above for propyl chlorides. No 2,2,3,3 tetramethyl butane was ever detected in the products. It was found that the products from the two butyl chlorides were the same and, surprisingly, they were very similar to the products from propyl chloride. The compositions and qualities were not significantly different.

Ethyl chloride-isobutane reaction was attempted but HCl liberation could not be obtained.

Other efforts to synthesise highly branched paraffins were made in Germany but none had resulted in a practical process. For technical interest the following documents, transmitted to the Bureau of Ships, relate to the chemistry of these studies:

VI. Die Herstellung von Trimethylbutan. (I.G. - Ludwigshafen - review by Dr. Baeren of 22 October 1943).

VII. 2,2,3 Trimethylbutan und andere verzweigte Kohlenwasserstoffe durch Hydrierung von Trialkylessigsäure.

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4. Synthesis of Isoparaffins (c)(VII.)(Cont'd.)

(I.G.-Ludwigshafen - report by Dr.
Bueren of 15 February 1944)

VIII. Die Wichtigsten Daten und Herstellungsweisen einiger Isoparaffin unter besonderer Berücksichtigung ihrer Verwendung als Motortreibstoffe.
(I.G.-Ludwigshafen-tabulation of
16 March 1944).

(d) Isomerization of Normal Paraffins.

Normal butane isomerization plants producing isobutane for alkylation had been built in Blechhammer, Böhlen, Leuna, and Scholven.

The plants employed a vapor phase process over aluminum chloride as contact. The installations were not greatly different from the vapor phase plants in wide use in America.

The German reactors were operated at 200 to 210 degrees fahrenheit under 16 atmospheres pressure. The normal butane feed to the reactor contained 10 percent weight HCl. The $AlCl_3$ catalyst (technical grade) was put into the reactors in crude lump form. At 200 degrees fahrenheit and a liquid hourly space velocity of 3.0 (volumes liquid normal butane per volume of catalyst per hour), a conversion of ca. 30 percent was obtained and a 96 percent weight recovery of total C_4 was obtained. The aluminum chloride consumption was not above 1.2 percent weight, based on isobutane produced, and the corresponding figure for anhydrous HCl was 0.6 percent weight.

The conversion of normal to isobutane could be increased to 40 percent by raising the operating temperature to 210 degrees fahrenheit, but the C_4 recovery dropped to 95 percent weight and catalyst consumption increased somewhat.

There are attached quite complete descriptions and a flow diagram of the process. The reactor design described is interesting. The lump aluminum chloride catalyst was put in on top of a section of Raschig rings, and both below the rings and above the catalyst layers there were large free spaces (volumes) in the vertical reactor. The feed butane-HCl mixture entered the bottom of the reactor and flowed upward. As the catalyst formed hydrocarbon complexes, it began to fluidize and

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4. Synthesis of Isoparaffins (d)(Cont'd.)

run down over the surface of the Raschig rings. By supplying an adequate height of ring layer, the fluid reaching the bottom and running off into the reactor free space was completely spent. The spent liquid collected in the bottom head of the reactor and was withdrawn. The free space above the layer of catalyst was to serve as a zone of "after reaction" in which sublimed catalyst would react with the butane mixture, form a liquid and return to the catalyst bed rather than be carried out as sublimed $AlCl_3$. (In practice this was not quite realised and $AlCl_3$ did carry over, causing condenser tube plugging.)

Although chrome-nickel steels were preferred for use in the reactor, condenser, piping, etc., only low carbon steels were available. Some corrosion difficulties were originally experienced in the plants, but with good drying of the feed, corrosion was no serious operating problem.

There was no commercial isomerisation of pentane in Germany, but the process had been extensively studied in the laboratory.

Of technical interest was some research conducted by I.G.-Leuna and by the Kaiser Wilhelm Institute in Mülheim on the isomerisation of C_6 paraffins.

Hexane isomerization was carried out on a normal hexane fraction (from Fischer-Tropsch) at I.G.-Leuna. A 50 atmosphere pressure of hydrogen was applied, and the temperature was 160 to 175 degrees fahrenheit. The catalyst was aluminum chloride with added HCl equal to ca. 30 percent weight of the $AlCl_3$ in the system. (The $AlCl_3$ was mixed with $SbCl_3$ or chlorinated hydrocarbons or phosgene to obtain a liquid phase catalyst at the operating temperature). A particular experiment with a contact time of 5 hours gave a 70 percent conversion, and the approximate yield structure was 15 percent weight of 2,2 dimethyl butane, 10 percent weight of 2,3 dimethyl butane, 10 percent weight of 3 methyl pentane, 15 percent weight of 2 methyl pentane, 30 percent weight unconverted normal hexane, and 20 percent weight of C_4, C_5 and other components. (Ethane and propane were usually absent in the products produced by cracking, and isobutane was the main product of disproportionation reactions).

Less cracking is obtained in paraffin isomerization when hydrogen pressure is high and temperature is low. Of course, as temperature is lowered a longer contact time is required in order to attain a given

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4. Synthesis of Isoparaffins (d)(Cont'd.)

conversion.

In a K.W.I. experiment at 100 atmospheres of hydrogen, 160 to 175 degrees fahrenheit, 0.2 mols of $AlCl_3$ and 2 mols of HCl per mol of normal hexane, and a contact time of about 18 hours, a 90 percent conversion of normal hexane was obtained and very little cracking or disproportionation occurred. Based on total hexanes, the yield was 57 percent of 2,2 dimethyl butane, 9 percent of 2,3 dimethyl butane, 31 percent of a mixture of the two methyl pentanes, and 3 percent of unconverted normal hexane.

I.G. consider that the practical application of normal hexane isomerisation would be under conditions to obtain perhaps a 30 percent conversion, and they estimated that at such a conversion the dimethyl butane isomers would be more than half of the total isomer yield.

Isomerization of normal heptane was studied under hydrogen pressures up to several hundred atmospheres. It was found impossible even under these conditions to avoid substantial cracking of heptane in contact with $AlCl_3$.

The production of branched hexanes by the isomerization of cyclohexane was studied. Cyclohexane was contacted with 15 percent weight of $AlCl_3$ and 7 percent weight of anhydrons HCl in the presence of 150 atmospheres of hydrogen. At a temperature of 210 degrees fahrenheit and a contact time of 6 hours, the product obtained was a mixture of one percent weight isobutane, 20 percent of 2,2 dimethyl butane, 6 percent of 2,3 dimethyl butane, 18 percent of a mixture of 2 and 3 methyl pentanes, a small amount of normal hexane, a small amount of methyl cyclopentane, and the rest was unconverted cyclohexane. It was stated in a patent application that the $AlCl_3$ can be recovered essentially unchanged from the operation.

The following documents transmitted to the Bureau of Ships, relate to paraffin isomerization:

IX. Die Isomerisierung von n-Butan
mit $AlCl_3$.
(I.G. - Leuna - report by Dr.
Pohl II, etc. of 22 February 1943)

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4. Synthesis of Isoparaffins (d[redacted])

X. Schema der Isomerisierung.
(I.G.-Leuna - flow diagram of butane isomerisation plant).

XI. Isomerisation.
(I.G.-Leuna - report by Dr. Strätz of early 1944).

XII. Über Isomerisierung von Paraffinen.
(KWI - Mulheim copy of speech by Dr. Koch on 24 June 1943).

5. Synthesis of Aromatics and Production of Base Stocks.

Since isoparaffins constituted only 10 to 15 percent volume of C-3 gasoline and none of B-4, and since components other than synthetic isoparaffins and base stocks were used only in small quantities in these aviation fuels, the base stocks themselves then consisted at least 85 percent of Germany's total aviation gasoline volume.

Most of these base stocks originated in coal and coal tar hydrogenation plants. Only a very small volume of carefully selected petroleum fractions was blended directly into aviation gasolines. The large high pressure hydrogenation plants at Leuna, Scholven, Pölitz, Brüx, Gelsenkirchen, Böhlen, Magdeburg, Blechhammer, and Wesseling all produced aviation base stocks. These plants consist of three stages of hydrogenation, the first (sump) phase being the bulk destruction operation to produce an intermediate boiling distillate from the coal or heavy tar, the second being a purifying treatment of the distillate, and the third being a fine hydrogenation step producing directly (as the only product) a gasoline of the required end point. All material boiling above the gasoline end point is recycled back to the third stage feed.

The B-4 aviation gasoline of Germany was this hydrogenated gasoline, stabilized to the specified vapor pressure (refer Table II). The quality varied somewhat, depending upon the raw material to hydrogenation, and individual gasolines needed some quality correction, either with small amounts of isoparaffin or outside base stocks. In general, however, the straight hydrogenation gasolines constituted the total supply of B-4 quality. In Table IV are given a few average data

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5. Synthesis of Aromatics and Production of Base Stocks (Cont'd.)

for these gasolines obtained from four (4) different hydrogenation plant feeds, all of which were used in Germany during the war.

TABLE IV

Properties of B-4 Base Stocks from High Pressure Hydrogenation Plants

Feed to Hydrogenation	Brown Coal	Stein Coal	Brown Coal Tar	Stein Coal Tar
B-4 Base Stock				
Density at 59°F.	0.723	0.730	0.725	0.725
Volume percent Distilled at 212°F.	65	57	58	65
End Point, °F.	270	308	302	320
Paraffin Content, percent volume	53	40	60	37
Naphthene " " "	42	52	30	55
Aromatic and Olefin Content, percent volume	5	8	10	8
Octane Number, Motor Method, Unleaded	71	73	69	76
Octane Number, Motor Method, with 4.35 cc Tetraethyl Lead/Gallon	90	91	89	94

The supply of the high quality 85 percent base stock component to C-3 grade aviation gasoline involved additional processing of the hydrogenated gasolines. In order to obtain gasolines that were high in antiknock performance throughout the whole range of air-fuel ratios, aromatizing processes were invoked.

By applying a particular set of operating conditions to the second stage of hydrogenation, the Ruhröl - Welheim installation produced a high aromatic content base stock directly. Distillate from the sump phase hydrogenation of coal tar pitch was fed to a second stage operating at 700 atmospheres pressure over a new catalyst containing molybdenum, chromium, and lead on an inert carrier. At 930 degrees fahrenheit and in one step, a 350 degrees fahrenheit end point gasoline was produced which contained 40 to 45 percent volume aromatics and which was used directly as the base stock ingredient of C-3 gasoline. This base

5. Synthesis of Aromatics and Production of Base Stocks (Cont'd.)

stock had an unleaded octane number of 80, and with 4.35 cc. tetraethyl lead per gallon it was 92. This process of producing directly in hydrogenation plants a highly aromatic aviation gasoline base stock was a new development in Germany and was being widely discussed. It is likely that applications to locations other than Welheim would have been made had earlier conditions continued to prevail in Germany.

Perhaps the most important aromatizing operation was the "DHD Process", an operation used on hydrogenated gasoline to increase their aromatic contents. Hydroforming was also used, but on a small scale only. Catalytic cracking was studied but no plant was in operation. Also, several processes were in operation synthesizing individual aromatics, but they made a small contribution only to the total gasoline volume. There are discussed below these processes and their contributions to the German aviation gasoline supply.

(a) The DHD Process.

The DHD process (Dehydrierung unter Druck or dehydrogenation under pressure) was developed by I.G. in Ludwigshafen. It was a catalytic process for increasing the aromatic content of a gasoline, through both naphthene dehydrogenation and paraffin cyclization.

At the end of the war there were four (4) DHD plants in operation; Ludwigshafen, Leuna, Scholven and Pölits. The combined intake capacity of these four plants was about 20,000 barrels per day. These plants were fed gasolines produced from both coals and coal tars. There were about ten (10) other DHD plants and plant extensions planned which were never completed. It was planned that ultimately nearly all of the hydrogenation plant gasolines, and certain crude oil factions as well, would have been processed through DHD plants.

Because of their high naphthene contents, gasolines from stein coal and stein coal tars were preferred feeds to DHD. By altering operating conditions to encourage paraffin cyclization as well as naphthene dehydrogenation, gasolines from brown coal and brown coal tars were also greatly increased in aromatic content by this operation.

The feed gasolines to the process had end points of about 360 degrees fahrenheit. These feeds were first stabilized to remove ca. 15 percent volume overhead which was the non-naphthene containing

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5. Synthesis of Aromatics and Production of Base Stocks (a)(Cont'd.)

fraction boiling to about 160 degrees fahrenheit. The stabilized gasoline was then pumped together with recycled hydrogen gas through a feed-product heat exchanger and a preheater which raised the temperature to 930 degrees fahrenheit. The vapor mixture entered the top of the first of a series of five (5) reactors. The operating pressure was 25 atmospheres total, of which 10 atmospheres was the hydrogen partial pressure, when the feed gasoline originated from brown coal (or its tar). For stein coal gasolines, the total pressure was 50 atmospheres, of which 35 was hydrogen. (The lower pressure with brown coal materials was used to encourage paraffin cyclisation).

The reactors were filled with a catalyst consisting of 10 percent weight MoO_3 on Al_2O_3. The alumina was precipitated and impregnated with molybdenum oxide and formed into cubes of about ½ inch on a side. (Catalyst was made from "Tonerde" (hydrated alumina earth). The earth was first dissolved in caustic and then precipitated at 120°F., with HNO_3 at a pH of 5.5 to 6.5. The precipitate was filtered, washed and dried up to an 80 percent Al_2O_3 concentration, pilled into ½ inch cubes, and calcined at 840°F. The catalyst cubes were then washed with an ammonium molybdate solution of such concentration that the final dried catalyst contained 10 percent wt. of MoO_3. The catalyst was dried at 400°F. for a short period and then at 750°F., until all ammonia liberation ceased. The apparent density of the finished catalyst was about 0.8.) Each reactor contained about 280 cubic feet of catalyst. The reactors had steel shells lined with fire brick and an internal liner of N8 steel. The space velocity employed was about 0.5 volumes of liquid feed per volume of total catalyst in the system per hour.

The endothermic heat of reaction caused the temperature to drop from 930 degrees fahrenheit at the top of the first reactor to 840 degrees fahrenheit at the bottom exit. A heater was therefore supplied after each of the first four reactors, raising the temperature back to 930 degrees fahrenheit at the top of the second and third reactors. With the extent of reaction subsiding, the entering temperature in the fourth reactor was raised to 950 degrees fahrenheit, its exit temperature was ca. 930 degrees fahrenheit, and the fifth reactor feed was 970 degrees fahrenheit with very little temperature drop occurring through it.

A sixth reactor was used for saturation of olefins. After leaving the fifth reactor, the temperature was lowered to about 650 degrees

[redacted]

5. Synthesis of Aromatics and Production of Base Stocks (a)(Cont'd.)

fahrenheit. The sixth reactor was filled with DHD catalyst except for the bottom fifth which was filled with Florida earth.

After 40 hours of operation on brown coal gasoline, or 250 hours with stein coal products, a regeneration for carbon removal was necessary. A 20 to 24 hour period was required for the complete regeneration. In regeneration, exit gas was recycled to control burning rate and limit the temperature to a maximum of 1,030 degrees fahrenheit. The carbon deposition on catalyst was equivalent to about one percent weight of brown coal gasoline and 0.1 percent weight of stein coal gasoline, which corresponded to a coke content on spent catalyst of about 3 percent weight.

The life of the catalyst was at least a year and perhaps would become considerably longer with more operating experience. Sulfur was a definite catalyst poison, but this was a problem in Germany only when operating on crude oil fractions. In general, stocks with the lowest possible sulfur content should be chosen as feeds.

Operating under the above described conditions, the yield of redistilled, stabilized gasoline was 75 to 85 percent by weight of the stabilized gasoline fed to the DHD unit proper. (The higher yield was obtained from stein coal gasolines).

The DHD outturn contained 65 percent volume of aromatics, so that when the original 15 percent of low boiling fraction was reblended, the final gasoline contained about 50 percent volume of aromatics. The overall weight yield, based on the original hydrogenated gasoline, was therefore 78 to 87 percent, and the corresponding volume yield figures were 75 to 83 percent.

The final product from this DHD operation had the following average properties:

Density at 59° F.	0.780
Volume percent distilling at 212° F.	48
End Point, ° F.	340
Paraffins, percent volume	30
Naphthenes, percent volume	20
Aromatics, percent volume	50

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5. Synthesis of Aromatics and Production of Base Stocks (a)(Cont'd.)

Olefins, percent volume	less than 0.5
Octane Number, Motor Method, unleaded	80
Octane Number, Motor Method, with 4.35 cc. Tetraethyl Lead/Gallon	92
Octane Number, Motor Method, unleaded, of Residual Oil after Aromatic Extraction	70

There appears on the following page a photostat of an I.G. tabulation showing the properties of DHD gasolines made from various raw materials.

A copy of a speech by Dr. Pier of I.G. in 1941 was transmitted to the Bureau of Ships. This paper gives some of the background of German aviation gasoline developments leading up to the manufacturing position existing at the end of the war:

XIII. Über Fliegerbenzine und ihre Herstellung.
(I.G.-Ludwigshafen-speech by Dr. Pier on 21 November 1941)

There was also transmitted the following document describing the DHD process:

XIV. Technische Entwicklung des DHD-Verfahrens.
(I.G.-Ludwigshafen-Report of 15 October 1942)

(b) Hydroforming.

There were two (2) hydroforming plants in operation in German territory. Both were located in the Moosbierbaum refinery near Vienna. A straight run petroleum gasoline boiling from 140 to 330 degrees fahrenheit was hydroformed in conventional discontinuous units. (The process and design data were obtained from America.) Both Roumanian and Austrian crudes were processed at this refinery.

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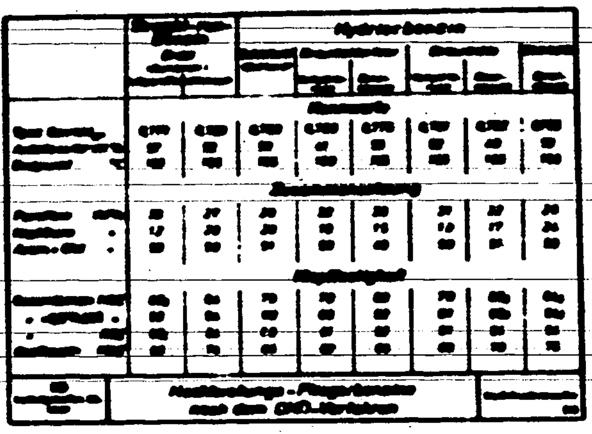

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5. Synthesis of Aromatics and Production of Base Stocks (b)(Cont'd.)

The operation was carried out at 15 to 30 atmospheres pressure, of which the hydrogen partial pressure was 65 to 70 percent. The reaction temperature was 930 degrees fahrenheit and the space velocity was 0.5 volumes of oil per volume of catalyst per hour. The catalyst was 5 to 10 percent weight MoO_3 on alumina.

The operating cycle was from 17 to 30 hours with 9 hours required for regeneration.

The hydroformed product was used in the same manner as was DHD gasoline; i.e., as the base stock for C-3 grade aviation gasoline.

In Table V are given some yield and analytical data for the average Moosbierbaum operation.

TABLE V.

Yield and Analytical Data on Moosbierbaum Hydroforming of Straight Run Gasoline.

Yield Data	Feed	Product
Gasoline, percent wt.	100.0	79.0
Redistillation Residue, percent wt.	---	3.5
Coke, percent wt.	---	1.1
Hydrogen, percent wt.	---	1.4
C_1 plus C_2 plus C_3, percent wt.	---	11.0
Isobutane, percent wt.	---	1.3
Normal Butane, percent wt.	---	2.7
Total	100.0	100.0
Analytical Data		
Density at 68° F.	0.750	0.776
Distillation, ° F., I.B.P.	144	112
Distillation, ° F., End Point	330	330
Distilled at 212° F., percent Volume	18	36
Distilled at 320° F., percent Volume	95	94
Olefin Content, percent Volume	0.5	1.5
Aromatic Content, percent Volume	14	54
Naphthene Content, percent volume	44	8

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5. Synthesis of Aromatics and Production of Base Stocks (b)(Cont'd.)

TABLE V. (Continued)

Yield and Analytical Data on Moosbierbaum Hydroforming of Straight Run Gasoline.

Analytical Data	**Feed**	**Product**
Reid Vapor Pressure, lbs.	5.3	5.1
Octane Number, Motor Method, unleaded	58	80
Octane Number, Motor Method, with 4.35 cc. Tetraethyl Lead/Gallon	79	91

The following documents transmitted to the Bureau of Ships, relate to hydroforming:

XV. HF-Verfahren und Anlage Moosbierbaum.
(I.G. - Leuna - report by Dr. Kaufmann of 9 December 1941).

XVI. Das HF-Verfahren.
(I.G.-Leuna-report by Dr. Wels of 12 February 1943).

(c) Synthetic Alkyl Aromatics.

The only important commercial synthesis of alkyl aromatics in Germany was of diethyl benzene. The chemical plants of I.G. at Hüls and Schopau produced together about 300 barrels per day of this material, named "Kybol", as a by-product in the manufacture of styrene. Benzene was alkylated with ethylene and the product, containing some diethyl benzene, was fractionated to separate into one fraction all of the diethyl compound together with a small amount of higher boiling alkylated benzenes. This fraction boiled from 325 to 350 degrees fahrenheit.

No cumene (isopropyl benzene) was being made, but one installation was being considered for producing a mixture of alkyl benzenes which would have contained cumene. Propane was to have been cracked thermally, yielding ethylene and propylene, and the olefins would then have been selectively absorbed with a copper nitrate-ethanol amine solution. The mixed olefins were to be used to alkylate benzene,

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5. Synthesis of Aromatics and Production of Base Stocks (c)(Cont'd.)

obtaining thereby a mixture of mono- and di-ethyl and isopropyl benzenes.

Of technical interest is a new German process, developed but never applied on large commercial scale, to dealkylate high boiling aromatics and reduce their boiling points down into the gasoline range. The process, known as the "Arobin Verfahren", was considered for application on high aromatic content hydroforming and DHD residues boiling from 340 to perhaps 600 degrees fahrenheit (50 percent points of ca. 380 degrees fahrenheit). A catalyst of synthetic aluminum silicate containing one percent weight of MoO_3 was used at a temperature of 750 to 780 degrees fahrenheit and under a hydrogen pressure of 200 atmospheres. At a space velocity of one volume total liquid feed (of which 50 percent is recycle) per volume catalyst per hour, an 85 to 87 percent weight yield of 330 degrees fahrenheit end point product containing 70 percent volume aromatics was obtained. A hydrogen consumption equal to 3 percent weight of the product gasoline was incurred. Through the use of the high hydrogen pressure, coke deposition on the catalyst was very low and long operating cycles (i.e., several hundred hours) were predicted. In Table VI are given some typical yield and analytical data for this operation.

The following documents, transmitted to the Bureau of Ships, relate to this subject:

XVII. Das Arobin - Verfahren.
(I.G. - Leuna - report by Dr. Wels
of 22 October 1943).

XVIII. Arobin-Anlage.
(I.G.-Leuna-material flow diagram
of 13 July 1943).

XIX. Bericht über die erste
Fahrperiode des Arobinofens.
(I.G.-Leuna-memorandum of
27 March 1944).

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5. Synthesis of Aromatics and Production of Base Stocks (c)(Cont'd.)

TABLE VI.

Yield and Analytical Data on Feed and Products of Arobin Process.

Yield, Percent Wt.	Feed	Product
Gasoline	100.0	85.7 to 87
Methane	---	0.2 to 0.3
Ethane	---	1.7 to 2.0
Propane	---	4.8 to 5.2
Isobutane	---	3.8 to 4.2
Normal Butane	---	2.4 to 2.6

Analytical Data	Feed	Product
Density at 68° F.	0.91	0.807
Distillation, °F., I.B.P.	340	120
" " 50 percent	380	260
" " E.P.	600	330
Aromatic Content, percent volume	95	65
Naphthene Content, percent volume	--	27
Paraffin Content, percent volume	--	8
Bromine Number	ca.8	0.8
Octane Number, Motor Method, unleaded	--	86
Octane Number, Motor Method, with 4.35 cc. Tetraethyl Lead/Gallon	--	93.5

(d) Catalytic Cracking.

There were no commercial scale catalytic cracking units in operation in German areas. One was being planned for operation at Moosbierbaum in Austria, a plant to carry out an operation referred to as catalytic cracking was being processed for Rucrchemie at Holten, and a large underground refinery planned for Niedersachswerfen (near Nordhausen) was to have a catalytic unit.

The Moosbierbaum and Niedersachswerfen units were to process crude oil fractions to produce aviation gasoline base stocks. The development work on the process was done by I.G. at Leuna, and a large pilot plant had been built at Deuben (south of Leuna).

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5. Synthesis of Aromatics and Production of Base Stocks (d)(Cont'd.)

The catalytic cracking process that was developed for plant application was quite similar to the TCC process in use in America. A silica-alumina catalyst, in the form of small spheres, was to be used at a temperature of 840 degrees fahrenheit and atmospheric pressure to crack straight run gas oil boiling up to about 750 degrees fahrenheit. The silica-alumina catalyst was made as follows: (A caustic aluminate solution was acidified at 220° F., with nitric acid to a pH of 6.5. The Al_2O_3 precipitate was washed free of sodium ion and dried at 210° F., to a water content of 25 to 30 percent wt. The dried Al_2O_3 was then mixed with 15 percent of its weight of SiO_2 (Kieselguhr). The mixed oxides were then ground until 90 percent passed through a screen containing 10,000 openings per meter. The powder was moistened with water acidified with nitric acid, well mixed, and then heated to 150° F., for 24 hours. It was extruded into cylindrical pellets, and put between two counter revolving plates which rolled the cylinders into small spheres of ca. 0.2 inches diameter. The spheres then were heated at 750 to 840° F., for 8 to 12 hours.) The main yield was to be a 340 degrees fahrenheit end point distillate for use directly, without repassing or other treatment, in C-3 quality aviation gasoline. A 30 percent weight yield of this fraction, a 3 percent weight yield of hydrogen plus methane plus ethane-ethylene, and a coke yield of 4 percent wt., all based on feed, were anticipated. A conversion of 50 percent volume; i.e., a disappearance of one-half (½) of the feed from its initial boiling range, was expected while employing a space velocity of 0.6 volumes of liquid feed per volume of catalyst (in reactor) per hour.

Catalyst regeneration was to be carried out at a temperature not exceeding 1020 degrees fahrenheit.

The plant design was to employ one catalyst elevator only. The regenerator would be mounted directly above the reactor, and regenerated catalyst would be dropped directly through control valves into the top of the reactor. Spent catalyst from the bottom of the reactor would then be elevated to the top of the regenerator.

A set of test data was reported for the catalytic cracking of 355 to 670 degrees fahrenheit fraction from a mixed base crude, using a 0.5 space velocity and 790 degrees fahrenheit reactor temperature. A 36 percent weight yield of 330 degrees fahrenheit end point gasoline was obtained which contained 20 percent weight aromatics and 4 percent weight olefins. The unleaded octane number was 75, and with 4.35 cubic

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5. Synthesis of Aromatics and Production of Base Stocks (d)(Cont'd.)

centimeters tetraethyl lead per gallon it was 94. The yield of low boiling components through butanes was 6.7 percent weight of which 3.1 percent was isobutane.

It was the opinion of most German technical people interrogated that catalytic cracking of the above type or of the other types employed in America, could have only limited applications in Europe. The process was being considered during the war only because it represented a method of making aviation gasoline directly from crude oil fractions. (The hydrogenation of such fractions of crude oil does not give high quality gasolines). Catalytic cracking is not considered applicable to coal tars directly because of high carbon deposition on catalyst, and the process has no obvious application in high pressure hydrogenation systems.

The following documents transmitted to the Bureau of Ships, pertain to this process of catalytic cracking:

XX. Flugbenzin durch Katalytisches Kracken. (I.G.-Leuna-report by Dr. Kaufmann of July 1942).

XXI. Flow Diagram of I.G. Experimental Catalytic Cracking Unit.

The Ruhrchemie process referred to as catalytic cracking was an operation designed initially to crack the normal paraffin residues of intermediate Fischer-Tropsch fractions used for various olefin-consuming chemical syntheses. A plant was being constructed at Holten on the basis of development work carried out there.

The reaction was designed to obtain the maximum yield of low boiling olefins for synthesis of high octane aviation gasoline ingredients. It had been concluded that the normal paraffins did not respond adequately to conventional catalytic cracking, that their isomerization was not a promising possibility, and hence that destruction to low boiling molecules (synthesis raw materials) over a catalyst was the most attractive method of converting them to high performance fuels.

The operation was to be at low (atmospheric) pressure and 930 degrees fahrenheit over a synthetic silica-alumina catalyst of 0.7 apparent density. A liquid space velocity of ca. 0.1 was to be employed in

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5. Synthesis of Aromatics and Production of Base Stocks (d)(Cont'd.)

order to obtain a 40 percent conversion per pass (disappearance from the original boiling range) of a 340 to 660 degrees fahrenheit Fischer-Tropsch fraction. Of the converted feed material, 75 percent appeared as C_3, C_4 and C_5 fractions, of which about 90 percent were olefins. Gasoline was only 15 percent of the converted yield.

By employing a recycle, a 75 percent weight ultimate yield of usable materials could be realized.

The process was to be discontinuous, with catalyst regeneration after operating cycles of 20 to 25 minutes. The carbon yield was estimated to be 1.5 percent weight of reactor feed.

In Table VII is given a set of of yield and product composition data characteristic of this operation. A copy of a report by Ruhrchemie, which describes quite completely the development of the process and its planned application, was forwarded to the Bureau of Ships:

XXII. Herstellung von Isogasolen
und Flugbenzin aus Synthese-
produkten.

(Ruhrchemie report by Dr.
Kolling in January 1943).

TABLE VII

Yield and Product Composition Data - Ruhrchemie Catalytic Cracking.

Feed to process is Fischer-Tropsch fraction of 340 to 660 degrees fahrenheit boiling range.

Yields of Components, Percent wt. of Feed	
Total Conversion	40 percent wt. of feed
Gasoline (C_6 to ca. 320° F.)	6-8
C_5 Fraction	7.6-9.6
C_4 Fraction	10-12
C_3 Fraction	8-10
C_2 Fraction	2-2.8
Methane & Hydrogen	0.4-0.8
Coke	1.2-1.6

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5. Synthesis of Aromatics and Production of Base Stocks (d)(Cont'd.)

TABLE VII. (Continued)

Yield and Product Composition Data - Ruhrchemie Catalytic Cracking.

Olefin Contents, percent volume

C_5 Fraction	85-90
C_4 "	90-95
C_3 "	90-95
C_2 "	60-65

Iso-Contents, percent volume

C_5 Paraffins	60-65
C_5 Olefins	45-50
C_4 Paraffins	60-65
C_4 Olefins	38-43

6. Conclusions.

(a) The maximum rate of production of total aviation gasolines achieved by Germany during the war was roughly 50,000 barrels per day, of which essentially the entire volume came from coal and coal tar hydrogenation plants. Of this total volume of liquid, about 10 percent was synthetic isoparaffins, 40 percent was high aromatic content base stocks produced by processing of hydrogenation plant gasolines, and the remaining 50 percent was almost entirely hydrogenation plant gasolines of aviation gasoline endpoint and volatility.

(b) Two grades of aviation gasoline were produced, one with a motor method octane number of 91, and the other of 95. The former, labeled B-4 (blue) contained about 10 percent volume aromatics, while the latter, known as C-3 (green), contained about 40 percent volume aromatics and would thus allow much higher power output under rich mixture conditions. Both grades contained 4.35 cc. tetra-ethyl lead per gallon (American). The 50 percent distilled specifications were 221 and 230 degrees fahrenheit, for B-4 and C-3, respectively.

(c) The B-4 grade was produced directly by the addition of tetraethyl lead to the entire liquid product from the large coal and coal tar hydrogenation plants. The volatility was adjusted to about 7 pounds Reid vapor pressure by stabilizing and no further refining or blending

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6. Conclusions (c)(Cont'd.)

was done.

(d) The C-3 grade was a leaded blend of about 15 percent volume of synthetic isoparaffins and 85 percent volume of a base stock containing 45 to 50 percent volume aromatics, produced by further processing of a hydrogenated gasoline almost identical to unleaded B-4. The C-3 grade represented at least two-thirds (2/3) of the combined volume of the two grades.

(e) Small amounts of synthetic aromatic compounds such as diethyl benzene, were used as components, but with unimportant exceptions, no additives or components other than those mentioned above were included in the commercial blends. No inhibitors of any kind were normally used.

(f) Had raw materials and manufacturing facilities been available, more isoparaffins would have been produced to improve the lean mixture performance of both grades and, ultimately, to allow a decrease in the aromatic content of the C-3 grade. The rich mixture performance of the gasolines was satisfactory for the engines being built and used.

(g) Synthetic isoparaffins were manufactured primarily by the alkylation of butylenes and isobutane. Some isobutylene polymerization and polymer hydrogenation was being carried out. No propylene or amylene alkylation was being done. No triptane synthesis had been developed, and no isoparaffin syntheses other than those mentioned above were being used.

(h) Isobutylene for polymerization was made by dehydrogenation of isobutyl alcohol which was synthesized directly from carbon monoxide and hydrogen. Normal butylene for alkylation was produced by catalytic dehydrogenation of normal butane produced by the coal and tar hydrogenation plants. Isobutane for alkylation came in part directly from the hydrogenation plants and in part by catalytic isomerization of some of the normal butane.

(i) To produce the bulk of high aromatic content base stock used in C-3, a process known as DHD was employed. This process produced aromatics both by dehydrogenation of naphthenes and by cyclization of paraffins. Hydroforming was used at one refinery to produce base stock, of quality eligible for use in C-3 grade, from Austrian and Roumanian crude oil fractions.

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6. Conclusions (Cont'd.)

(j) No catalytic cracking units existed in the German area, but the process had been studied and two plants installations were being planned. It is generally agreed that catalytic cracking of the type employed today in America will not find wide application in the synthetic oil industry. It was of interest to Germany only as a wartime means of producing aviation gasoline. The units being planned were similar in general design to a TCC unit and were to use a synthetic silica-alumina catalyst.

(k) Some new processes developed in Germany during the war years but which were not in commercial operation included:

(1) A specific and efficient catalytic process for dealkylating aromatics;

(2) A catalytic cracking process for normal paraffins boiling in the kerosene range, producing primarily C_3, C_4 and C_5 olefins;

(3) A catalytic process for producing an ultimate weight yield of 70 to 78 percent of toluene from normal heptane, and

(4) A process for producing high quality gasoline isoparaffins by combining propane and isobutane via chlorination.

(l) Jet fuels were being produced in Germany at a rate of ca. 1,000 barrels per day in 1944. The fuel was a mixture of gasoline and diesel oil fractions. The specifications for jet fuel were lenient; no unusual quality was demanded and no unusual specifications were forthcoming.

Prepared by:

M. E. SPAGHT,
Technician.

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APPENDIX I

THE DEHYDROGENATION OF BUTANE TO BUTYLENE.

Two (2) methods for the dehydrogenation of butane to produce feed for polymerization and alkylation plants were studied in Germany. One involved the direct release of hydrogen over a catalyst, and the other was via chlorination and HCl splitting. The catalytic dehydrogenation process was developed by I.G. and plants were built at three locations. The chlorination process was also developed by I.G. but no commercial installation was made or planned. For general information, however, there is attached a process flow diagram of a hypothetical plant employing the chlorination process.

The catalytic dehydrogenation process was carried out at 1020 to 1100 degrees fahrenheit at practically atmospheric pressure, using a catalyst consisting of 2 percent weight K_2O, 8 percent weight Cr_2O_3, and 90 percent weight Al_2O_3. The conversion to olefins was ca. 18 percent per pass when a space velocity of 8 volumes of liquid butane per volume of catalyst per hour was used.

The catalyst was made by first precipitating alumina from an aluminum sulfate solution, then drying and grinding the precipitate. The ground alumina was then soaked in a chrome solution, pilled, dried, and put into the reactor. The finished catalyst had an apparent density of 1.0.

The reactor was a vertical bundle of 2½ inch tubes with flue gas circulated around the tubes. The tubes were made of 17 percent chrome, 17 percent nickel, "high" molybdenum content steel. The flue gas circulated around the tubes was at a temperature about 200 degrees fahrenheit above that of the inside catalyst.

Catalyst was continually added at the top of the bundle and continually withdrawn at the bottom. The time required for the catalyst to pass through the tube was about 200 hours. Catalyst deactivation occurred primarily through carbon formation and deposition. The spent catalyst contained 2.5 percent weight carbon and in regeneration with air it was reduced to 1.5 percent weight and returned to the system. In the regeneration, care was taken that the temperature did not exceed the operating level of 1020 to 1100 degrees fahrenheit.

The same space velocity and conversion were used for both normal

[redacted]

and isobutane, but with normal butane the operating temperature was 1100 degrees fahrenheit compared with 1020 degrees fahrenheit for isobutane.

The exit stream from the dehydrogenation furnace was first cooled and then hydrogen, methane and other low boiling materials were separated. The butane-butylene mixture then was fed directly to alkylation. Acid life in alkylation was markedly influenced by the quality of dehydrogenation product. Small amounts of butadiene adversely affected acid life. Butadiene formation was minimized by carefully controlled dehydrogenation furnace operation, particularly avoiding tube plugging with resulting catalyst overheating.

In obtaining a product containing 18 percent olefins, a total weight loss of about 5 percent is incurred. That is, a 95 percent weight recovery of total C_4 fraction is obtained. On this basis, an ultimate weight conversion of 78 percent butane to butylene is realized. Losses through fractionation and alkylation plants will of course reduce this figure.

Dehydrogenation under hydrogen pressure was studied, and the low pressure system was chosen in preference. (This decision was influenced by the difficulty of obtaining high pressure equipment in Europe during the war).

The following documents, transmitted to the Bureau of Ships, relate to this subject:

XXIII. Dehydrierung
(I.G. - Leuna - report of Dr. Herbert)

XXIV. Materialfragen in der Dehydrierung.
(Politz - report of Dr. Hüttner)

XXV. Mengenschema zur AT Anlage mit katalytischer Dehydrierung.
(I.G.-Leuna - flow diagram and material balance of system including catalytic dehydrogenation of normal butane)

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[redacted]

Appendix I (Cont'd.)

XXVI. Die Katalytische Dehydrierung von Propan zu Propen. (I.G. - Leuna - report by Dr. Nowotny of 16 March 1944)

XXVII. Chlor-Dehydrierung nach Bähr (I.G. - Leuna - process flow diagram of butane dehydrogenation plant)

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APPENDIX II

THE MANUFACTURE OF NITRATION GRADE TOLUENE.

The German supply of nitration grade toluene came from several sources. In addition to coal tar fractionation and refining of DHD fractions, there were employed the Witol process, the Leutol process, and aromatization of heptanes.

The DHD process is fundamentally a device for producing aromatics, and it was logically seen to be a potential source of toluene. Some nitration grade toluene was made directly from the normal DHD product by separation of a C_7 fraction and application of methanol in an azeotropic distillation process. In another instance, a C_7 fraction was separated from the DHD product and repassed again through the same process. The repassed product was then fractionated directly without the aid of added agents to produce toluene of nitration grade. In both cases, sulfuric acid treatment and redistillation were employed as a finishing operation.

The Witol process was a synthesis of toluene by the combination of methanol and benzene. A four to one ratio of benzene to methanol was reacted, and the alkylated benzenes consisted of 70 percent toluene and 30 percent higher homologues.

To produce toluene from the poly-methylated benzenes, the Leutol process, which was quite similar to the Arobin process (discussed in this report), was employed. In the Leutol process, an aluminum silicate-molybdenum oxide catalyst is used, with a hydrogen pressure of ca. 200 atmospheres, to dealkylate the higher boiling compounds.

Perhaps of widest technical interest, however, is the heptane aromatizing process developed by Ruhrchemie. A plant was being built at Holten but it had not been completed by the end of the war.

The Ruhrchemie cyclizing process is specially designed for heptane - heptene fractions from the Fischer-Tropsch synthesis. These fractions would consist largely of normal heptane, with perhaps 10 percent of heptene-1 and 5 percent of other heptenes. This mixture was to be carefully fractionated from C_6 and C_8 components; i.e. to 99.5 percent purity. It was then to be passed over a chrome-alumina catalyst at atmospheric pressure and a temperature of 860 degrees fahrenheit. The chrome-alumina catalyst was made as follows:

[redacted]

Appendix II (Cont'd.)

(Al_2O_3 was precipitated, washed, dried, and ground in conventional manner, but careful washing was considered important. The ground alumina was then mixed with pure chromic nitrate salt with adequate water to make a viscous mixture. This mass was extruded into small cylinders, dried and finally roasted at a temperature of 1200 degrees fahrenheit. Small amounts of cobalt, nickel, manganese, and thorium had been used in individual tests as activators.) By using a liquid hourly space velocity of 0.1, a 50 percent conversion to toluene was anticipated. By the recycle of unconverted heptane - heptene, an ultimate yield of toluene equal to 78 percent weight of the feed was obtained in a pilot plant; this figure was expected to decrease to 70 percent in the commercial plant.

In the pilot plant, in obtaining a 50 percent weight yield of toluene in one pass, the total loss to other materials was ca. 1.2 percent weight hydrogen, percent weight methane and other low boiling materials, and 3 to 4 percent weight of light gasoline, high boiling residues, etc.

The reaction cycle in this process was one-half (½) hour on production, about one-quarter hour oxidizing off carbon, and one-quarter hour reducing the catalyst after oxidation. In the reduction step, hydrogen produced in the operation is used.

The toluene is separated from the reactor product liquid by simple fractionation, and after acid treating and redistillation it meets nitration grade specifications.

The use of a low pressure operation without hydrogen recycle is possible because of the absence of cyclopentanes in the feed. At low pressure cyclopentanes would decompose extensively to carbon and result in very rapid catalyst fouling.

Ruhrchemie was planning the application of this process to a wide boiling (190 to 390° F.) Fischer-Tropsch fraction to improve it as a motor gasoline component. Such a fraction could be reformed by this method to give a 93 percent weight yield of material of the same boiling range as the feed. With a 47 percent volume aromatic content, the octane number of the product would be 68 compared with 18 for the feed.

The catalyst life was estimated to be about one year, which would be equivalent to a catalyst consumption of roughly one pound per barrel

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Appendix II (Cont'd.)

of liquid throughput.

A general description of the process as announced by Ruhrchemie in 1943 was transmitted to the Bureau of Ships:

XXVIII. Die Aromatisierung von gradkettigen aliphatischen Kohlenwasserstoffen aus der Fischer-Tropsch - Synthese. (Ruhrchemie - report by Dr. Rottig in January 1943).

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Serial 327P23
dated 22 Oct. 1945

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8C432

TECHNICAL REPORT No. 146-45

THE MANUFACTURE AND APPLICATION OF LUBRICATION IN GERMANY

July 1945

U·S·NAVAL·TECHNICAL·MISSION·IN·EUROPE

ADDRESS NAVY DEPARTMENT,
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FOR VICTORY BUY WAR

CNO ltr Op-337
Serial 337P23
22 Oct. 1945

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10 SEP 19[illegible]

To: Commander, Naval Technical Mission in Europe

Via: Chief of Naval Operations
(Op-16-PT)

Subj: Technical Report No. 146-45 - Errata.

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1. Two errors appear in the subject report and correspondence with Technician M. E. Spaght discloses the following corrections should be made:

(a) The title of the report should read "The Manufacture and Application of Lubricants in Germany".

(b) Paragraph 2, page 49, should read, "The Leuna process gives an ethylene yield in the plant of 70% wt. based on charged ethane. The ethane to be reacted (three volumes) is heated to 1100°F, oxygen (one volume) is separately preheated to 750°F. and the two are combined under slight vacuum in a carefully designed burner wherein the temperature rises to 1470 to 1560°F. The product of the furnace is cooled by exchange and the ethylene is separated and purified to a minimum of 95% wt. in the final product."

2. It is requested that these corrections be circulated to the distribution list for this report.

D. L. Hooper
By direction of
Chief of Bureau

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Serial: 732

80434

7 August 1945.

[redacted]

From: Chief, U.S. Naval Technical Mission in Europe.
To : Chief of Naval Operations (OP-16-PT).

Subject: U.S. Naval Technical Mission in Europe Technical Report No. 146-45, The Manufacture and Application of Lubrication in Germany - Forwarding of.

Enclosure: (A)(HW) Copies of subject report.

1. Enclosure (A) is forwarded herewith.

2. It is requested that CNO (OP-16-PT) make up additional copies for such other agencies as may be interested in this report.

Harry D Hoffman
HARRY D. HOFFMAN,
Captain, U.S.N.,
Acting.

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TECHNICAL REPORT No. 146-45

THE MANUFACTURE AND APPLICATION OF LUBRICANTS IN GERMANY

July 1945

U. S. NAVAL TECHNICAL MISSION IN EUROPE

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SUMMARY

This report records and summarizes technical information, obtained by U.S. Naval Technical Mission in Europe investigators, on the quantity, quality, composition, and manufacture of German lubricants during the past war years.

Figures for the quantities of oils produced from all sources are presented. The properties and specifications of some of the important commercial lubricants are discussed.

The methods by which lubricating oils are produced from petroleum are outlined, and the several processes that were in use for producing synthetic oils are described. The manufacture and application of a new synthetic lubricating oil component are described.

The preparation and use of several new additives are outlined. The position of lubricating grease manufacture is covered briefly.

An appendix describes the manufacture of ethylene, the raw material for one of the synthetic oils.

There have been transmitted to the Bureau of Ships several German documents which will serve to elaborate in more detail some of the subjects covered herein.

Samples of the most promising new oils and additives were obtained and forwarded to the Naval Research Laboratory at Anacostia, D. C.

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TABLE OF CONTENTS (CONT'D.)

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THE MANUFACTURE AND APPLICATION OF LUBRICANTS IN GERMANY

1. Introduction.

In allied nations there have been many technical developments during recent years in the manufacture and application of lubricants, both because of new demands and because this field has been a subject of extensive chemical research. Because of its highly industrialized and mechanized economy, it was to be anticipated that Germany also would have given great attention during recent years to the development and manufacture of lubricants.

Whereas in America and in most other nations petroleum is the source of essentially all liquid fuels and lubricants, in Germany the bulk of liquid fuels and some lubricants were known to have come from synthetic processes. It was expected that new developments would have occurred at least in the field of synthetic lubricants.

To obtain a comprehensive view of German developments in this field, technical personnel of all of the producers of synthetic lubricants were found and interrogated and most of the plants producing these synthetic lubricants were visited.

To augment and substantiate the information gained from interrogation and observation, many documents, reports and descriptive papers were accumulated, and samples of some of the newer synthetic materials were obtained.

In the following sections are discussed the supply and composition of German lubricating oils, the manufacturing methods used for mineral oils, and the development and production of synthetic oils and their components. New additive developments are described and discussed.

It should be pointed out that in reporting herein the information gained from many sources and under many different circumstances, the opinions of those contacted were obviously reflected in the information given. Further, in some cases it has not been possible to obtain or present documents with test data to confirm opinions and contentions.

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1. Introduction (Cont'd.)

Substantiating data will be desirable in many instances using analyses and test procedures that are in standard use in America.

2. Commercial Supply and Composition of German Lubricating Oils.

In Table I is shown an approximate breakdown of the German supply of lubricating oils from petroleum and the various synthetic processes. These figures were obtained from documents and from interrogation of a government oil planning board official (Dr. Butefisch). The volume figures apply to the period of about 1942. Subsequent to 1942, efforts were made to increase by four-fold the production of aviation oils, and for this program many plants were still being constructed in 1944, when the Allied bombing raids began to be concentrated on the oil industry. Hence, in 1943 the supply of oils may have exceeded somewhat the figures in Table I.

Despite the development of several types of synthetic lubricating oils, it will be seen that the bulk of the commercial volume still came from petroleum. The crude petroleum used for the production shown in Table I was from Germany, Austria, Hungry and Rumania.

With the exception of the small volume produced by Rheinpreussen, the synthetic lubricating oils went almost entirely to aircraft oil. The aircraft oil supplied to the Luftwaffe was normally a mixture of equal parts of synthetic and highly refined mineral oil. The specifications for aircraft oil and some approximate analytical data on the synthetic and mineral oil components and the blend thereof are shown in Table II. This mixed oil was normally used without additives or inhibitors.

For engines other than aircraft, in general, refined mineral oils only have been used in Germany. An exception was the use by the German Navy of the Rheinpreussen synthetic lubricating oil in diesel engines. Gasoline and diesel engines were normally supplied with the same grades of oils with no effort being made to supply a special oil for diesels. It was the general opinion of both oil and engine people in Germany that the well refined mineral oils were adequate for today's diesel engine requirements. Again, no special additives

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TABLE I

SUPPLY OF GERMAN LUBRICATING OILS
(all figures are in barrels per day)

SUPPLIER	METHODS OF MANUFACTURE	VOLUME OF SUPPLY	DISPOSITION	
			AIRCRAFT OILS	OTHER
Various mineral refiners	Conventional refining methods	15750	750	15000
Brabag Zeitz	TTH Hydrogenation of tars	600	-	600(1)
Pölitz	Olefin Polymerization	250	250	-
Rhenania Ossag	Olefin Polymerization	200	200	-
Ruhrchemie	Olefin Polymerization	200	-	200(2)
Rheinpreussen	Aromatic-Parrafin condensation	50	-	50(3)
IG-Leuna	Ethylene Polymerization	300	300	-
IG-Leuna	Ester Synthesis	100	100	-
	Totals	17,450	1,600	15,850

(1) Relatively low quality, used for industrial and automobile lubricants.
(2) Used by Army for trucks, tanks, etc.
(3) Consumed entirely by German Navy for Diesel engines.

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2. Commercial Supply and Composition of German Lubricating Oils. (Cont'd.)

or inhibitors were included.

Two (2) grades of motor oil were supplied to the Wehrmacht, one for winter and one for summer use. The winter grade had a viscosity of approximately 52 S.S.U. at 210 degrees fahrenheit and a viscosity index of about 100, while the corresponding values for the summer grade were 62 and 95. The great difficulty encountered in Russia in the winter of 1941-42 with cold starting of trucks and tanks when using these winter motor oils was an impetus to the synthetic ester oil development which is discussed later.

It will be noted in Table II that the synthetic component is much more viscous than the mineral oil component. Since the viscosity of the synthetic oils can be rather easily controlled, these oils were made viscous so that mineral oil bright stocks (high viscosity fractions) could be released for industrial purposes.

The synthetic oils have been applied in small volume to many specialty uses which are discussed in connection with the individual syntheses.

Because of the low temperatures encountered in Germany's war campaign, lowering of the pour point of lubricating oils was desired for almost every application. Special problems concerned the supply of a low temperature lubricant for torpedoes, a low temperature oil for weapons, a water-soluble oil for use with torpedoes, and a journal oil for the German railroad. Those problems all were solved through the supply of special synthetic products.

The lubricating oils used in normal automobile service and for general industrial equipment apparently were little different from those used in America.

3. Lubricating Oil from Petroleum.

It was seen in Table I that raffinates from mineral oil were still the preponderant source of lubricants in Germany. These oils came from a variety of crudes and via many different refining processes.

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TABLE II

PROPERTIES OF GERMAN AIRCRAFT OIL

	Air Ministry Specifications for Aircraft Oil	Typical Synthetic Oil from Olefin Polymerization	Typical Refined Mineral Oil Fraction	Typical Mixture of Equal Parts of Synthetic & Mineral Oils
Density at 68°F.	0.895 max	0.84	0.89	0.875
Viscosity, SSu at 212°F.	95 min	215	57	105
Viscosity, SSu at 122°F.	580-660	1450	250	590
Viscosity Index	98 min	120	98	110
Pour Point, °F	-4 max	-7	± 0	-13
Flash Point, °F	437 min	604	437	464
Fire Point, °F.	437 min	670	500	534
Conradson Carbon % wt.	0.25 max	0.38	0.16	0.22
Ash Content, % wt.	0.01 max	0.001	0.00	0.001
Neutralization Number, Mg. KOH/g.	0.06 max.	0.03	0.03	0.03
Saponification Number, Mg. KOH/g.	0.2 max.	0.11	0.11	0.08

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3. Lubricating Oil from Petroleum. (Cont'd)

The crude oils processed for lubricating oil manufacture included Hannover (Germany), Zistersdorf (Austria), Rumanian Pakura (distillation bottoms from Rumanian crude), Hungarian and Galizian.

Dewaxing and solvent extraction were employed by all of the major producers. Propane and ethylene dichloride dewaxing were employed. Solvent extraction methods included furfural, SO_2- benzol, phenol and propane (Duo-sol), and phenol as a single solvent.

Aside from the medium and low VI oils made for industrial uses, the bulk of the lubricating oil processed from petroleum was refined to a VI in the region of 80 to 100. Because of the good native quality of the lubricating oil fraction in the crudes being processed, the production of high VI products did not entail large losses to selective solvent extracts. For example, in the refining of Zistersdorf crude, the final yield of deasphalted, dewaxed, solvent extracted, acid treated, clay filtered lubricating oil was 50 percent by weight of the gas oil free residue from the crude topping units.

Many of the German crude oil refineries were built by American construction firms and most of the lubricating oil refining processes were operated under license from American or Allied companies.

The following documents transmitted to the Bureau of Ships, relates to this subject:

I. Brochaus Plan
(Material balance and flow diagram of a refining system manufacturing lubricating oil from an Austrian crude oil).

4. Mixed Polymerization Process applied to Lubricating Oils from Petroleum.

A new synthetic process involving mineral oil lubricating fractions is that of "mischpolymerisation" or mixed-polymerization. It was developed primarily by I. G. and was described by them in reports of 1942 and 1943.

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4. Mixed Polymerization Process applied to Lubricating Oils from Petroleum.

A deasphalted and dewaxed but not solvent extracted lubricating oil distillate is reacted with a synthetic polymer of ethylene or other olefins, such as those obtained from the thermal cracking of waxes. A mixture of roughly equal parts of the two components is allowed to react in the presence of $AlCl_3$. The product is an oil of superior quality. The yield exceeds substantially that which could be obtained by mixing the olefin polymer and the mineral oil fraction after such solvent extraction that the mixture would have the same VI as the product of mixed polymerization.

An application worked out by I.G. involved the treatment of a lubricating oil distillate from a German crude oil. To prepare 1.0 volumes of oil meeting aircraft oil specifications by solvent extraction, 1.5 parts of lubricating oil distillate (deasphalted and dewaxed) were needed. This would require the discard of 0.5 parts as extract. However, by mixed polymerization of the 1.5 volume of distillate with 1.5 volumes of ethylene polymer, an approximately 3.0 volume yield of oil could be obtained equal in quality (both by laboratory and full scale engine tests) to either the ethylene polymer itself or the solvent extracted mineral oil fraction. Thus, the yield of aircraft oil could be increased from 2.5 to 3.0 volumes; i.e., 0.5 volumes of low grade extract could be made into aircraft oil.

To accomplish the mixed polymerization reaction, ethylene is first polymerized with $AlCl_3$ (described in detail in a later section on manufacture of Ethylene Polymers) The polymer product - $AlCl_3$ mixture, containing about 5 percent weight $AlCl_3$ is mixed in an autoclave with an equal weight of mineral oil. A temperature of 210 to 250 degrees fahrenheit is maintained and the mixture is agitated for 3 to 4 hours. The reaction is explained as being primarily between aromatics, (and any olefins present) in the mineral oil and the olefin polymers of ethylene. The reaction product is then freed of $AlCl_3$ and neutralized. Fractionation may or may not be necessary, depending upon whether or not any low boiling components entered the ethylene polymerization system.

The mixed polymerization process is claimed to yield oils which are actually superior in engine ring-sticking performance to a mixture of the ethylene polymer and a heavily extracted mineral oil

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TABLE III

MIXED POLYMERIZATION TREATMENT OF A LUBRICATING OIL DISTILLATE FROM PETROLEUM

	Deasphalted and Dewaxed Petroleum Distillate	Ethylene Polymer	Mixed Polymerization Product of equal parts of Ethylene Polymer and Petroleum Distillate
Input, parts by wioght	52.5	47.5(1)	-
Outturn, parts by weight	-	-	93.5(2)
Density at 68°F.	0.915	0.855	0.870
Viscosity, S.S.u. at 100°F.	540	2950	1200
Viscosity, S.S. u. at 210°F.	58	205	108
Viscosity Index	54	109	108
Flash Point, °F.	428	428	428
Pour Point, °F.	±0	-22	-22
Conradson Carbon, % wt.	1.09	0.08(est)	0.15

(1) The input is expressed as the amount of ethylene polymer of this quality that would have been produced by the ethylene charged. To produce 47.5 weights of this polymer oil, 63.3 weights of ethylene is required.

(2) In addition 5.1 weights of low molecular weight material is produced.

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4. Mixed Polymerization Process applied to Lubricating Oils from Petroleum, (Cont'd.)

raffinate. (See section on "Ethylene Polymers as Lubricating Oils" for description of ring-sticking test.)

Some brief yield and analytical data on the mixed polymerization treatment of a fraction of Hauskirchen crude oil are given in Table III.

In 1943 the German government had ordered I. G. to proceed with plants at Leuna, Heydebrek, and Moosbierbaum to produce a total of about 1500 barrels per day of aircraft lubricating oil by the mixed-polymerization process. The olefin raw material was to be ethylene. However, because of subsequent war developments, none of these plants was completed.

The following documents, transmitted to the Bureau of Ships, relate to this process:

II Uber das Prinzip der Schmierol - Mischpolymerisation. (
(I.G. Leuna-Aktennotiz of January 12, 1942).
III Mischpolymerisation non SS-Ol mit Mineralol (I.G. Leuna
February 1, 1943).
IV Herstellung von Flugmotorenol durch Mischpolymerisation.
(I. G. Leuna-Bericht of March 29, 1943).

5. The TTH Process for Lubricating Oil Manufacture

The TTH process will be mentioned here only because it was a source of some of Germany's lubricating oil (see Table I). The process is being fully described in a report of the U. S. Navy Technical Mission in Europe entitled "The Production of Synthetic Fuels by the Hydrogenation of Solid and Liquid Carbonaceous Materials."

The TTH process (Tief-Temperature Hydrierung) is a mild high pressure hydrogenation of braun coal tar. Instead of yielding gasoline as the main end product, as is the case with most coal and coal tar high pressure hydrogenation operations, this process is a milder hydrogenation and yields substantial volumes of diesel fuel, lubricating oil, and wax. The only commercial installation in Germany was the Brabag plant in Zeitz. The lubricating oil produced there had a

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5. The TTH Process for Lubricating Oil Manufacture, (Cont'd.)

viscosity index of 50 to 60. It was separated from the hydrogenation product and without further treatment was sold for use as a motor lubricating oil.

This source of lubricating oil was invoked only because of the shortage of lubricants in Germany during the war.

6. Synthesis of Lubricants by Polymerization of Olefins using Aluminum Chloride.

The polymerization of low boiling olefins to compounds boiling in the lubricating oil range using $AlCl_3$ as a catalyst was the process used to produce most of Germany's synthetic lubricants. There are two different applications of the process, one developed and employed by I. G. using ethylene as the olefin raw material, and one employed by Ruhrchemie, Rhenania Ossag, and Politz (Stettin), using a mixture of olefins boiling in the 80 to 570 degrees fahrenheit range as raw material. The products from the two types of operations are chemically and in performance very similar. It is maintained by I. G. technologists that ethylene can be polymerized to yield oils of higher viscosity than those that are prepared from higher boiling olefins. They believe that under normal economic conditions ethylene would be the preferred olefin for polymerization.

The choice by I. G. technologists of ethylene for raw material rather than higher boiling olefins, which are prepared from Fischer-Tropsch fractions and from petroleum wax, may have been due in part to their particular company position. As operators of coal and tar hydrogenation processes, they could perhaps make low boiling olefins available more readily than higher boiling ones of the necessary quality.

Both types of application used commercially in Germany will be described.

(a) Ethylene Polymers as Lubricating Oils.

The I. G. organization in Leuna has devoted much thought to the fundamental questions underlying the syntheses of a high quality lubricating oil. It was reasoned that a crude oil fraction, however well refined, still contains carbon atoms in perhaps every hydro-

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6. Synthesis of Lubricants by Polymerization of Olefins using Aluminum Chloride, (a) (Cont'd.)

carbon configuration, and that some of these configurations must be undesirable as lubricating oil components. These people believed therefore that a molecular type should be chosen which shows itself to contain the maximum number of properties desired in a lubricating oil, and that a synthesis for that molecule should then be developed.

The basic requirements of a lubricant are that it shall (a) have a low rate of change of viscosity with temperature (high VI); (b) have a low pour point, allowing low temperature use; (c) have good lubricating properties; and (d) be stable (unreactive) under the conditions of use. I.G. believed that a hydrocarbon molecule could be designed which would satisfy at least (a), (b) and (d), and if (c) were not adequate, then additives could be considered to improve that property.

To have a high VI, an oil must consist of molecules which can absorb energy without breaking away from each other. A long straight paraffin chain with no side chains, or with very short side chains, does not have a shape which allows it to interlock itself with other molecules. Aromatic and naphthenic nuclei agglomerations are easily forced apart. Paraffin molecules consisting of a few long chains, however, should be more difficult to pull apart. Paraffins consisting of long chains, which will repulse one another and tend to occupy a large space volume, should be high VI components. Long

side?

paraffin chains on aromatic nuclei should also give molecules which tend to interlock themselves with one another, and hence be high in VI. In designing a molecule for high VI, therefore, a paraffin consisting of long side chains on a central structure, or an aromatic or naphthene nucleus with long paraffin chains, should be preferred forms.

If the viscosity of an average high VI oil follows an extrapolated curve, the slope of which is obtained from measurement between 30 and 210 degrees fahrenheit, then quite low temperatures are reached before the oil is so viscous that it seriously hinders or prevents the operation of the mechanism employing it. However, normal mineral lubricating oils show wide deviations from this extrapolated viscosity curve, and as their pour points are approached plastic flow characteristics manifest themselves. To obtain an oil which follows the extrapolated viscosity curve, and does not exhibit plastic

6. Synthesis of Lubricants by Polymerization of Olefins using Aluminum Chloride. (a) (Cont'd.)

flow or crystal formation, it was reasoned that the oil should be a mixture of compounds, none of which is outstandingly high melting and all of which form complete and true solutions with the other components. To obtain low melting compounds, and thereby a pour point which corresponds simply to a high viscosity, disymmetry within the individual molecules is necessary.

Compounds which have highly symmetrical molecules are characterized by high melting points. Thus, normal octane has a melting point of -57 degrees centigrade the mono-methyl heptanes have melting points between -110 and -120 degrees centigrade and 2,2,3,3 tetramethyl butane has a melting point of plus 102 degrees centigrade. In the design of a lubricating oil molecule, therefore, a disymmetry or unbalance should be planned. A normal paraffin is unsatisfactory, and a branched molecule of high symmetry may also be unsatisfactory.

To possess good lubricating properties, a molecule must be able to adhere to the surface it is lubricating. If its use is under very low load; i.e., far in the region of so-called hydrodynamic lubrication, it needs to possess little more than the ability to wet the surfaces and retain a film between them. If the load is higher, then a more tenacious adherance to the surface is necessary. In this region, a molecule should be supplied which has a configuration allowing close contact between the mass of the molecule and the metal being lubricated. By this close contact, "adhesion forces" cause the molecule to be firmly held by the metal, or one may supply the lubricating molecule with a point or points of activity (called by I.G. an "active electron field") such as particular "strained" carbon configurations or combined oxygen, nitrogen, or sulfur atoms in particular arrangements. If operation is under extreme pressure, then even tenacious surface adherance may be inadequate and materials must then be supplied which enter into active and perhaps irreversible combination with the surfaces. A lubricating oil to be used for aircraft, automobile, and diesel engine service perhaps doesn't need extreme pressure properties, but it should contain a molecule which can combine quite firmly, if reversibly, with metal surfaces.

Lastly, the ideal lubricant will be unreactive in service, undergoing no oxidation, no deterioration, and forming no degredation products. To approach this quality, I.G. reasoned that, above all,

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6. Synthesis of Lubricants by Polymerization of Olefins using Aluminum Chloride. (a) (Cont'd.)

aromatic carbon atoms should be excluded. Aromatics characteristically form carbon and high molecular weight condensation products upon decomposition. Aromatic oils are, however, good solvents for their degredation products. Paraffin type compounds, while they may crack at high temperatures, form less harmful degredation products. In other respects, paraffins are notable unreactive. No hydrocarbon will be totally resistant to decomposition or chemical change, but a paraffin must be chosen as the nearest approach to the ideal unreactive lubricating oil molecule.

In deciding then what type of synthetic lubricating oil molecule is to be produced, it is seen that it should be possible to design a paraffin with a high VI, a low pour point, good resistance to oxidation, and perhaps lubricating properties satisfactory for all but extreme pressure conditions.

In setting out to synthesize paraffin molecules in the lubricating oil range the polymerization of many low boiling olefins was studied. Propylene alone could never be made to give a product of higher than 70 to 80 VI (I.G. found that by incorporating 1 to 2 percent of polystyrene in the polymerization feed, propylene can be made to yield oils with a VI above 100. This fact was observed several years ago but was not further developed, presumably because the introduction of styrene produced oils with unsatisfactory stability. Polystyrene in polymerization feed gave the same characteristic improvement in VI to polymers of other olefins.) Isobutylene gave high VI products, but its polymers have extremely poor lubricating properties. Normal olefins of the type of octylene -1 however, give high quality polymers. Such olefins are the type used in the synthetic processes of Ruhrchemie, Rhenania-Ossag, and Pölitz. However, due at least in part to its particular supply position, I.G. preferred to concentrate on the use of gaseous olefins.

Efforts to polymerize ethylene to high quality lubricating oil had been made by many groups, but none had been able to produce a polymer with a VI above zero. Through very tedious research I.G. found that by careful selection of feed stock and of operating variables, the VI could be raised to about 120. Polymers of up to approximately 300 S.S.U. at 210 degree fahrenheit viscosity were made in yield equal to 78 to 80 percent weight of the ethylene feed.

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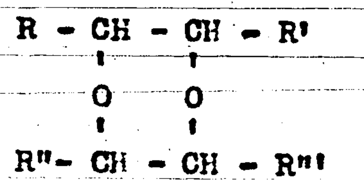
6. Synthesis of Lubricants by Polymerization of Ole fins using Aluminum Chloride. (a) (Cónt'd.)

The pour point was -30 degrees fahrenheit. The lubricating properties of this material were roughly equal to those of high quality mineral oil, hence, satisfactory for most general uses.

Regarding the stability of ethylene polymers against oxidation and other chemical changes, these materials were found to absorb oxygen but their properties were not greatly altered hereby. A mineral oil, being a mixture of many molecular types, forms a great multiplicity of oxidation products. An olefin polymer, however, being simply a paraffin with one olefin linkage per molecule, forms only a few specific oxidation products. One is a fatty acid which, in this molecular size, is non-corrosive and is itself a very good lubricant. The other is a so-called peroxide linkage, wherein two (2) molecules form oxygen bridges with each other of the nature of



$$\begin{array}{c} R - CH - CH - R' \\ \quad\;\; | \qquad\; | \\ \quad\;\; O \qquad O \\ \quad\;\; | \qquad\; | \\ R'' - CH - CH - R''' \end{array}$$

This process of oxygen bridging and growing molecular size does not continue indefinitely, however, because as the size of the aggregate grows, its reactivity toward further oxygen absorption decreases rapidly. Thus, the final state may be aggregates of perhaps two (2) or three (3) of the original molecules, each bridged to a neighbor with two (2) atoms of oxygen. Again, these oxidized aggregates are very good lubricants, actually better than the original material and quite stable. In use, the viscosity of a straight ethylene polymer increases noticeably (perhaps 33 percent) at first but soon reaches a plateau beyond which it does not further change.

The manufacture of ethylene polymers was started by I.G. at Leuna in 1937 in a small plant producing 15 barrels per day. By 1944 plants in Leuna and Schopau (near Leuna) were producing a total of 325 barrels per day. Plans had been laid for extensions and other plants to produce ultimately 925 barrels per day.

Since 1941, all ethylene polymer had been made to a viscosity of approximately 220 S.S.U. at 210 degrees fahrenheit and had been

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6. Synthesis of Lubricants by Polymerization of Olefins using Aluminum Chloride, (a) (Cont'd.)

used in equal volume with highly refined mineral oil for aircraft oil. The ring-sticking test which is used to evaluate air-craft oils shows ethylene polymers to be very outstanding.

(1) The ring-sticking test was used widely in Germany and had become a specifications measurement for aircraft lubricating oils. It had been first used in 1926 but subsequently many improvements were made to increase reproducibility and to make its results more indicative of full scale performance.

(2) The test device is a single cylinder aircraft engine, BMW 132 (Bayerische Motoren Werke). The cylinder is set up for test block operation with appropriate control and measureing devices. It is operated at 1900 revolutions per minute with a power output of 57 horsepower. The cylinder head temperature is 500 degrees fahrenheit, the fuel inlet temperature is 90 degrees fahrenheit the oil inlet temperature is 210 degrees fahrenheit, and the oil outlet temperature is 230 degrees fahrenheit. An initial oil charge of ca. 2.5 gallons is used and the oil circulation rate is about 26 gallons per hour.

(3) A pressure recorder on the crankcase shows when gas by-passing begins as the result of piston ring-sticking. The power output drops at the same time and the cylinder becomes hotter. Once gas by-passing begins, a very short time only is required before complete sticking of the rings occurs.

(4) It was specified by the German Air Ministry that all aircraft oils must have a minimum ring-sticking time of 8 hours. A mineral oil normally would just reach 8 hours, but ethylene polymers would run for 20 hours and often longer. The synthetic oils from wax olefins normally gave test times between 10 and 20 hours.

(5) The ring-sticking test was considered to be a good prediction of aircraft oil stability under performance conditions. The test was not considered necessary for evaluating motor or diesel oils, because in these engines ring-sticking rarely occurs.

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6. Synthesis of Lubricants by Polymerization of Olefins using Aluminum Chloride. (a) (Cont'd.)

A highly refined mineral oil deteriorates after 8 hours of test to such an extent that the rings of the test engine are stuck. Ethylene polymers give a test time as high as 40 hours, normally at least 20 hours, and equal mixtures of mineral oil and ethylene polymers give a test time longer than the average for the two components. The high VI and low pour point of the ethylene polymers are of course desirable properties for aircraft use.

Prior to 1941 a lower viscosity polymer (about 100 S.S.U. at 210 degrees fahrenheit) had been made as well as the more viscous grade. In addition to these two (2) main products, in either operation a small volume (about 10 percent of the total yield) of a 60 to 100 S.S.U. at 122 degrees fahrenheit fraction was recovered by product fractionation. This fraction had recently been highly valued as a lubricant for jet aircraft. It had a pour point of -95 degrees fahrenheit and was mixed with other ingredients to produce various lubricants for low temperature operation. An ingredient of a journal lubricant used by the German Reichsbahn (railroad) was recovered by hydrolysis of the $AlCl_3$ sludge produced in the polymerization.

In Table IV are shown typical yield and quality data for the operations producing both viscosity grades of ethylene polymers.

(b) Manufacture of Ethylene Polymers.

An attached document ("Das Athylen Schmieröl Verfahren") describes in detail the process that was in use in Leuna, but a brief outline of the operation is supplied below.

To obtain high viscosity and high VI products, the ethylene raw material should be minimum 95 percent pure. An inert content above a few percent disrupts the chain formation and prevents polymerization from proceeding to the formation of high viscosity products. A very serious poison is carbon dioxide, and unless this contaminant is almost entirely absent, polymerization will not proceed. (Reaction with CO_2 apparently seals off the olefin chains.) While carbon monoxide is undesirable, 0.005 percent can be tolerated. Nitrogen (as ammonia), sulfur and oxygen are also poisons, and all should be completely removed. A propylene

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TABLE IV

TYPICAL YIELDS AND PROPERTIES OF ETHYLENE POLYMERS

	Low Viscosity Polymer Product.	High Viscosity Polymer Product.	Low Viscosity Distillate Oil Fraction	Oil from $AlCl_3$ Sludge by Hydrolysis
Yield, % wt. of charged ethylene	-	76.0	6.8	7.2
Yield, % wt. of charged ethylene	ca. 70	-	ca. 10	ca. 10
Density at 68° F.	0.850	0.853	0.817	0.857
Viscosity, S.S.U. at 100° F.	1050	3200	44	1170
Viscosity, S.S.U. at 210° F.	106	215	-	106
Viscosity Index	124	111	-	107
Pour Point, °F.	-36	-33	below -100	-35
Flash Point, °F.	375	446	293	356
Conradson Carbon per-cent wt.	0.08	0.08	0.01	0.20
Molecular weight *	640	825	ca. 250	325

[redacted]

* Determined by boiling point elevation method

6. **Synthesis of Lubricants by Polymerization of Olefins using Aluminum Chloride, (b) Cont'd.)**

contaimination of a few percent can be tolerated, but above perhaps 5 percent the quality (particularly VI) of the product begins to decrease.

To obtain ethylene of the required purity from a process of ehtane dehydrogenation, a system of selective absorption or Linde fractionation is employed. The production and preparation of ethylene by this system is described in Appendix I to this report.

The polymerization operation is a batch process and proceeds in two steps, first, the catalyst preparation and second the polymerization itself. A stirred autoclave (carbon steel) of about 30 barrels capacity was used in Leuna. Into this autoclane was first run about 400 gallons of a recycle oil, which was a 260 to 520 degrees fahrenheit fraction separated from the polymerized product. This recycle oil, which was an incompletely polymerized product, was used as a slurrying oil for 275 pounds of $AlCl_3$ (equal to 5 to 6 percent weight of the ethylene to be charged) (The $AlCl_3$ used normally contained 2 to 4 percent weight of $FeCl_3$ to limit the activity.) Ethylene gas then was introduced until a pressure of 30 atmospheres had been established. The temperature then was raised to 160 degrees fahrenheit by means of hot water coils in the autoclave. Ethylene polymerization began and the temperature rose rapidly to 360 to 430 degrees fahrenheit. Cooling water then was put through the coils to bring the temperature down to 230 to 250 degrees fahrenheit which was the opereting level. This ended the catalyst preparation step. The ethylene pressure had dropped practically to zero in the operation, and the product of this step was a catalyst compound of $AlCl_3$ and polymerized ethylene. The temperature to which the system rises in the catalyst preparation step determines the activity of the prepared catalyst mass. The higher this peak temperature, the less active the catalyst.

Ethylene then was introduced into the system as a vapor at the maximum rate possible while maintaining the temperature at the desired level. This rate was governed only by the ability of the cooling system to remove the heat of reaction. As the

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6. Synthesis of Lubricants by Polymerization of Olefins using Aluminum Chloride, (b) (Cont'd.)

reaction proceeded, the catalyst would begin to lose activity so that a steadily increasing pressure of ethylene was used to consume the system's heat removing ability. At the end of about six hours, the ethylene pressure had risen to 20 to 30 atmospheres, and a total of 4800 pounds of ethylene had been introduced and reacted. The catalyst was considered spent at this point and further use of it resulted in a depreciation of the product.

To produce the more viscous grade of oil a very active catalyst was prepared by limiting the peak temperature in formation to 360 degrees fahrenheit. A low operating temperature, 230 degrees fahrenheit then was used. To make the less viscous grade, a less active catalyst was prepared (peak temperature in formation was 430 degrees fahrenheit) and an operating temperature of 250 degrees fahrenheit was used.

The operating temperature and not the catalyst activity determines the chain length; the higher the temperature the shorter the length the chain is allowed to attain before it is thrown off the catalyst. When a more viscous oil is desired and a lower temperature therefore is necessary, an active catalyst is required in order to accomplish the polymerization. When the temperature is raised in producing a less viscous grade, a less active catalyst is required, both because its activity increases with temperature and because less extensive polymerization is possible before the temperature forces the particle off the surface of the catalyst and thereby ends its growth. Actually, apart from the lack of necessity of the more active catalyst at the higher temperature, the lower activity catalyst is desirable in order to limit the cracking reaction which begins to be noticeable near the 250 degrees fahrenheit level.

In addition to catalyzing the simple addition of ehtylene molecules to the end of chains, an important accomplishment of the $AlCl_3$ catalyst is that of olefin isomerization; i.e. shifting of the double bond toward the center of the molecule. Through this isomerization, polymerization continues from a centralized double bond, thus producing molecules possessing long side chains and therefore a high VI. It is considered that this is the important isomerization capacity of $AlCl_3$ in ethylene polymerization, although some paraffin isomerization undoubtedly occurs,

6. Synthesis of Lubricants by Polymerization of Olefins using Aluminum Chloride. (b) (Cont'd.)

giving branches on the end of the long chains and again yielding a molecular design which would be expected to have a high VI.

During the course of the described 6 hour process, the molecular weight of the polymers being formed gradually decreases. The formed polymers act as diluents which characteristically lower the size of the particles being formed. Thus, the product of a batch polymerization of ethylene is a mixture of many molecular sizes.

At the end of the 6 hour period, the ethylene pressure on the system was released and the temperature was lowered to Ca. 175 degrees fahrenheit. The $AlCl_3$ slurry phase was centrifuged from the oil layer. A small volume of methanol (20 to 30 gallons) was then added to the oil phase to react with $AlCl_3$ - unsaturated hydrocarbon complexes which remained dissolved. This methanol reaction product separated out and was removed; the oil layer thereby being almost completely freed of $AlCl_3$. The oil was neutralized and then fractionated into recycle oil, the low viscosity distillate oil fraction (normally boiling up to about 660 degrees fahrenheit), and the main polymer oil. This residual polymer oil, the main yield, was treated with bleaching earth and filtered.

The separated $AlCl_3$ sludge layer was hydrolyzed to yield and oil phase which was further polymerized by a subsequent $AlCl_3$ stage of treatment and made into a low temperature railroad journal lubricant.

A typical weight balance for the polymerization step is shown in Table V.

The following documents transmitted to the Bureau of Ships relates to ethylene polymerization:

V. Das "Athylen - Schmierol - Verfahren (I. G. Leuna
Dr. H. Zorn report of about July 1943)

80459 [redacted]

TABLE V

HYDROCARBON WEIGHT BALANCE FOR BATCH POLYMERIZATION OF ETHYLENE

(Volume of Autoclave = ca. 30 barrels)

Input	**Pounds**	**Percent**
Ethylene	4860	100.0
(Recycle Oil)	(2650)	—
Total Input	4860	100.0
Outturn		
Polymerized Lubricating Oil Product	3690	75.9
Low Viscosity Distillate Oil Fraction	330	6.8
Oil from $AlCl_3$ Sludge Hydrolysis	360	7.4
(Recycle Oil)	(2650)	—
Unreacted Ethylene	130	2.7
Treating Losses, etc.	350	7.2
	4860	100.0

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[redacted]

6. Synthesis of Lubricants by Polymerization of Olefins using Aluminum Chloride. (Cont'd.)

(c) Polymerization of Higher Olefins:

As indicated before, olefins boiling in the 80 to 570 degrees fahrenheit range were used in Germany for the synthesis of high grade lubricants. This synthesis is not new, having been applied elsewhere in the world prior to the war. The most suitable olefins for such synthesis are normal (straight chain) compounds with the double bond in the alpha position, and two (2) sources of such raw materials were used in Germany; olefins from the thermal cracking of a Fischer-Tropsch synthesis fraction and olefins from the thermal cracking of paraffin wax.

This lubricating oil synthesis was practiced by Ruhrchemie in Holten, by Rhenania-Ossag in Hamburg-Harburg, and at the Politz refinery near Stettin.

At Ruhrchemie, a 360 to 600 degrees fahrenheit fraction from the Fischer-Tropsch plant was cracked thermally at a temperature of 1020 to 1110 degrees fahrenheit. A fraction boiling from 85 to 360 degrees fahrenheit was separated out as polymerization feed. Heavier components were recycled to feed. The ultimate yield of polymerization feed thereby was 60 percent weight of the thermal cracking unit charge.

This polymerization feed contained 60 to 70 percent olefins, largely normal alpha compounds. The naphthene content was only a few percent and the aromatic content was "extremely low"

At Rhenanas-Ossag, the polymerization raw material was prepared by cracking paraffin wax from Austrian crude oil. The thermal cracking was carried out at low pressure and 1040 to 1100 degrees fahrenheit. A 60 percent weight yield of liquids above C_4 was obtained. The liquid was highly olefinic and best suited for lubricating oil synthesis if the wax from which it was prepared was low in oil content. A fraction boiling from 85 to 590 degrees fahrenheit was separated for polymerization feed.

Politz also used Austrian waxes as a source of olefins. The wax was cracked there at low pressure and 910 to 950 degrees fahrenheit. A fraction boiling from 95 to 570 degrees fahrenheit was

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6. Synthesis of Lubricants by Polymerization of Olefins using Aluminum Chloride, (c) (Cont'd.)

separated and heavier components were recycled to extinction. Based on the raw wax feed, a yield of 70 percent of polymerization feed was obtained thereby.

In all cases, the polymerization was carried out in a stirred antoclane at temperatures of 140 to 175 degrees fahrenheit. $AlCl_3$ equal to approximately 6 percent weight of the feed was added and the reaction required 15 to 20 hours. Rhenania began the reaction at near room temperature, after 5 hours the temperature was raised to 175 degrees fahrenheit, and the reaction proceeded for 7 hours more.

In the polymerization, approximately 95 percent of the olefins were converted to material in the lubricating oil range. Of the total polymer, about 75 percent was recovered as primary product. A low viscosity spindle oil normally was separated. Some oil was recycled as $AlCl_3$ slurrying oil back to the polymerization step. This oil comprised approximately 15 percent of the total yield. Politz prepared in addition a cylinder oil by hydrolysis of the $AlCl_3$ sludge phase. The other two operators apparently did not.

Both Rhenania and Politz used fresh $AlCl_3$ for only one batch polymerization operation. Ruhrchemie, however, started with a 6 percent weight addition of $AlCl_3$, but in the second batch only one percent weight of fresh $AlCl_3$ was added and sludge from the first batch was used to make up the volume of slurry. This was repeated for each subsequent batch, withdrawing only enough sludge to keep the catalyst phase constant in volume. At the end of 60 batches, the total sludge was discarded and the process was then repeated for each 60 batches.

After completion of the polymerization step and removal of the $AlCl_3$ sludge phase, the oil phase was treated for removal of $AlCl_3$, neutralized, and fractionated over clay.

The Phenania and Politz oils were used in mixture with mineral oils as aircraft lubricants. The polymer oils were both approximately 210 S.S.U. at 210 degrees fahrenheit, viscosity, 110 to 120 VI, and with pour points of about -15 degrees fahrenheit. They were in general quite similar in properties to the ethylene polymers and were used in the same manner.

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6. Synthesis of Lubricants by Polymerization of Olefins using Aluminum Chloride, (c) (Cont'd.)

The main Ruhrchemie product was a less viscous material of 285 S.S.U. at 122 degrees fahrenheit, viscosity and was sold exclusively to the Army for motor vehicles and tanks. This oil had an average molecular size of C_{26} and hence was only a trimer or tetramer of the original olefins. The Ruhrchemie oil was described as having excellent VI and pour point, but with oxidation stability and lubricating ability not quite equal to those of the best Pennsylvania mineral oils.

Some published data on three different viscosity oils previously marketed by Ruhrchemie showed them to have densities of 0.85 to 0.86, pour points of approximately -40 degrees fahrenheit, VI between 105 and 115 and Conradson carbon values of 0.07 to 0.15 percent weight.

While in recent years the supply of olefins to these $AlCl_3$ polymerization systems has been from thermal cracking of normal paraffins, there were plans that in the future they would be produced at least in part directly from Co plus H_2 synthesis. At Ruhrchemie, a modification of their Fischer-Tropsch plant to employ the "Kreislauf" (recycle) principle was planned to increase the content of olefins in the product. A fraction of this product was to be used directly as polymerization feed without thermal cracking. Further, the application of iron catalysts with increased pressure in Fischer-Tropsch processes was forthcoming. From such operations polymerization feeds containing 60 percent olefins, of which approximately 85 percent is normal olefins, would be obtained directly.

7. Synthesis of Lubricants by Condensation of Aromatics and Paraffins.

A lubricating oil was synthesized by Rheinpreussen in Homberg by condensing naphthalene with paraffins, to make a molecule consisting of an aromatic nucleus with a long paraffin chain.

The Rheinpreussen people were of the opinion that lubricating oils made from a Fischer-Tropsch fraction, as practiced by Ruhrchemie, were not satisfactorily stable to oxidation, and they set out to make a more stable product. They argued that

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7. Synthesis of Lubricants by Condensation of Aromatics and Paraffins, (Cont'd.)

Pennsylvania oils, which they considered to be a standard of stability, contained some aromatic rings and hence that aromatics need not be avoided in order to have a good lubricating oil. Further, Rheinpreussen had large coal and coal tar operations, and they were receptive to any developments that would supply new uses and outlets for aromatics.

The material ultimately developed and manufactured by Rheinpreussen (via a paraffin chlorination and condensation with aromatic process) was a molecule consisting of a naphthalene nucleus and one straight, or only slightly branched, paraffin side chain containing on the average about 16 carbon atoms. This type of molecule gave oils with a VI of about 105 and pour points of + 20 degrees fahrenheit.

In producing their average molecule, Rheinpreussen wanted one paraffin chain per molecule. They had found that one long chain gave a higher VI product than two (2) or more shorter chains. Also, they wanted only one aromatic group attached to each paraffin chain, since molecules consisting of a chain bridging two (2) naphthalene groups were poorer in VI.

Rheinpreussen produced a spindle oil, a turbine oil, a steam cylinder oil of 250 S.S.U. at 210 degrees fahrenheit, viscosity and as their main product a diesel oil of 570 S.S.U. at 122 degrees fahrenheit viscosity. **Rheinpreussen sold this diesel oil exclusively to the German Navy** and was the largest of three (3) suppliers of diesel oil to the Navy.

Rheinpreussen diesel oil enjoyed a very good reputation with the Navy and with Daimler-Benz who supplied the Navy with diesel engines. It was claimed that very good performance was obtained, not exceeded by any other oil available. While the ring sticking test, used to evaluate aircraft oils, showed Rheinpreussen oil to be only equal to refined mineral oils, it was claimed that in diesel engine tests it was definitely superior to mineral oil. No direct comparison with polyethylene was available, but it is generally acknowledged that the Rheinpreussen products are poor aircraft oils, that they decompose to coke and other degredation products more rapidly than synthesized paraffins, and that at the same time they are lower in VI and higher in pour point.

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7. Synthesis of Lubricants by Condensation of Aromatics and Paraffins. (Cont'd.)

For evaluating diesel oil, the Navy used the **MAN** test. This test consisted of heating a sample of oil in an open Erlenmeyer flask in a drying cabinet for 140 hours at 250 degrees fahrenheit and then measuring the asphalt content (insoluble in petroleum ether). A value of less than 0.01 percent weight was required for acceptance.

The Rheinpreussen diesel oil had a Conradson Carbon value of about 1.0 percent weight. It was argued, however, that formation of carbon or asphaltic products was less serious with their type of oil because an aromatic material is able to dissolve and retain in solution such degradation compounds.

The Rheinpreussen process is carried out in two (2) stages. In the first stage, a 430 to 660 degree fahrenheit fraction of Fischer-Tropsch product oil is chlorinated, no catalyst being employed. A temperature of 160 to 210 degrees fahrenheit is used and the reaction time is several hours. At the end of the reaction period, the chlorinated oil contains approximately 18 percent weight chlorine. (This quantity of chlorine is equivalent to somewhat more than one chlorine atom per molecule.)

In the second stage, the chlorinated paraffin is reacted with naphthalene in the presence of gasoline as a diluent and $AlCl_3$ plus aluminum metal (shavings) as catalyst. The naphthalene supplied was 10 percent in excess of a one to one molal ratio with the paraffin present, but slightly less than a one to one equivalent ratio with the combined chlorine. The $AlCl_3$ consumption is about 0.2 percent weight based on the polymerized product. The reaction is carried out in a stirred reactor at 250 degrees fahrenheit; a time of 2.5 to 3 hours is required until no combined chlorine remains in the oil. The product oil is separated, neutralized, treated with clay, and fractionated.

There are attached hereto the following documents relating to the Rheinpreussen process:

VI Beschreibung der Schmierolanlage Rheinpreussen.
(Lurgi Gesellschaft-May 31, 1945)
VII Fliessbild der Schmierolsynthese Rheinpreussen.

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8. Esters as Lubricating Oil Components:

(a) Development and Application

Following development of the ethylene polymer lubricating oils, the I. G. research people resurveyed the field of lubricant application to ask them what were the most important shortcomings of available oils and by what methods could they be improved.

It was always possible, of course, to ask for further VI improvements. Also, for low temperature applications, the pour points of mineral oils, and even ethylene polyers, could be lowered advantageously. The oxidation stability of ethylene polymers was not satisfactory, in that their viscosity increased upon use and they absorbed oxygen to form fatty acids and peroxides, but they did nevertheless give very long operating times in the ring sticking test and did not decompose or deteriorate to give troublesome products. The lubricating ability or "oiliness" of ethylene polymers was only equal to that of mineral oils, and, although this was adequate for most applications, here was a property that could be improved. Ethylene polymers and other similar synthetic oils were non-corrosive in use, gave only average engine wear, were adequately viscous, and had no outstanding shortcomings in other directions.

Thus, a better lubricant would be useful, one which would result in lower friction in the range of hydrodynamic lubrication, and one which would behave somewhat as an extreme pressure lubricant in the range of boundary lubrication. This property should be combined if possible with high VI, low pour point, resistance to oxidation and decomposition, and should otherwise be compatible with general lubricating oil requirements.

For a molecule to be effective as a true extreme pressure agent, it must either adhere very tenaciously to the metal surfaces, or, more commonly, react chemically with the metal surfaces and wear away those high temperature spots or areas operating under the highest loads. However, it should be possible to import good lubricating quality, if not actually extreme pressure properties, to an oil by designing molecules which would securely but reversibly attach themselves to the surfaces being lubricated.

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8. Esters as Lubricating Oil Components. (a) (Cont'd.)

Many organic molecular types were considered for this role, with attention finally being centered on oxygenated hydrocarbons. Of the oxygen forms the ester linkage was particularly interesting. Ethers and ketones have poor lubricating properties, and peroxides and aldehydes are unstable. Esters, however, have very surface-active groups and are stable.

A long program of research on esters ensued. It was found that esters of secondary alcohols were unstable, and the field narrowed to combinations with primary alcohols only. A triester of trimethylol ethane and C_8 to C_{10} fatty acids gave a ring-sticking test time of 100 hours, hence very outstanding for its stability in an engine. It had a VI of approximately 150, a pour point of -95 degrees fahrenheit, but its lubricating properties were not outstanding. Through study of many ester compounds, it was found that the space pattern of a molecule such as the above was so massive that only a sparse covering of the surface with absorbed ester groups could be obtained. It was concluded that the ideal ester would be a simple one wherein the attached members are straight thin chains (unbranched) and the surface could thereby obtain a dense covering by the adhering ester groups.

Monoesters of straight chain acids and alcohols are good, but outstanding in quality are diesters of molecules wherein the two ester groups are separated by a straight chain of several carbon atoms. A diester of adipic acid and normal C_8 alcohol was made and its properties were outstanding. The VI was 238, the lubricating properties were excellent, but the symmetry of the molecule was too great and the pour point was +40 degrees fahrenheit. Disymmetry was introduced by using beta-methyl adipic acid instead of adipic acid, and this product had a VI of 228, excellent lubricating properties, excellent oxidation and engine stability, and the pour point had dropped to -33 degrees fahrenheit.

Thus originated the use of esters as lubricating oil components. The production of 200 barrels per day of adipic and methyl adipic acid esters was being planned in Germany, but the attained rate did not exceed 100 barrels per day. The alcohols for esterification came almost entirely from the "Isobutyl Synthesis" in Ludwigshafen. Different fractions of alcohol were used for the several grades of esters produced, but they were in

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8. Esters as Lubricating Oil Components, (a) (Cont'd.)

general those boiling from 280 to about 570 degrees fahrenheit. These alcohols were primary compounds with some branching, but not enough to interfere with close spacing of molecules on the surface being lubricated. Adipic acid was produced in Germany as a raw material in the manufacture of Perlon, a nylon type material. It was produced by oxidation of cyclohexanol with nitric acid. Methyl adipic acid was produced likewise by oxidation of methyl cyclohexanol, the product being a mixture of the alpha and beta compounds.

The new small production of esters by I. G. was in great demand for specialty oils requiring high VI and low pour points. These demands were largely associated with the German war compaign in Russia, where failure of machines due to high lubricant viscosity during the winters was a very serious problem. An ester of adipic acid and 280 to 360 degrees fahrenheit, alcohols was used in 50 percent concentration in an oil for lubricating weapons. An ester of adipic acid and 320 to 390 degrees fahrenheit alcohols was used as an ingredient of a low temperature journal lubricant for railroad cars. A special hydraulic lubricant for aircraft contained 5 to 10 percent of an ester of adipic acid and cyclohexanol, an ester with an unusually low pour point. There were these and several other specialty uses, but the main volume offtake was for some aircraft lubricating oils, where ester of adipic acid and 360 to 570 degrees fahrenheit alcohols were used in ca. 25 percent concentration.

Because of the shortage in Germany of both acids and alcohols, some of the I. G. raw materials were admittedly not the ones that would have been chosen otherwise. It was planned that ultimately the main alcohol source would be from the new "Synol" process, which can produce primary straight chain alcohol in the desired C_8 to C_{12} range directly from CO and H_2. While adipic and methyl adipic acids are good starting materials, higher acids in the same series, such as sebacic, were considered to be more desirable and active research on the manufacture of higher dicarboxylic acids was in progress.

Another ester research development in Germany meriting note was one by the Deutsche Fettsaure Werke in Witten (Ruhr). This company, which works with fatty acids and produces synthetic butter and other esters, studied the use of esters as normal lubricating

[redacted]

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8. **Esters as Lubricating Oil C**[redacted] **(a) (Cont'd.)**

oil components. They concluded that an ester of pentaerythritol and C_6 to C_{10} fatty acids was well suited for such an application. These compounds had the same desirable properties as the I.G. esters. (DFW proposed to make pentaerythritol from formaldehyde and acetaldehyde). It was the opinion of DFW that the best lubricating oil that can be manufactured today is one consisting of a synthetic base material such as polyethylene and 5 to 10 percent of an ester such as those described above.

(b) **Manufacture of Esters:**

The esterification operation of I.G. is quite simple and does not require unusual purities of raw materials. The acid and alcohol and pumped into a stainless steel limed, agitated reactor, Benzene or naphthalene sulfonic acid is used as a catalyst, about one percent weight of the total mixture being required. A 10 percent stoichionetric excess of alcohol is used. The temperature is 300 to 360 degrees fahrenheit.

During the reaction the water formed continually distills off and progress of the reaction is judged by the rate of evolution of water. The reaction requires about 24 hours.

The product is washed with water and soda which removes the catalyst, unreacted acid, and half esters. It is next distilled to remove alcohol and low boiling secondary products. The ester oil then is contacted with 0.5 percent weight bleaching earth at 160 to 175 degrees fahrenheit and filtered. The product thereafter is handled like a normal refined oil. No stabilizers are added and no special handling precautions are necessary.

While the preferred catalyst for the above described esterification was a sulfonic acid, for more difficult esterification, such as with trimethylol ethane wherein a temperature of above 390 degrees fahrenheit is used, the best catalyst is zinc metal (dust).

Some properties of a few typical lubricating oil esters are given in Table VI.

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[redacted]

TABLE VI

PROPERTIES OF SOME SYNTHETIC LUBRICATING OIL ESTERS

Acid	Adipic	Beta Methyl Adipic	Sebacic	Mixed C_7 Acids-Monocarboxylic
Alcohol	Iso and Normal Octyl*	Normal Octyl	Isooctyl	Trimethylol Ethane
Density 68° F.	0.922	0.920	0.912	0.958
Viscosity, S.S.U. at 122°F.	45.5	48	54	62
Viscosity, S.S.U. at 100°F.	50	55	65	81
Viscosity Index	191	228	189	157
Pour Point °F	-11	-33	Under -98	-94
Flash Point °F.	405	440	455	465

* Half ester of each alcohol.

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[redacted]

8. Esters as Lubricating Oil Components, (b) (Cont'd.)

About 15 gallons of ester of methyl adipic acid and 360 to 480 degrees fahrenheit alcohol, and two (2) drums of the 360 to 480 degrees fahrenheit alcohol were obtained and sent to the Naval Research Laboratory in Anacostia, D.C.

The following documents transmitted to the Bureau of Ships, relate to the manufacture and use of lubricating oil esters:

VIII Die Wissenschaftliche Grundlagen der Schmierstoff Synthesen (I.G. - Leuna - DrH. Zorn report of 14 May 1943)

IX Ester als Schmierole (I.G. - Leuna - DrH. Zorn report of 11 November 1943)

X Esterole (I.G. - Leuna-Paper on properties and applications)

XI Ester als Schmierole (I.G. - Leuna-Dr.H.Zorn paper listing properties of esters)

XII FliessSchema fur Esterolanlagen Me 1016 (I.G. Leuna-Flow diagram and material balances for manufacture of several esters)

XIII E Ol Anlage Schema I Teil and II Teil (I.G. - Leuna - Two process flow diagrams for ester oil manufacture).

9. Other Synthetic Lubricating Oils

German developments in synthetic lubricants were not a result solely of requirements but were to some extent a by-product of the enormous research programs being carried out in all chemical fields.

An example of such a contribution is the polytetrahydrofuran development by I. G. at Leverkusen. Tetrahydrofuran can be produced easily from 1,4 butanediol, an intermediate in an I.G. process for butadiene manufacture. Tetrahydrofuran can be polymerized to yield oils which have been studied as motor lubricants.

[redacted]

9. Other synthetic Lubricating Oils.

The copolymerization of tetrahydrofuran with smaller amounts of ethylene oxide has also been carried out and this product has been considered both as an engine lubricant and a steam cylinder oil.

In polymerization, the tetrahydrofuran ring opens and allows chains to form, with the oxygen becoming an ether in the chain. The copolymerization with ethylene oxide to produce lubricant was carried out at 85 degrees fahrenheit using two (2) moles of tetrahydrofuran to one mole of ethylene oxide. The catalyst found to be most suited was a few percent of thionyl chloride containing some ferric chloride. After reaction the oil is washed free of iron salts with sodium bisulfite, treated with sodium methylate to replace terminal chlorine groups with methoxy groups, neutralized and distilled to remove unreacted components, etc. The physical properties of this material included a pour point of zero degrees fahrenheit, a VI of 150, and a viscosity of 130 S.S.U. at 210 degrees fahrenheit.

The above synthesis has been described in more detail in U.S. Naval Technical Mission in Europe Letter Report No. 123-45 (S) of 12 June 1945.

The development of tetrahydrofuran polymers is relatively new and not many data on their properties as lubricants had been obtained. A total of 18 tons was produced in 1943. An active program of development including engine testing was in progress at Leuerkusen.

A water-soluble torpedo lubricant developed by the Deutsche Fettsaure Werke is an example of another new type of synthetic compound. The DFW was requested by the German Navy to produce a lubricant which would allow a torpedo to operate without danger of leaving an oil smear on the water surface in its wake. A compound was developed which was a salt of triethanol amine and an approximately C_8 fatty acid. The salt was formed by direct congination without water separation. Such a compound is water soluble, has a pour point of -40 degrees fahrenheit, a high VI, and is an excellent lubricant. These salts apparently are not stable by the standards of lubricating oils, but for short duration use extreme stability is not necessary. The viscosity of

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[redacted]

9. Other Synthetic Lubricating Oils. (Cont'd.)

the triethanol amine salts can be varied widely by the use of fatty acids of varying molecular weight. A sample of this water-soluble oil was obtained and forwarded to the Naval Research Laboratory.

10. Additives to Lubricating Oils:

With the necessity of supplying lubricants to new and exacting uses, and with the ever present urge to upgrade low quality materials to increase the volume of lubricants, it was expected that Germany had given attention to the development of additives. It was found that many companies had been studying additives and that, parallel to the situation in America, hundreds of compounds had been synthesized and tested. From this mass of research there were developed some new compounds that were being used commercially and which perhaps could be useful to America.

The use of inhibitors and additives in lubricating oils was less extensive in Germany than it is today in America. Mineral oils were used uninhibited, and no inhibitors or additives were used in the synthetic lubricating oils or in the aircraft oils containing esters. As stated before, no special attention was given to diesel oils, and again no inhibitors or additives were used in them.

The use of additives was limited therefore to special oils but since it was the practice to specify special oils for a great many needs, there were large numbers of special compounded oils marketed. Natural fats and oils were used, but their shortage encouraged the development of substitutes. The shortage of natural esters, for example, was one of the reasons for the study of synthetic esters which lead to the extensive development previously described.

Some outstanding new additives are described briefly below, classed according to their effect on lubricating oil properties.

(a) Oxidation Inhibitors:

An oxidation inhibitor developed by I. G. - Leuna was claimed to be the most effective one that had been tested for improving

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[redacted]

10. Additives to Lubricating Oils, (a) (Cont'd.)

the stability of polyethylene-mineral oil mixtures. No test data were found, but this compound was the subject of patent applications, and was repeatedly discussed in interviews. It was not used in commercial practice. The material is a tin compound, made by the following synthesis:

See p. 41-42

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[redacted]

10. Additives to Lubricating Oils. (Cont'd.)

(b) Corrosion Inhibitors:

A compound developed by I. G. - Leuna, known as KSE (Korrosionschutzester), shows very good corrosion resisting properties. In a cutting oil study a soap that was being tested was observed to protect iron surfaces against rusting. An ester of the acid was then prepared and studied as a lubricating oil ingredient. Extensive test data and field experience were accumulated, and this compound was being manufactured and included in several special machine oils, torpedo oils, and weapon oils. The compound is prepared from a normal C_{12} to C_{18} paraffin, obtained in Germany by selecting a fraction of Fischer-Tropsch liquid. The synthesis was then carried out in the following steps:

$$R - CH_3 + SO_2 + Cl_2 \longrightarrow R - CH_2 - SO_2 Cl + HCl$$

$$R - CH_2 - SO_2 - Cl + NH_3 \rightarrow R - CH_2 - SO_2 NH_2 + HCl$$

$$R - CH_2 - SO_2 - NH_2 + Cl CH_2 - COOH \longrightarrow$$
$$R - CH_2 - SO_2 NH - CH_2 COOH + HCl$$

$$R - CH_2 - SO_2 - NH - CH_2COOH + R^1 - OH \longrightarrow$$
$$R - CH_2 - SO_2 - NH - CH_2 - COO - R^1$$

(R is C_{12} to C_{18} and R^1 is from C_4 to C_{16})

The reaction of the paraffin with SO_2 and Cl_2 is catalyzed with ultraviolet light. The NH_3 and the chloracetic acid reactions proceed without catalysts.

As an emulsifying soap in cutting oils, the soap usage is 4 to 6 percent weight. For the other applications, the ester is used in concentrations of about 3 percent weight.

[redacted]

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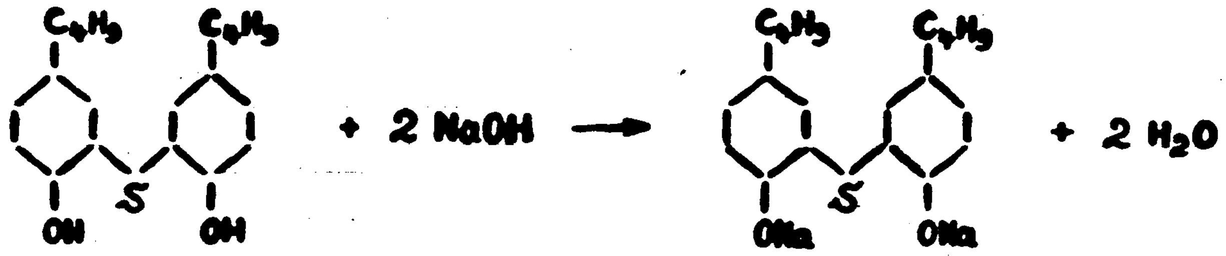
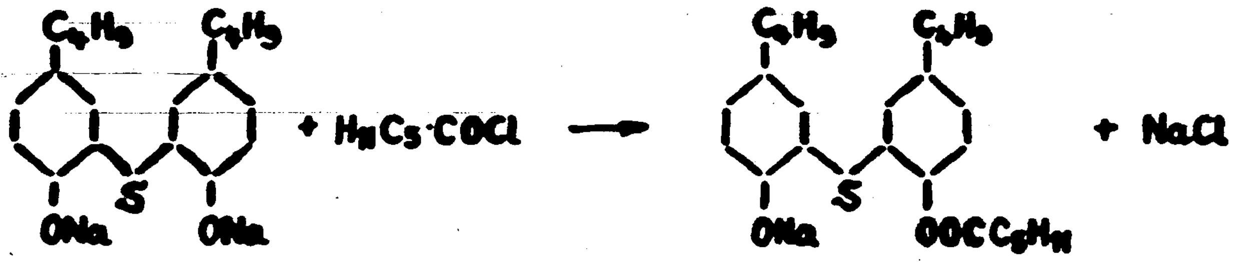
~~Reaktionsschema für Inhibitor~~ ([redacted])



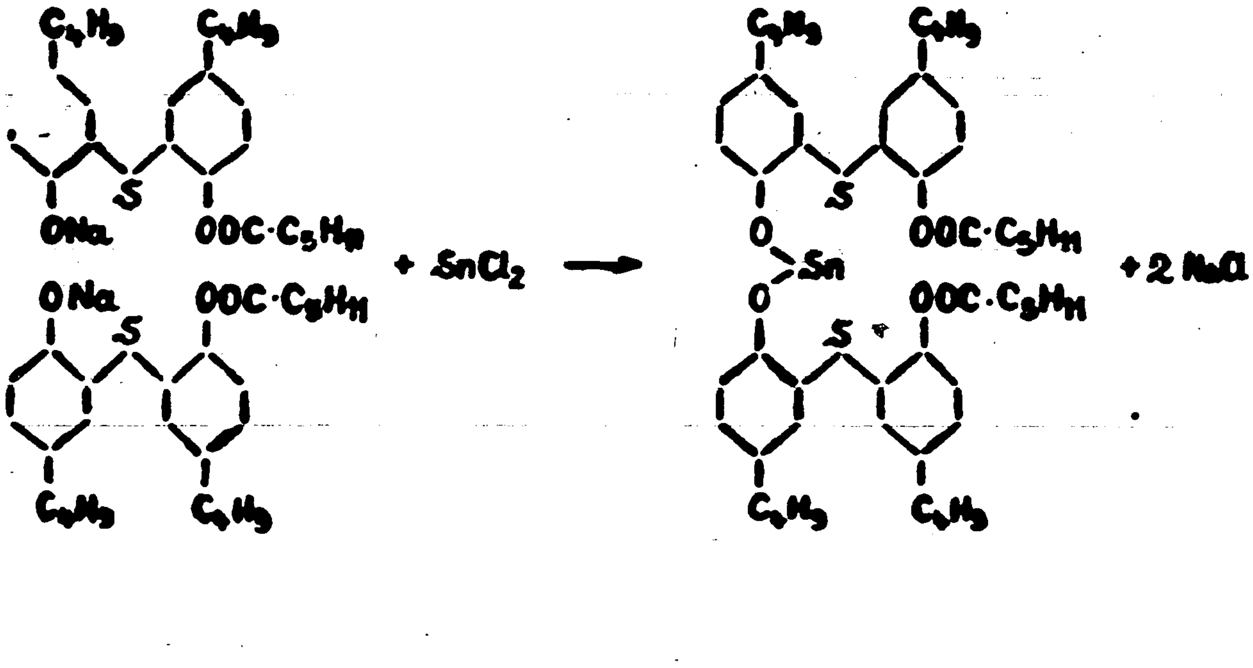
$C_{20}H_{26}O_2S$ + 2 NaOH → $C_{20}H_{24}O_2Na_2S$ + 2 H_2O

330 + 80 → 374 + 36



$C_{20}H_{24}O_2Na_2S$ + $C_6H_{11}OCl$ → $C_{26}H_{35}O_3NaS$ + NaCl

374 + 134 → 450 + 58



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10. Additives to Lubricating Oils, (b) (Cont'd.)

Test data have shown that 3 percent of the ester in a lubricating oil will reduce iron corrosion rate to 2 percent of that observed with uninhibited oil. Although particularly effective for iron protection, zinc, aluminum, and lead also show greatly decreased corrosion rates from the use of this material.

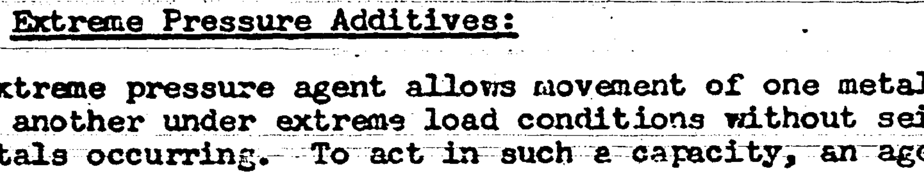
A sample of several gallons of KSE was obtained and forwarded to the Naval Research Laboratory in Anacostia, D. C.

(c) Extreme Pressure Additives:

An extreme pressure agent allows movement of one metal surface over another under extreme load conditions without seizure of the metals occurring. To act in such a capacity, an agent must effect a reduction in friction by providing some moving layer between the two (2) surfaces. Most extreme pressure additives accomplish this effect by reacting irreversibly with the surfaces, forming a metal compound which rubs off the metal and provides a moving layer which departs from the surfaces with less friction than that accompanying the motion of one pure metal surface over the other.

However, an extreme pressure agent should be "corrosive", forming metal compounds, only under the conditions of extreme load. Therefore, an agent should be chosen which is non-corrosive at low temperatures but which becomes suddenly corrosive at some elevated temperature. With such an agent, those spots or areas which become warm from friction will be attacked by the agent, forming a metal compound which will privide the "lubrication" necessary to prevent overheating and seizure.

One compound prepared b I. G. - Leuna possesses such a temperaturecorrosivity relationship and was used as an ingredient of their extreme pressure lubricants. The compound, known as Mesulphol, was synthesized as follows:



$$C_4H_9 - CH_2OH + CS_2 + NaOH \longrightarrow C_4H_9 - CH_2 - O - C\begin{matrix} \nearrow S \\ \searrow S - Na \end{matrix} + H_2O$$

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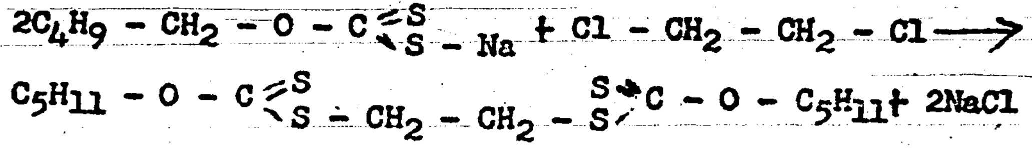
[redacted]

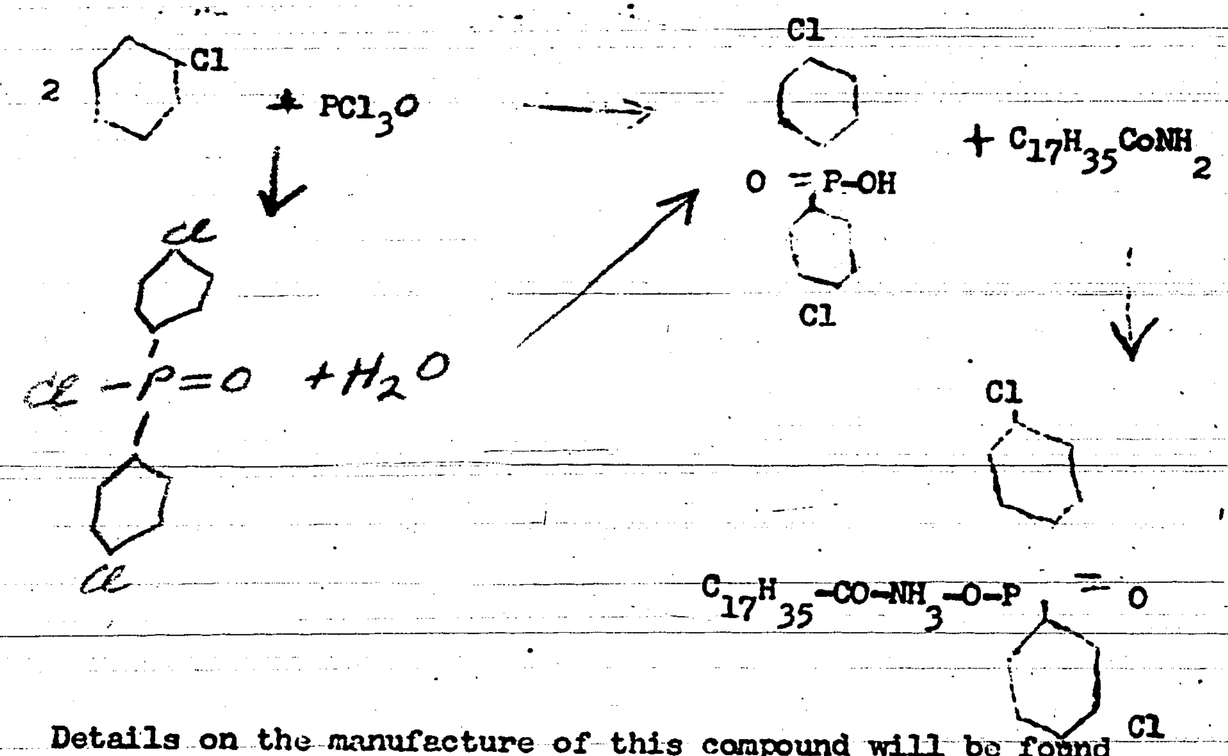
10. Additives to Lubricating Oils. (c) (Cont'd.)



$$2C_4H_9 - CH_2 - O - C\begin{matrix}\nearrow S\\ \searrow S - Na\end{matrix} + Cl - CH_2 - CH_2 - Cl \longrightarrow$$

$$C_5H_{11} - O - C\begin{matrix}\nearrow S\\ \searrow S\end{matrix} - CH_2 - CH_2 - \begin{matrix}S\searrow\\ S\nearrow\end{matrix}C - O - C_5H_{11} + 2NaCl$$

A new compound was being manufactured by I.G. Leuerkusen for use as an ingredient of aeroplane engine break-in oils. The agent is a phosphorous compound manufactured from chlorbenzene phosphorus trichloride and stearyl amine. The use of 0.5 to 1.0 percent weight of this compound in oil reduced the break-in time for aeroplane engines from 50 hours to 10 hours. It had been in small production at Leuerkusen since 1943, the total output having gone to Daimler-Benz and Junkers for the above use. The compound was prepared as follows:



Details on the manufacture of this compound will be found in U. S. Naval Technical Mission in Europe Letter Report No. 119-45 (s) of 12 June 1945.

In Germany, testing of extreme pressure lubricants and additives was carried out with various test devices. The four-ball machine was used, but was not regarded as a good device. The Alman-Wieland test

[redacted]

10. Additives to Lubricating Oils, (c) (Cont'd.)

machine was also used. A test apparatus recently developed consisted of a slowly revolving metal drum, partly immersed in oil, with a metal wire under tension in contact with 180 degrees of the drum. The wire is put under such tension that the area of contact is under very high load. The friction drag is measured by the difference in tension between the two (2) ends of the wire. This machine then measures friction against speed of rotation at constant temperature, or against temperature at constant speed.

(d) Pour Point Depressors:

Paraflow was being manufactured in Germany. The process consisted of condensing 80 parts of chlorinated paraffin with 15 parts of naphthalene and one part of polystyrene, using $AlCl_3$ as a catalyst and a temperature of 85 degrees fahrenheit. The polystyrene inclusion was said to "double the effect" of the Paraflow addition to lubricating oils. In 1942, about 10,000 barrels of Paraflow was manufactured and sold in a concentrate containing 8 percent Paraflow and 92 percent oil.

(e) Viscosity Index Enhancers:

Polyisobutylene was being manufactured and sold in Germany under the trade name of Oppanol (I. G. - Oppau). Its use was limited to the increase of VI of a few low grade lubricating oils to make them salable as motor oils.

(f) The Principle of Two-Phase Lubricants.

It is perhaps worthwhile to mention that work was in progress in one research laboratory on a two-phase lubricating liquid. The goal was the supply to the engine or device a lubricating medium that would not change viscosity with temperature. The principle was to use a two-phase system, wherein phase A is a lubricant and phase B is a more viscous liquid, with or without lubricant properties. As temperature increases the solubility of phase B in phase A increases at such a rate that the viscosity of phase A remains constant. No commercial application of the principle has been made or have, in fact, specific phase compositions of such a system been worked out.

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11. Lubricating Greases:

Very few new developments in grease manufacture or use were found. The components of greases are no different from those that are in conventional use in America .

Soaps for grease manufacture were made largely from synthetic fatty acids. These fatty acids were made by the Deutsche Fettsaure Werke (Witten), I. G. (Oppau and Heydebrek), and a plant in Magdeburg by oxidizing normal paraffins from waxes. The total fatty acid production for this use was about 120,000 tons per year. The soaps used in greases were primarily sodium, calcium, and aluminum. The use of Lithium soaps for greases was known and a very small volume was being produced, but there was apparently only little interest in and no plans for extended use of them.

The oil components of German greases were almost exclusively refined petroleum fractions and, most commonly, of Pennsylvania origin. No important use had been made of the synthetic lubricating oils produced in Germany as grease components.

One development that was found was the use of finely divided silicon dioxide to produce gels with lubricating oils. It was a development by the Degussa Company (Deutsche Gold und Silber Scheide-Anstalt). The finely divided SiO_2 is prepared by burning silicon tetrachloride and directing the flame against a cooled metal surface. The silica product has a particle size distribution similar to that of carbon black and a settled density of only 0.015. Used in 5 to 10 percent concentration with certain lubricating oils, particularly those containing an appreciable content of polar compounds, a stable gel was set up which could be used as a grease. The gels were said to be stable over a temperature range of -65 to +570 degrees fahrenheit.

The following document, transmitted to the Bureau of Ships, pertains to German Lubricating greases:

XIV Technische Lieferbedingungen fur Flieger-Sonderfette. (Specifications for greases supplied to the German Air Ministry).

[redacted]

12 Conclusions.

(a) The total volume of lubricating oils produced for German use during the last war years was about 17,500 barrels per day. Of this total, only 1,700 barrels per day came from synthetic processes and the remainder was obtained from petroleum.

(b) The refining methods employed to obtain finished lubricating oils from petroleum were largely conventional and are well known in America. A new process not yet applied commercially was known as Mixed-Polymerization. It invalues the addition of ethylene and its polymers to petroleum lubricating oil distillates as a refining process, thereby obviating the necessity of solvent extraction.

(c) The synthetic oils came from the following processes and locations:

(1) The TTH process at Brabag-Zeitz produced 600 barrels per day of industrial quality lubricating oil. This process hydrogenates brown coal tar under such conditions that a lubricating oil fraction of average quality only is obtained directly as a main product.

(2) At I. G. Leuna polymerization of ethylene to produce high quality oils was being carried out. Using a new process of I. G. origin, oils of 120 VI, low pour point, and good stability in use, were being made. These oils, produced at a rate of 300 barrels per day, were being used in 50/50 admixture with refined petroleum fractions as 100 VI aircraft oils.

(3) At Ruhrchemie-Halten, Rhenania Desag-Hamburg, and Politz, olefins produced by thermal cracking of high boiling paraffins were polymerized to high quality oils of 110 to 120 VI. Of these oils, produced at a combined rate of 650 barrels per day, most were used with refined petroleum fractions to produce aircraft oils.

(4) Using a process of their own development, Rheinpreussen-Homberg produced 50 barrels per day of oils by alkylating a naphthalene with a C_{16} paraffinic chain. Their production was teken entirely by the German Navy for use in diesel engines.

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[redacted]

12 Conclusions (Cont'd.)

(d) Several esters were being synthesized by I. G. - Leuna for use as components in special oils requiring low pour points and high VI. Esters impart good lubricating quality ("oiliness") to a mixture, at the same time fulfilling other requirements of a good lubricant. The VI of esters are 150 to 250, and their pour points are about -40 degrees fahrenheit. The ester development is considered to be of outstanding interest. The I.G.- Leuna ester production rate was 100 barrels per day.

(e) Synthetic oils developed, but not produced commercially, included a polymer of tetrahydrofuran and ethylene oxide (I.G.-Leverkusen), and a water-soluble salt of triethanol amine and a ca. C_8 fatty acid (Deutsche Fettsaure Werke-Witten). The former compound has a high VI and low pour point, but little information is available on its performance. The water-soluble oil was developed for torpedo use and was said to have been accepted by the German Navy.

(f) Several new additives had been developed, including an oxidation inhibitor (an organic tin compound), a corrosion inhibitor especially effective on iron, and two (2) extreme pressure compounds.

(g) No outstanding new developments in the field of lubricating greases were found.

(h) Of the new synthetic oils and components disclosed, the polyethylene oil and the ester additives are considered to be of particular interest and their study and test by the U.S. Navy is recommended. The new additives described should also be tested by methods in standard use in America.

Prepared by:

M. E. SPAGHT
Technician

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APPENDIX I.

THE MANUFACTURE OF ETHYLENE FROM ETHANE

Ethylene for the manufacture of ethylene polymer lubricating oils was produced at Leuna by the partial oxidation of ethane.

The Leuna process gives an ethylene yield in the plant of 70 percent weight, based on charged ethane. The ethane to be reacted is three (3) volumes is heated to 1110 percent weight, oxygen one volume is separately preheated to 750 degrees fahrenheit, and the two are combined under slight vacuum in a carefully designed burner wherein the temperature rises to 1470 to 1560 degrees fahrenheit. The product of the furnace is cooled by exchange and the ethylene is separated and purified to a minimum of 95 percent weight, in the final product.

On a hydrogen and nitrogen free basis, the product from the reaction burner is:

48.1 percent vol.	Ethylene
30.5 percent vol.	Ethane
16.0 percent vol.	CO
0.6 percent vol.	CO_2
1.6 percent vol.	O_2
2.4 percent vol.	Propylene and Higher Olefins
0.8 percent vol.	Acetylene
100.0	

Based on ethane recycle to extinction, the above analysis corresponds to an ultimate ethylene yield of 79 percent. This figure is reduced, of course, by losses in the recovery and separation system

The ethylene was purified at Leuna by a Linde fractionation system. Before fractionation, CO_2 was removed with an alkazid plant (regenerative alpha-amino-propionic acid) and acetylene was hydrogenated over a nickel-chrome catalyst down to a content of 0.1 percent volume. The first Linde column separated overhead materials lighter than C_2, a second column separated the

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Appendix I (Cont'd.)

C_2 fraction overhead, and a third column separated ethane and ehtylene. Through this fractionation, CO was also separated quite completely from the ethylene.

A second method for ethylene manufacture from ethane was worked out at Leuna and a plant was being built at Heydebrek. The dehydrogenation step in this system employs straight thermal cracking at atmospheric pressure. In a two stage counterflow of flue gas and ethane feed through two furnaces, the ethane temperature is raised to 1200 degrees fahrenheit in the first coil and to 1550 degrees fahrenheit in the second. The cracked gas is quenched, acetylene is selectively hydrogenated out, and the gas passes to a selective solvent ethylene concentration system.

In the thermal cracking operation, a conversion of 30 percent per pass is obtained (design figure for Heydebrek). In pilot plant work, coke deposition in the 27 percent chrome tubes required a cleanout only once in 40 days.

With a thermal cracking method for the ethane dehydrogenation, a system of selective absorption was to be used for ethylene recovery. The solvent is a copper - diethanol amine complex, prepared by saturating diethanol amine with cuprous nitrate and adding thereto 3 to 4 percent weight of ammonia water. This solvent is used at 80 degrees fahrenheit and under 10 to 20 atmosphers pressure. Ethylene is released by reducing pressure and increasing temperature to 105 degrees fahrenheit.

When recovering ethylene from a 30 percent concentration gas mixture, one volume of solvent at 15 atmospheres is adequate to scrub 30 volumes of gas down to an ethylene content of 0.2 percent volume.

This solvent will separate ethylene from paraffins but is not selective between ethylene and propylene. It will not separate CO from ethylene, and hence is not used when ethylene is produced by partial combustion of ethane. Sulfur compounds in a gas being treated with this solvent react with the solution and precipitate copper sulfide which then must be filtered out periodically. If CO is to be separated, Linde fractionation is considered to be the most practical method. Removal of CO with a KNi CN_2 solution had been studied, but the process is not

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Appendix I (Cont'd.)

regenerative and hence is costly for high CO concentrations.

The following documents transmitted to the Bureau of Ships, pertain to the manufacture and concentration of ethylene by the two systems outlined:

XV Die Herstellung lines Athylenhaltigen Gases durch thermische Spaltung von Althan oder Propan und Aufarbeitung dieses Spaltgases auf Reinathylen in einer Gastrennanlage nach Linde. (I. G. Leuna - Report).

XVI Gestehkostenvorausschatzung fur Athylen aus Athan durch thermische Spaltung im Rohrenofen nach Hauber. (I.G. - Leuna - Bericht of 11 June 1941)

XVII Schema zur Spaltanlage. (I. G. - Leuna - Flow diagram of Ethane Thermal Cracking Unit-20 April 1943).

XVIII Olefinabsorption mittels Cuprosalzlosungen II Mitteilung. (I. G. - Leuna - Dr. Hauber report of 22 July 1942) y no. 18.

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U·S·NAVAL·TECHNICAL·MISSION·IN·EUROPE

Unclassified by
CNO ltr. Op-23-PT
Serial no. 327P23
dated 22 October 1945

8C485

TECHNICAL REPORT No. 147-45

INTERNAL COMBUSTION ENGINES
(Use of a chemical as ignition agent)

JULY 1945

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S41-3

U·S·NAVAL·TECHNICAL·MISSION·IN·EUROPE

80486

U. S. NAVAL TECHNICAL MISSION IN EUROPE
c/o Fleet Post Office,
New York, N.Y.

File: A9-16(3)(10/Ms)

Serial: 672

28 July 1945.

[redacted]

From: Chief, U. S. Naval Technical Mission in Europe.
To : Chief of Naval Operations (OP-16-PT).

Subject: U. S. Naval Technical Mission in Europe Technical Report No. 147-45, Internal Combustion Engines (Use of a chemical as ignition agent) - Forwarding of.

Enclosure: (A)(HW) Copies of subject report.

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TECHNICAL REPORT No. 147-45

INTERNAL COMBUSTION ENGINES
(Use of a chemical as ignition agent)

SUMMARY

A method by which ignition, in an internal combustion engine, is obtained not by means of spark plugs but by self-ignition of a liquid finely atomized into the combustion chamber at the proper moment of the cycle.

This method is designated as "Ring-process".

Key Personnel interviewed:

Dr. Fritz Penzig, of the I.G. FarbenIndustrie A.G. at Ungstein, near Bad-Durkheim.

Dr. K. Peter, of the Baierische Motoren Werke, at Munich.

July 1945

U. S. NAVAL TECHINICAL MISSION IN EUROPE

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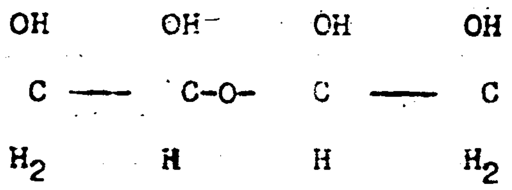
INTERNAL COMBUSTION ENGINES

1. Purpose of the Ring Process.

In the German aircraft gasoline engine it was recognized, up to very recently, that the weakest part especially for high-altitude operation was the spark-plug. Not only was it necessary to take unusual precautions to avoid ignition difficulties at high altitudes (for instance special high-altitude spark plugs, dual ignition, specially insulated cable, restricted air circulation) but it was also necessary to avoid fouling of the spark plugs by limiting the lead content of high-test gasoline. The "Ring-Process" is an invention for the elimination of the spark plugs. Ignition is produced by spraying into the combustion chamber, at the right moment of the gasoline-air compression stroke, a liquid that will spontaneously ignite at the temperature of the cylinder, and thus ignite the combustible charge.

The process, already mentioned in the writings of Dr. Rudolf Diesel in 1898 was developed by Dr. Fritz Penzig of I. G. Farben Industrie A.G. at Oppau in 1940-41 and perfected in cooperation with the Baierische Motoren Werke of Munich in 1942-43.

The ignition liquid used, called "R-Fluid" is an ETHER such as Butadiol diethyl ether, or Diethyl diglycol ether of formula:



$$\begin{array}{ccccccc} \text{OH} & & \text{OH}^- & & \text{OH} & & \text{OH} \\ \text{C} & — & \text{C-O-} & & \text{C} & — & \text{C} \\ \text{H}_2 & & \text{H} & & \text{H} & & \text{H}_2 \end{array}$$

It is designated in Germany under the symbol R-300 and has the following properties:

[redacted]

1. Purpose of the Ring Process. (cont'd)

COMPARISON OF R-300 with AVIATION GASOLINE

	R-300	Aviation Gasoline
Spec. gravity	0.91	0.75
Viscosity CS at 20°C	1.5	0.6
Distillation E. P.	180°C	200°C
Calorific Value Kcal/kg.	6900	10400
Theoretical air required kg/kg.	9.3	14.8
Ignitability in Cetane rating	185	up to 35

It is to be noted that R-300 can also be used as starting fluid for Diesel engines, in which case it is designated as KS II.

The self-ignition quality of R-300 appears to be due to a rapid disintegration of the molecule under the action of heat, an exothermic reaction producing a rapid rise in temperature which causes the products of decomposition to ignite, at about 70 degrees centigrade.

On account of its high ignitability, R-300 is not particularly affected by changes in the compression-ratio, and operates down to a compression ratio of 1:7. In practice 1:8 is the minimum compression ratio selected.

2. Various Features of the Ring-Process.

(a) Ring-Process operates over entire range of air-fuel mixtures.

One of the interesting features of this process is that it operates with correct ignition from the leanest up to the richest air-fuel mixtures. This can be explained by the high energy of spray of R-fluid, estimated at 70 kcal. as against an energy release of 10^{-6} kcal. coming from a spark plug. The only condition for the ignition of very lean mixtures is a

2. Various Features of the Ring-Process. (a)(cont'd)

slight increase in the quantity of R-Fluid. Figure 1 illustrates the economy of the process when the air-fuel ratio is varied. As slightly more R-fluid is used for the lean mixtures, the power output curve is also slightly raised. On the other hand for very rich mixtures the ignition delay seems to increase resulting in a power reduction. In other words, as the temperature of self-ignition of the R-fluid is not reached quite as fast for a rich mixture, a slight power-loss occurs. To obviate this, the injection timing of the gasoline is slightly advanced so as to permit the R-fluid particles to completely permeate the air-fuel mixture.

(b) Ring-Process and Knock.

The Ring-process has proven to reduce to a considerable extent the knocking tendency of a fuel. This seems to be due to the fact that the particles of R-fluid penetrate thoroughly throughout the mass of air and fuel and, when they ignite, start the ignition uniformly. It is as if an infinitely large number of small spark plugs were all operating simultaneously.

(c) Ring-Process and Timing.

The timing of the injection of R-fluid into the cylinder does not seem to have the same effect upon the operation of the engine as the timing of the ignition has upon a spark plug engine. This is explained on Figure 2 on the theory that, as soon as the spark is produced ignition takes place and the rate of pressure rise is modified when the timing of the spark is changed. On the other hand the injection of the R-fluid does not instantaneously start ignition; ignition does not take place until near Top Dead Center. In other words a slight change in the timing of the injection of R-fluid does not affect the rate of pressure rise. A sudden rise in the pressure curve occurs at point A as soon as the spark is produced, in the spark-ignition engine while it does not occur until point B, for the Ring-process, regardless of the exact timing of the R-fluid injection; point B of the curve corresponds to the pressure and consequently temperature condition at which self-ignition of the R-fluid occurs. A comparison of the various

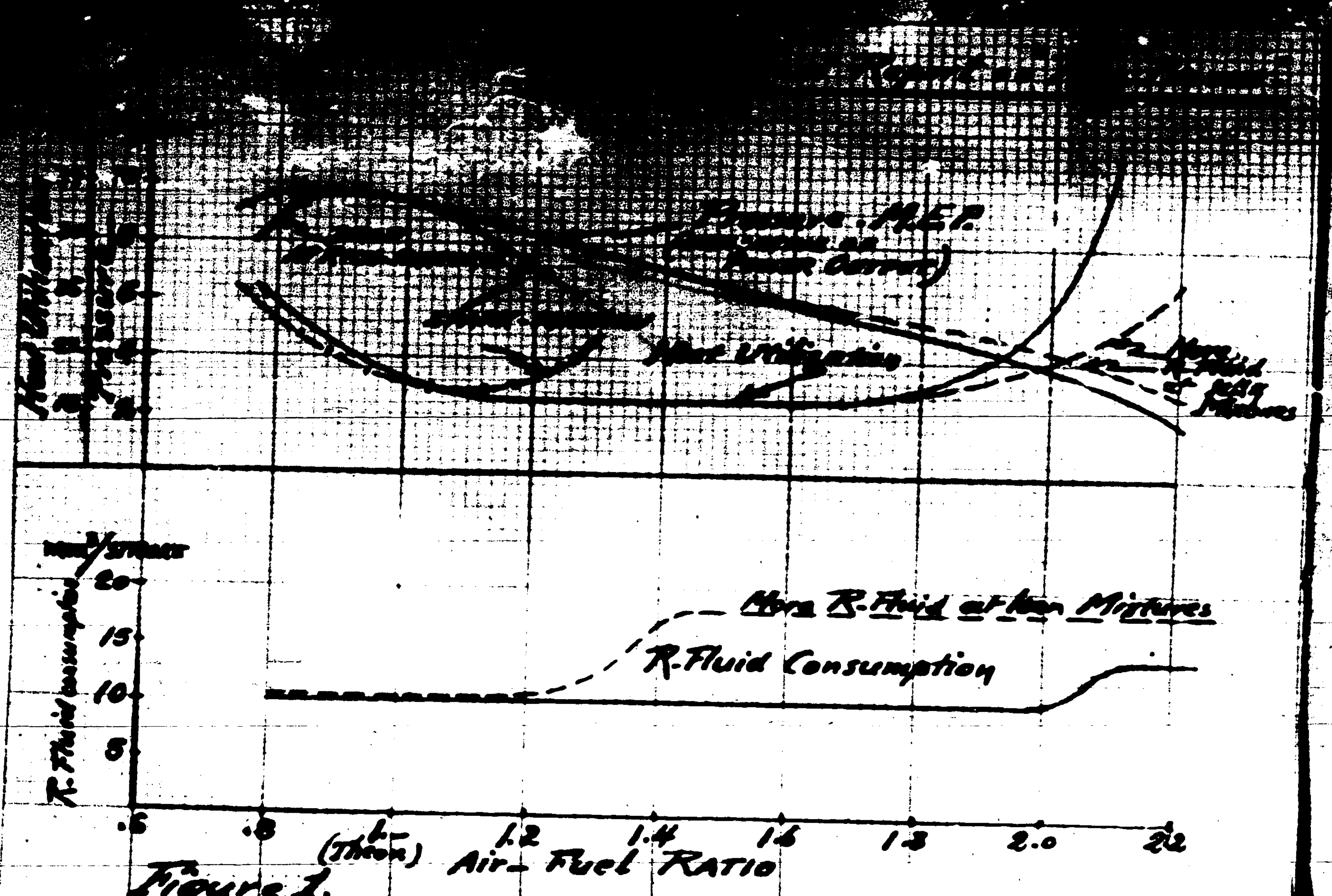

M.E.P.
Constant)
Utilization
More R-Fluid at lean Mixtures
R-Fluid Consumption
R-Fluid consumption
20
15
10
5
.6
.8
1.
(Theor)
1.2
1.4
1.6
1.8
2.0
2.2
Air-Fuel RATIO

Figure 1.

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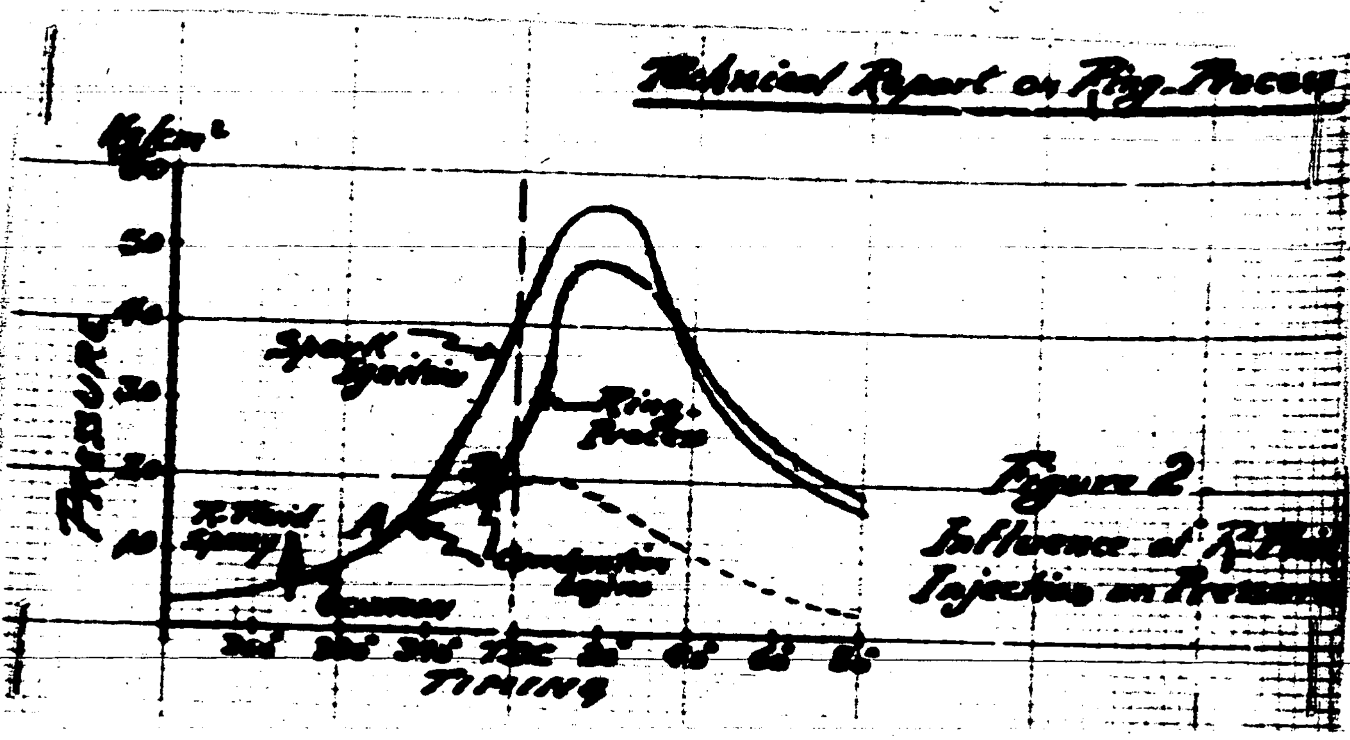

Figure 2.

[redacted]

2. Various Features of the Ring-Process (c)(cont'd)

pressures noted in the spark-ignition process and in the Ring-process, when varying ignition or R-fluid injection timing, is shown on Figure 4. Examination of the curves shows that, while the maximum M.E.P. indicative of maximum output of power is the same in both processes, peak pressures are different. In the Ring-process, M.E.P. and peak pressures are correlated, and independent from the timing.

(d) Ring-Process and Engine Temperatures.

Tests run with air-cooled engines as well as with liquid-cooled engines have demonstrated that the cylinder head temperatures were considerably lower with the Ring-process. In a liquid-cooled engine the heat carried away by the coolant was 15 to 25 percent lower with the Ring-process than with spark-plug ignition, at full load. Further tests were planned, but not completed, to determine how this difference in heat loss may be accounted for, particularly since the exhaust gases did not show an increased heat loss of equal amount.

(e) Ring-Process and Engine Speed.

Tests conducted at the HIRTH MOTOR CO. in Stuttgart Zuffenhausen proved that no difficulties in the injection of R-fluid need occur at any rate of speed. Velocities as high as 3800 rpm. were reached. The results of these tests are shown on Figure 3. Curves show that the timing of R-fluid injection must be slightly advanced at high speeds, as may well be expected, and that the fuel consumption expressed in grams per horsepower increases also with increasing speed, which is normal. A regular Diesel injection pump with a 6 m/m plunger will take care of the usual rate of R-fluid injection, which varies from 10 to 20 mm3 per stroke.

3. Flight Tests with the Ring-Process.

(a) Prior to the flight tests described below, preliminary tests were made on one cylinder of a 9-cylinder radial engine, the BMW 323, having a 3-liter cylinder capacity. An R-fluid injection nozzle was installed in place of the spark plug, and the

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3. Flight Tests with the Ring-Process. (a)(cont'd)

compression ratio was raised from 1:6.4 to 1:8 which is the minimum considered practical for self-ignition of R-300. No knocking was noticed with the various fuels used. Aviation gasoline C3 was selected for test purposes. The only difficulties experienced were an increase in fuel consumption and some ignition failures when the temperature of the air from the supercharger was below 50 degrees centigrade. This led to a study of the motor temperatures as it was expected that at high altitudes excessive cooling would cause further failure of the process. Figure 5 shows the temperatures at various places of this one cylinder engine.

1.-with spark ignition,
2.-with the Ring-process without any mechanical change,
3.-with the Ring-process after shield plates had been installed to protect the cylinder head from excessive cooling.

It also appeared advisable, in order to avoid ignition failures, to direct the spray of R-fluid against a real hot part of the combustion chamber. By causing the spray to impinge against the exhaust valve a considerable improvement was noticed throughout. This improvement, both in Fuel consumption and in Power output, is illustrated on Figure 6, where 3 conditions are shown: first, a straight spraying of R-300 into the combustion chamber, the air being cooled to 1°C; this condition is the worse of the three! Then the same direction of spray but with air slightly warmer; even this small difference shows an improvement. Finally, with air at -1 degree centigrade but with the spray of R-300 directed against the exhaust valve. A decided improvement is noticeable, power output higher, fuel consumption generally lower. Average consumption of R-300 was 2.5 kilograms per hour, which is rather high. The output, especially for rich mixture, was equally as good as for spark ignition, and the fuel consumption, especially at lean mixtures was decidedly better.

(b) Tests were then conducted with a BMW 323 9-cylinder engine in a Junker JU-52. Compression ratio was 1:8 Two-stage supercharger. Take-off power: 1000 to 1050 HP at 2500 rpm. Climbing power: 800 HP at 2250 rpm. The fuel consumption averaged 210 grams/HP. The R-fluid consumption was 1 to 1.2 per

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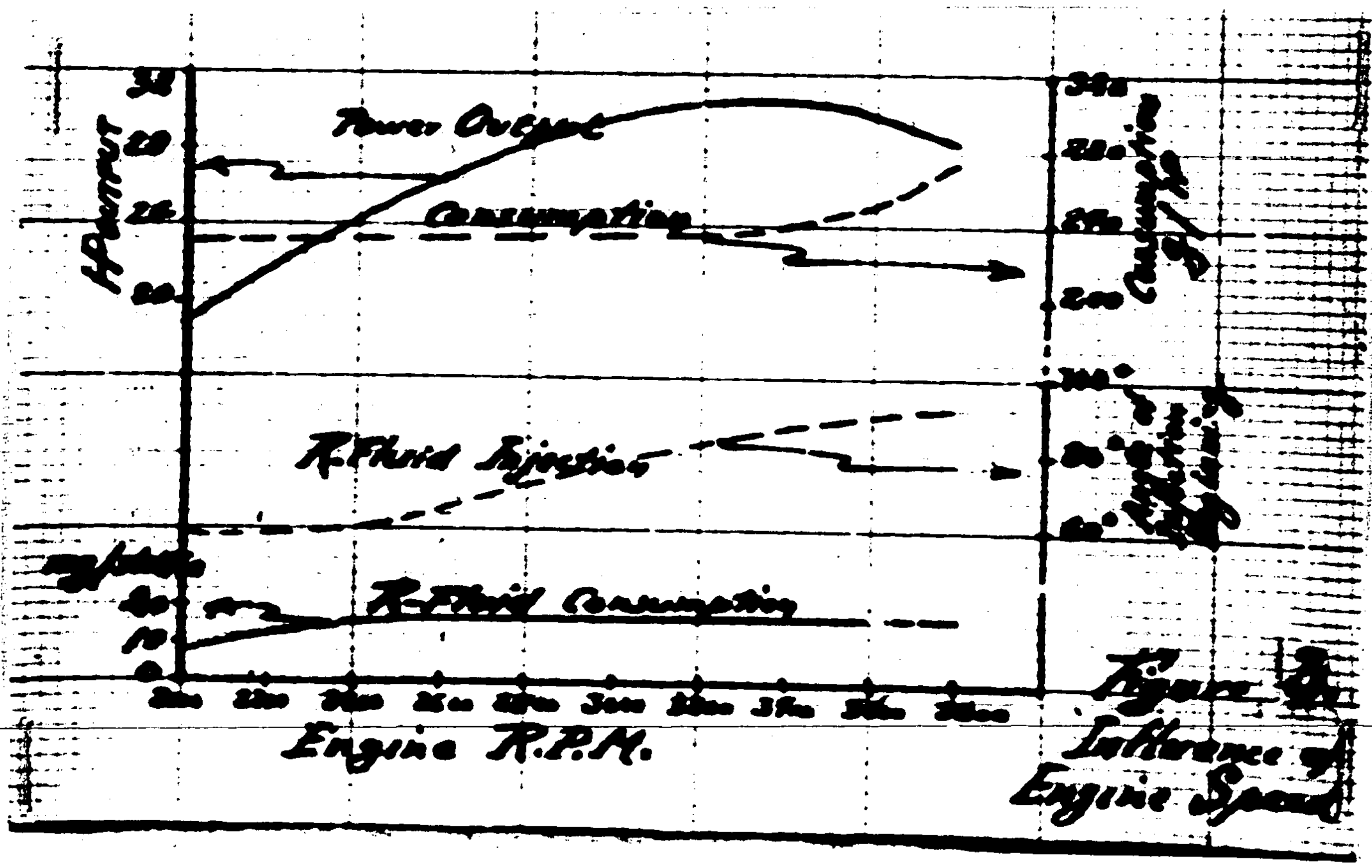
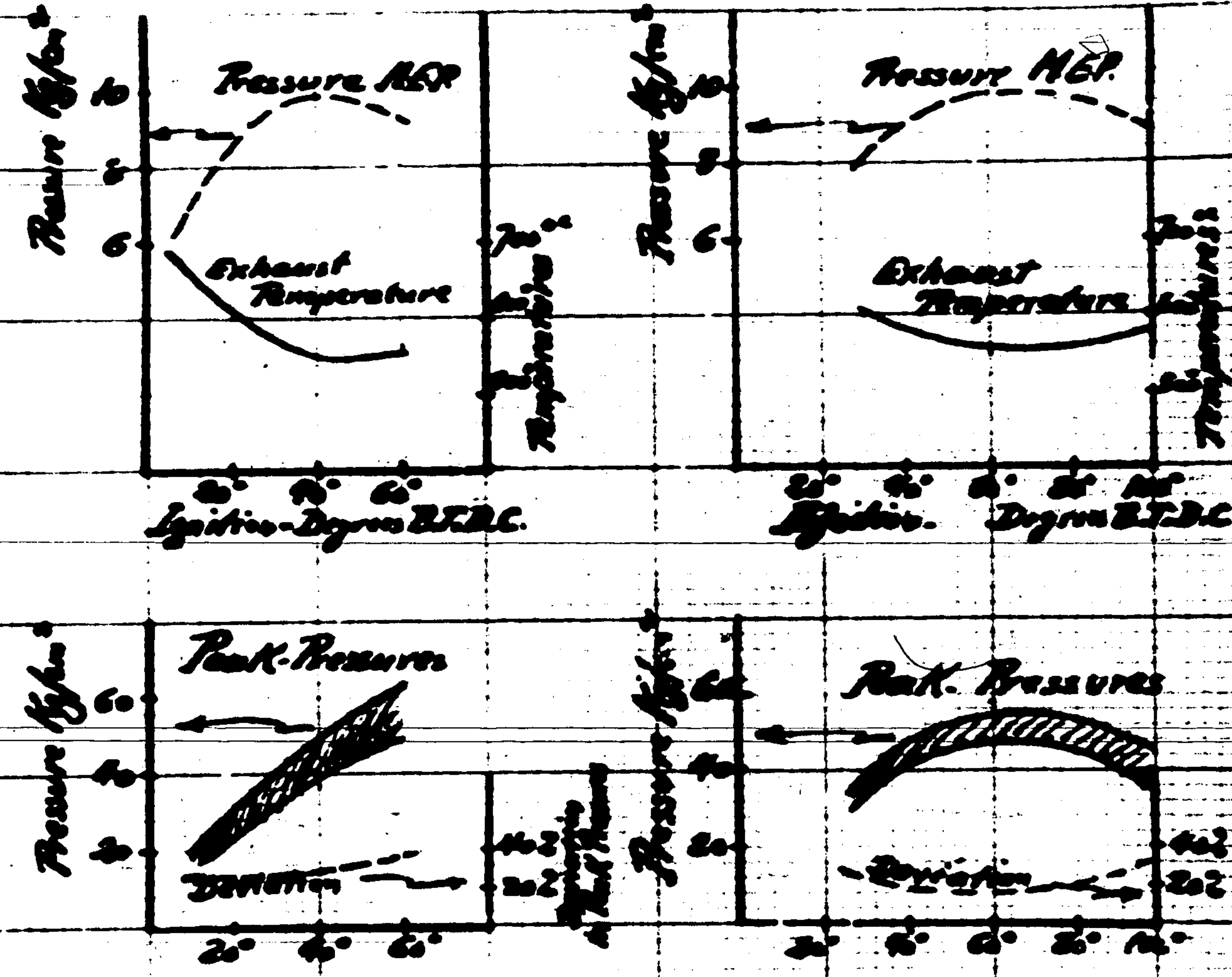


Figure 3.

Technical Report on Ring-Process.



A- With Spark plugs.
Peak Pressures rise with
Advanced ignition.—

B- Ring-Process.
Peak Pressures are
proportional to M.E.P.

Figure 4.

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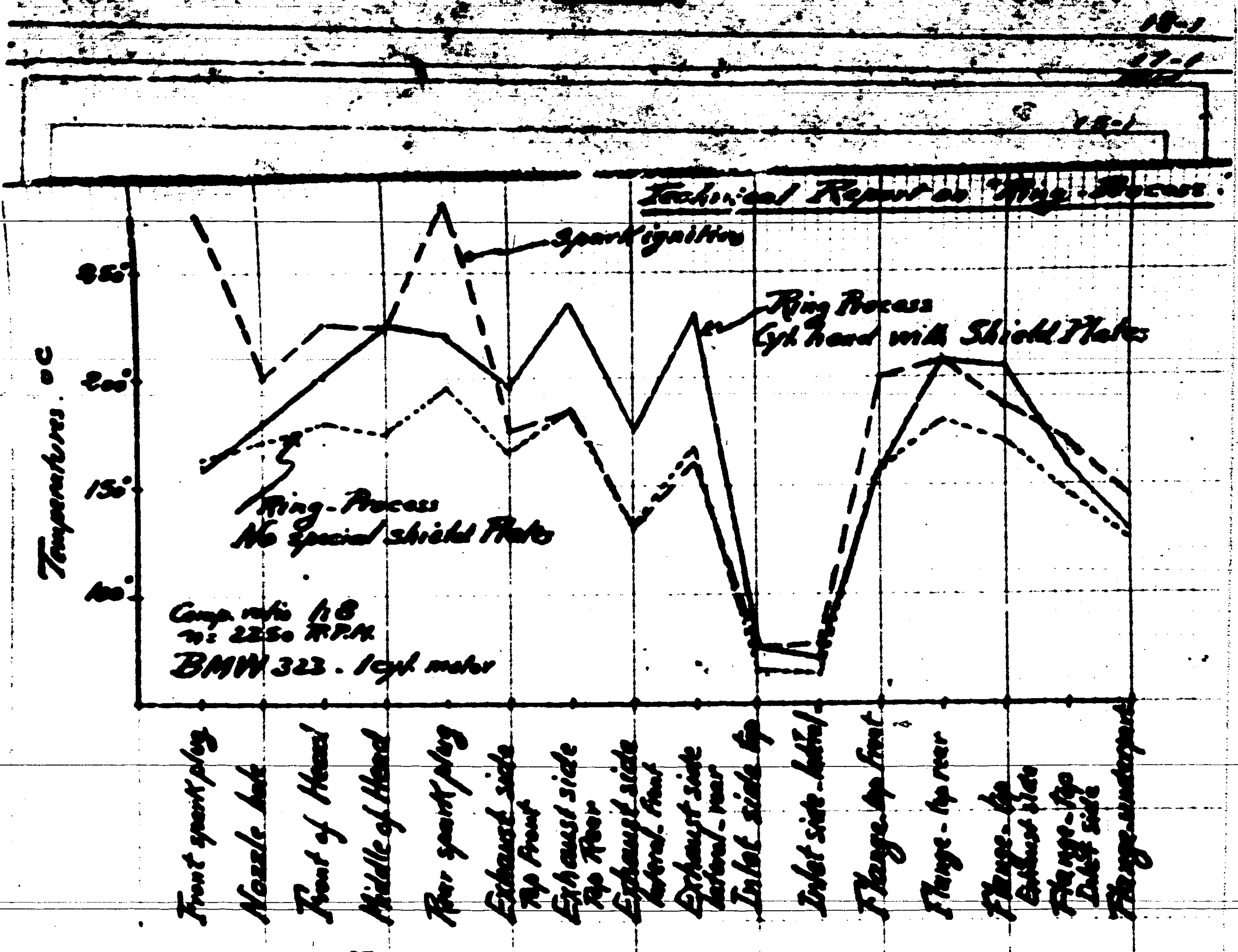

Figure 5. Metal Temperatures.

Technical Report on "King-Process."

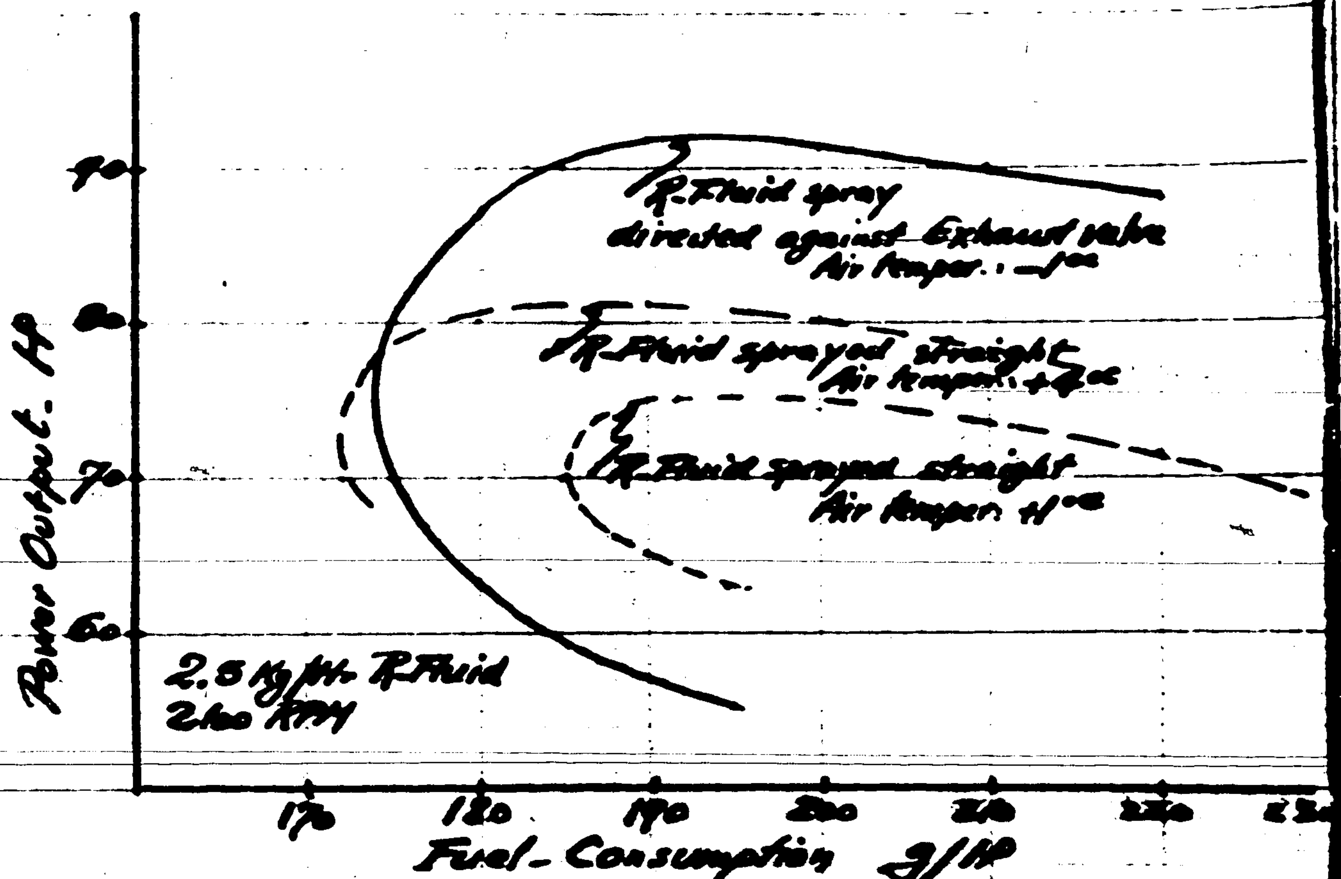

Figure 6.

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3. Flight Tests with the Ring-Process. (b)(cont'd)

hour per cylinder, that is 15 to 23 mm3 per stroke. At no-load the use of R-fluid increased to 40 mm3 per stroke.

The Ring-process was used in the middle engine of a group of three on the plane. Tests showed that the high rate of cooling would cause difficulties, and a different set-up had to be used.

(c) The next series of tests was therefore run, also in a Junker JU-52 but with a BMW engine having a compression ratio of 1:9 instead of 1:8. Average fuel consumption was 185 grams/HP. R-fluid consumption was 18 to 23 mm3 per stroke per cylindor and again 40 mm3 at no-load. It can be said that the R-fluid consumption is from 5 to 10 grams per HP.

Unfortunately this plane could not go above altitudes of 5,000 meters, where difficulties were really expected due to excessive cooling, and further tests were planned. But in the winter of 1943-44 perhaps due to some improvement in the spark ignition technique in Germany, perhaps due to greater interest in other types of plane propulsion, it was decided to interrupt this work on account of what was termed "more pressing interests".

4. Problems Related to the Ring Process.

Two (2) problems were given consideration in connection with this process. The first is the problem of starting the engine, especially at low temperatures. It soon became clear that a set of auxiliary spark plugs, used only for starting, were an indispensable accessory of the Ring-process, together with battery, distributor, and all the electrical equipment necessary.

The second problem was one of reducing the cost of installation of the Ring-process, definitely higher than the cost of spark-ignition, by eliminating some of the injection equipment. The Hirth Motor Company adopted an injection system developed by Prosper l' Orange for small Diesel engines, and similar to the pre-gasification injection of the Cummins Engine Company in the U.S.A. It is illustrated on Figure 7.

[redacted]

4. Problems Related to the Ring Process. (cont'd)

1. During the suction stroke, the operating valve opens and the delivery port is filled with R-fluid.
2. During the compression stroke, the gases passing through the Venturi into the chamber create a suction which causes the R-fluid to flow out of the delivery port into the chamber; there it is heated and ignites.
3. The flame created in the chamber comes out through the injection passage into the main combustion chamber and ignites the air-fuel mixture. The ignition of the R-fluid in the small chamber takes place at 10 to 20 degrees before Top Dead Center.

This solution worked out without mechanical difficulties, caused however a slightly higher consumption of R-fluid.

5. Conclusion.

It can be said that the main advantage of the Ring-process compared to the spark ignition method lies in the elimination of spark plug difficulties, serious in Europe at the time of the development of the process. A saving of fuel of approximately 5 percent can also be expected as a result of more knock-free performance and of more economical use of fuel in the "lean mixture" operating periods. The fact that less cooling is necessary may be considered either an advantage or a disadvantage inasmuch as a careful control of the cooling process must be provided to avoid excessive cooling and resultant failures. The cost of installation of an R-fluid injection system must be compared to the cost of electrical ignition, especially when it is considered that electrical ignition is required for starting at the present stage of the development.

An exact evaluation of the process can only be made after giving due thought to all new processes related to power production for aircraft: Diesel engines, jet-propulsion, turbines. In that light, the Ring-process appears to be a minor development.

Prepared by:

R. J. Bender,
Lieut. USNR.

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Technical Report on "Ring Process"

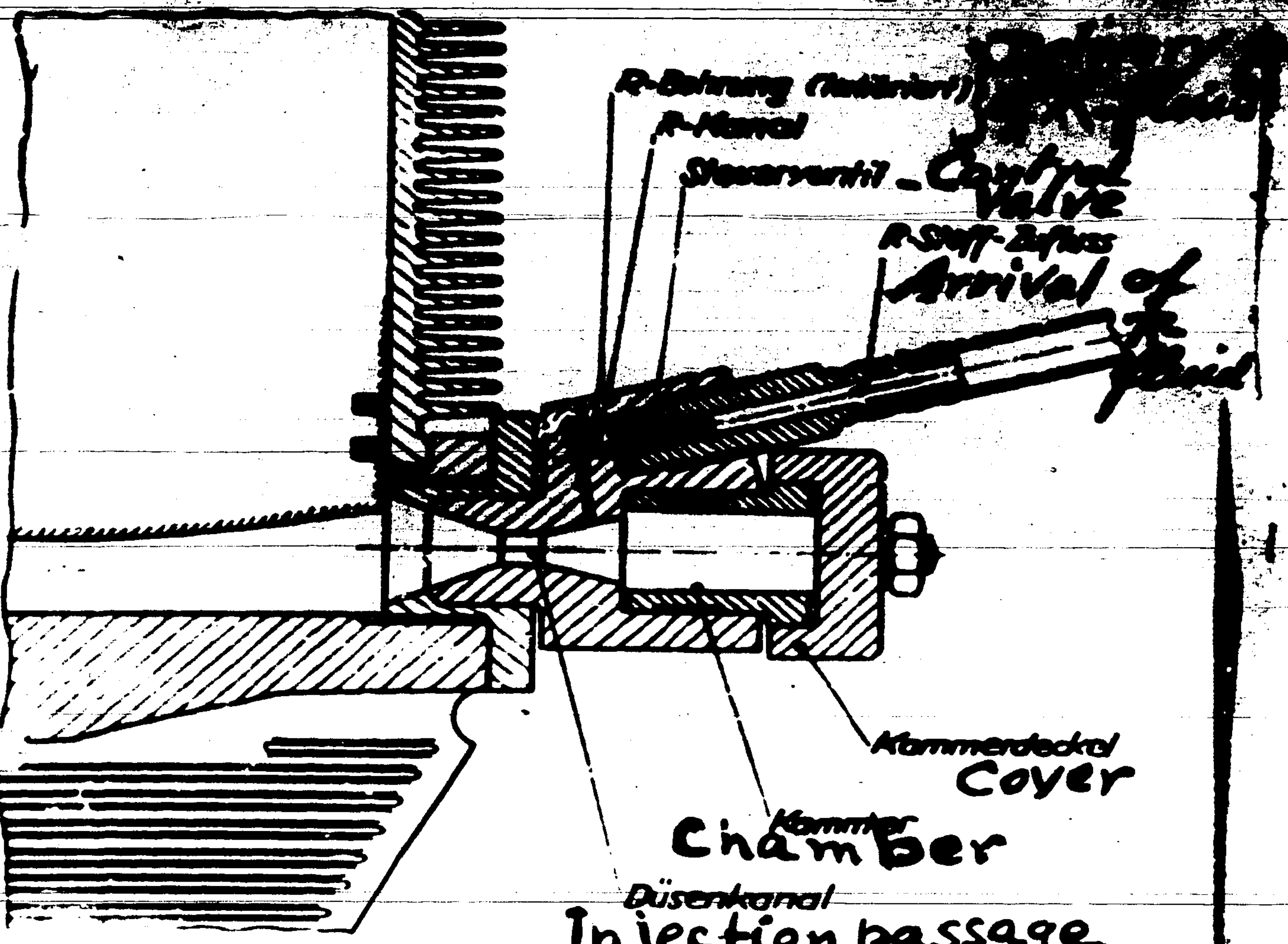

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Figure 7. Pumpless Injection - Hirth 1 liter cylinder.

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Unclassified by
CNO ltr. Op-23-PT
Serial no. 327P23
dated 22 October 1945

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TECHNICAL REPORT NUMBER 187-45

GERMAN DIESEL FUELS

AUGUST 1945

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U. S. NAVAL TECHNICAL MISSION IN EUROPE
c/o Fleet Post Office
New York, N.Y.

File: A9-16(3)(10/hn)

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Serial: 0862

[redacted]

17 August 1945.

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To : Chief of Naval Operations (OP-16-PT).

Subject: U.S. Naval Technical Mission in Europe Technical Report No. 187-45, German Diesel Fuels - Forwarding of.

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TECHNICAL REPORT No. 187-45

GERMAN DIESEL FUELS

SUMMARY

Review of the work done in Germany during the past few years to produce a satisfactory diesel fuel for high-speed engines, and the research conducted by scientists to investigate possibilities of further improvements. Study of additives such as: nitrates, nitrites, peroxides, alcohols, etc.; and of various processes such as "nitration" and "ozonisation" to raise the cetane rating of fuels.

August 1945

U. S. NAVAL TECHNICAL MISSION IN EUROPE.

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Sources of Information an[redacted]sons Interviewed

I. G. Farbenindustrie A.G.	Dr. Fritz Penzig (at Ungstein near Bad Durkheim) Dr. Mathias Pier (at Heidelberg)
Technische Hochschule Stuttgart	Dr. Otto Wiedmaier (at Heidelberg.
Technische Hochschule Munich	Dr. Fr. Kneule Dr. Beck (at Munich)
M.A.N. Diesel Works at Augsburg	Dir. Prof. E. Sorensen Dr. K. Zinner
Baierische Motoren Werke at Munich	Dr. Ammam
Klockner Humboldt Deutz A.G. at Oberursel	Dr. Schnurle, Director Dr. Emele
Rhenania-Ossag(Shell Petroleum Co) at Hamburg	Prof. Zorbe
Deutsche Vakuum Oel (Vacuum Oil) at Schulau near Hamburg.	
Intava	Mr. Syamken, Director (Hamburg, and Oldesloe near Lubeck)
Wifo No. I at Hitzacker on/Elba	

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GERMAN DIESEL FUELS

1. German Diesel Fuel Specifications.

Slow speed stationary diesel engines were operated on such liquid fuels as were available. These fuels included petroleum residues, petroleum crude, coal and lignite tars and crude shale oil. No specifications could be maintained as the fuels for these types of engines were inadequate at all times and became increasingly scarcer as the war progressed. So much so that attempts, only partly successful, were made to use these local supplies, alone or mixed with other diesel fuels, in automotive engines. The results are reported in the 1944 quarterly reports of the "Reichs Minister für Rüstung und Kriegs-produktion" (Department of Planning and War Production), Fuels and Lubricants Section, under direction of Dr. Bokemuller of the Daimler Benz Company in Gaggenau (Baden).

Diesel fuel specifications were prepared for the various armed forces. A comparison of the requirements of the "Wehrmacht", the "Luftwaffe" and the "Kriegsmarine" are tabulated on Table I. Small differences are apparent in this tabulation between the requirements of the various branches.

The German Navy (Kriegsmarine) in particular was definitely opposed to the use of any additive.in diesel fuels for fear of corrosion, and never did use specification KI of the Luftwaffe for fear of vaporlock.

In addition to these diesel fuels most generally used and recognized there came out, from time to time, certain fuels known as "Sonder Diesel Kraftstoff", "Leicht Diesel Kraftstoff", "Speziall Diesel Kraftstoff" prepared to order for a definite purpose or for certain experiments. Some were blends of various types of diesel fuels, others were blends of diesel fuels and gasolines. The latter could be classified in the United States as "tractor fuels".

2. Sources of Diesel Fuel in Germany.

Note: Whenever a production process is mentioned, such as Fischer-Tropsch synthesis, or hydrogenation, the reader is referred to the reports on these various processes prepared by the U. S. Naval Technical Mission in Europe.

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2. Sources of Diesel Fuel in Germany. (Cont'd)

(a) Natural Petroleum Distillates.

Crude oil was obtained from the Polish, Rumanian, Austrian and German fields, to serve as a base for the German fuels and lubricants industry. Although the quantity of these oils was continually decreasing under the impact of Allied air and land offensives, a surprisingly large amount was still on hand almost up to the end of hostilities.

(b) Synthetic Distillate known as Kogasin II.

The high boiling fractions distilled from the Fischer-Tropsch low pressure, low temperature, catalytic process for obtaining hydrocarbons from solid fuels has the following typical analysis (1945) and was used as blending product for the preparation of Diesel fuels:

Gravity	.76
Color	15 Saybolt
Odor	Sickly-Characteristic of F.T. products.
Cetane No.	90 and better
Bromine No.	13.8
Iodine No.	13
Aromatics	Nil
Unsaturates	15 - 20 percent
Flash Point (PM)	195°F
Fire Point	215°F
Ash Content	Nil
Comradson Carbon	Nil
Viscosity	2.8 centiskokes @ 68°F
Sulfur	.01 percent
Aniline Point	90°C

DISTILLATION

I.B.P.	192°C
200°C	3.5 percent
210°C	17 percent
250°C	82 percent
260°C	91 percent
270°C	95 percent
E.P.	276°C
Recovery	97 percent

(c) Synthetic Distillate known as Kogasin I.

The lighter fractions distilled in the Fischer Tropsch process, with boiling range below 225 degrees centigrade, known as Kogasin I, and with a cetane number from 35 to 60, according to the cut, have also been used as one ingredient in various mixtures, for the production of Diesel fuels. Some work, mentioned below has been done to improve their suitability.

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TABLE I. TABULATION OF DIESEL FUEL SPECIFICATIONS

<table>
<tr><th rowspan="2"></th><th rowspan="2">Wehrmacht Diesel Kraftstoff</th><th rowspan="2">Sonder Diesel Kraftstoff</th><th rowspan="2">Luftwaffe K_1</th><th colspan="2">KRIEGSMARINETREIBOEL</th></tr>
<tr><th>Mineral oil; F.T. Synthesis; Hydrogenation</th><th>Lignite Oil</th></tr>
<tr><td>Appearance</td><td colspan="5">The Fuel must be clear, free from all solid matter.</td></tr>
<tr><td>Gravity @ 15°C</td><td colspan="3">.81[illegible] to .865</td><td>.88 Max.
For U-Boats</td><td>.90 Max.
.84 to .87</td></tr>
<tr><td>Viscosity Engler @ 20°C</td><td colspan="3">1.1° to 2°</td><td colspan="2">1.2° to 2.6°</td></tr>
<tr><td>Pour Point</td><td colspan="2">Winter: - 30° [illegible] Max.
Summer: - 1[illegible]° C Max.</td><td>-45°C Max.</td><td colspan="2">Must flow freely and without separation @ 0°C</td></tr>
<tr><td>Filtering ability</td><td colspan="3">Winter: 200 cc min in 60 Sec @ -25° C
Summer: " " " " " " @ - 5° C</td><td colspan="2">No such specifications</td></tr>
<tr><td>Flash point P.M.</td><td>55°C min</td><td>21°C Min</td><td>50°C Min</td><td colspan="2">55°C Min</td></tr>
<tr><td>Neutralisation No</td><td colspan="2">.4 mg Max</td><td>1% Max.</td><td colspan="2">1.5% Max.</td></tr>
<tr><td>Zinc Corrosion</td><td colspan="3">Not over 4 mg of weight reduction</td><td colspan="2">Acidity Zero</td></tr>
<tr><td>Water</td><td colspan="5">.5% Max</td></tr>
<tr><td>Ash</td><td colspan="5">.05% Max</td></tr>
<tr><td>Sulp[redacted]</td><td colspan="3">1% Max.</td><td>1% Max.</td><td>1.3% Max.</td></tr>
<tr><td>Conr[redacted]on Carbon</td><td colspan="2">.05% Max
Or 2% coke and gum by the Hagemann Hammerich method</td><td>1% Max.</td><td>.8% Max.</td><td>1% Max.</td></tr>
<tr><td>Lowe[redacted]eat Value</td><td colspan="5">9900 Kcal/kg. Min.</td></tr>
<tr><td>Ignitability</td><td>45 Cetane Min.</td><td></td><td>50 cetane Min.</td><td colspan="2">No specifications
(in practice 50 - 55)</td></tr>
<tr><td>Volatility</td><td colspan="2">80% Min distilled at 360°C</td><td>95% Min @ 350°C</td><td colspan="2">60% Min. distilled @ 350°C</td></tr>
<tr><td>Compatibility</td><td colspan="5">All Diesel fuels must mix together without precipitation</td></tr>
</table>

NOTES:

1. The Kriegsmarine specified also an "Emulsibility Test" which was the following: 10^{cc} of the Diesel fuel was shaken in a 50^{cc} closed tube with 10^{cc} of water for 30 seconds. There must be no emulsion and the separation of oil and water should start within a minute after the shaking. After 1/2 hour separation must be complete (within 1^{cc} of mixture). Then 1^{cc} of a ^{n}/10 NaOH solution is added and the fuel and water are shaken again 1/2 minute. The coloring of the liquid within the next 24 hours must be at the utmost a very pale pink. If too dark the entire test is repeated with sea water.

2. All Kriegsmarine Diesel Fuels, called "TREIBOEL", except. SDK2 (Sonder Diesel Kraffstoff 2) which is actually a "tractor Distillate", had to be colored to a minimum of 4 - 5 Oswald. For oils which were too light in color a mixture of 13 mg of Sulan brown R and 1 mg of Japan black were added per 1 kg of fuel (colors made by I.G. Farben-industrie).

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2. Sources of Diesel Fuel in Germany. (Cont'd)

(d) Distillates obtained from the Low-Temperature Carbonisation of Coal and Lignite (Schwelteer).

Low-temperature carbonisation of lignite produces about 3 percent of an oil containing as much as 20 percent of "creosote" and, according to the refining process, varying in cetane rating from 38 to 48. Its composition makes it a rather poor diesel fuel, and it is not generally used without further treatment.

(e) Distillates from the Hydrogenation Process.

The oil obtained from the hydrogenation of coal, coal tar and lignite constitutes a good diesel fuel, whether it is the middle oil from the sump phase, or the residue of distillation from the gas phase. Typical analysis of these hydrogenation diesel fuels cover a wide variety according to their boiling range:

Gravity	.850 to .885
Aniline Point	31 to 53°C
Aromatics and Unsaturates	38 to 49 percent
Boiling Index**	255 to 265
Cetane Rating	30 to 45
Pour Point	Below -35°C and as low as -70°C
Viscosity E @ +20°C	1.45 to 1.81°

They are used either pure or mixed with Kogasin II.

** The Germans refer to "Boiling Index" as the sum divided by ten of the temperatures at which 10 percent, 20 percent, 30 percent, etc... of the liquid have distilled, including the end point, but not the initial boiling point. Some also divide by nine the sum of the 10 percent, 20 percent, etc... fractions but exclusive of both I.B.P. and E.P.

(f) Oils from High-Temperature Carbonisation of Coal.

In the Ruhr where large quantities of coal are coked for the metallurgical industry, a tar-oil is available, of high gravity and low ignitability which is not suitable as diesel fuel for high-speed engines. It can however, be processed and mixed with other products, as will be described below.

[redacted]

2. Sources of Diesel Fuel in Germany. (Cont'd)

(g) Shale Oil.

The distillation of shale yields about 3.5 percent of an oil suitable as a Diesel fuel after further treatment and mixed with other products, in a manner similar to the treatment of coal tar mentioned above. This will be described further. A typical analysis of shale oil, such as produced at Dotternhausen (near Rottweil) is:

		DISTILLATION	
Gravity	.916		
Cetane Rating	35		
Neutralisation Index	0	I.B.P.	124°C
Ash	.02 percent	10 percent	240°C
Water	.09 percent	20 percent	250°C
Sulphur	4.4 percent	50 percent	282°C
Saponification No.	2.63	70 percent	315°C
Conradson Carbon	.15 percent	90 percent	340°C
Asphalt	0.06 percent	E.P.	371°C
		Recovery	96 percent

3. Preparation of the Diesel Fuel Blends.

It is of interest to relate the manner in which all fuels, for aircraft as well as for ground forces, were prepared for consumption in war-time Europe.

The utmost secrecy was maintained at all times inside and outside Germany regarding sources of fuels and preparation of blends. Producers were ordered to ship certain quantities of products to locations designated by a number and were not informed of the disposition or ultimate destination of these products. Blending was accomplished upon the orders of certain organizations, without any knowledge of the identity of the products blended. People who had complete knowledge of the fuels and lubricants situation were, for automotive engines, the personnel of the "Zentral Büro für Mineral Oel" in Berlin and for aviation engines, the personnel of the "Oberkommando der Luftwaffe." Under these, the "Wirtschaftliche Forschung Gesellschaft" or WIFO, assisted by the "Reichs Amt für Wirtschafts Ausbau" in Berlin, took care, at strategic points throughout Europe, of the storage, blending and distribution of fuels and lubricants.

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[redacted]

3. Preparation of the Diesel Fuel Blends. (Cont'd)

WIFO Depots, such as the huge WIFO No. 1 at Hizacker, on the Elbe south of Hamburg, were equipped not only to store fuels and lubricants in underground tanks and in barrels, but also to make control analysis in a well-equipped laboratory, and to carry on a certain amount of research independently from the manufacturers. This set-up explains some of the difficulties encountered in the attempt to get a complete picture of the liquid fuel situation in Central Europe.

For diesel fuels the usual types of blends were prepared in WIFO depots. For the more elaborate mixtures only, necessitating preliminary treatment, did the manufacturer take a hand in the process.

From the point of view of ignitability alone, Kogasin II from the Fischer-Tropsch process is an ideal product. It has been demonstrated however that, used alone, it is far from being an advantageous diesel fuel. Tests have proven that, compared with a diesel fuel of petroleum origin having a cetane rating of 47 and a specific gravity of .856, Kogasin II with 86 cetane rating and .770 specific gravity, when used in engines adapted to low cetane fuel, the only engines available at this time, showed:

(1) an increase in consumption of around 5 percent (based on equal heat value).
(2) an increase in exhaust gas temperature of about 25 percent.

This was attributed to the fact that Kogasin II does not have enough "body", as it is referred to. It ignites too fast but burns too slowly and must be blended with some of the other products listed above. Therefore Kogasin II was used mostly to upgrade the ignitability of other fuels.

Typical blends used as Diesel Fuels, with the specifications indicated above, and obtained by simple mixing, were, for instance:

45 percent Fischer-Tropsch Kogasin II
50 percent Light petroleum gasoil
5 percent Spindle oil distillate or, as alternative:

75 percent of this 45 - 50 - 5 blend
25 percent of a slightly heavier petroleum gasoil.

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[redacted]

3. Preparation of the Diesel Fuel Blends, (Cont'd)

When the mixture involves tar oils from the carbonization of coal, or shale oil, serious complications arise from the fact that these oils contain high percentages of asphalt, gum and carbon-forming elements which rapidly clog the injection nozzles, especially in small high-speed engines. Furthermore these components have a tendency to segregate out of the liquid, when Kogasin II is added and to settle in storage tanks. Originally inhibitors were used to prevent this condition, either 2 cubic centimeters of cresol for 100 centimeters of fuel, or 0.02 grams of mono-benzyl-amido-phenol in weak alcohol solution per 100 centimeters of fuel.

It became therefore necessary to refine the mixtures, and Dr. H. Kölbel of the "Rhein-Preussen Company" in Homberg, Ruhr, developed several processes for that purpose. The initial process consisted of a 20 percent liquid sulfuric acid wash at atmospheric temperature followed by a caustic wash with fullers earth filtration. Later aluminum chloride was substituted for the sulfuric acid wash, followed by neutralization and filtration. The latest method, covered by Deutsche Reichs Patent No. 730853 dated 28 January 1943 for the "cleaning of mixtures of tar oils and aliphatic hydrocarbons" consists of a treatment by sulfur dioxide SO_2, in gas form, at atmospheric pressure. On the following tabulation can be seen a typical picture of the changes taking place in the fuel by the use of this process.

	Kogasin II	Tar Oil	Mixture of Diesel Fuels		Petroleum gas-oil (for comp)
			Before Treatment	After Treatment	
Spec. gravity	.760	1.060	.862	.855	.857
Color	Water Clear	Black	Brown; not translucid	Yellow; Translucid; Fluorescant.	Yellow
Boiling Index	218°C	260°C	260°C	260°C	275°C
Cetane Rating	96	20	60	60	50
Flash Point P.M.	48°C	114°C	70°C	70°C	90°C
Pour Point	-20°C	Zero	-20°C	-20°C	-30°C
Lower Calorific value	10500 Cal	9980 cal	———	10100	10100
Conradson Carbon	.03 %	.26%	no data	.004%	.05%

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[redacted]

3. Preparation of the Diesel Fuel Blends. (Cont'd)

	Kogasin II	Tar Oil	Mixture of Diesel Fuels		Petroleum gas-oil (for comparison)
			Before Treatment	After Treatment	
Hard Asphalt (Hagemann & Hammerich)	Zero	2.5%	.46%	.03%	.06%
Insoluble in Benzine	Zero	4.8%	.87%	.05%	.11%

Proportions of carbon and hydrogen in these mixed Diesel fuels are:

87-90 percent C, to 9-12 percent H with a fraction of one percent of sulfur compared with following proportions in the Kogasin:

C - 85 percent
H - 15 percent
No sulfur

The proportions of Kogasin II in the mixtures vary according to the results desired. It has been found that the cetane rating increases practically in proportion to the quantity of Kogasin in the mixture; thus 35 percent tar oil and 65 percent Kogasin has a cetane rating of 57 while a 50-50 mixture has a cetane rating of 52.

The refining process is said to be inexpensive, as the loss of SO_2 is extremely small, the bulk being used over and over again. The amount of heavy tar, asphalt, and carbon precipitated out of the fuel during the treatment is about 10 percent of the total in weight. The phenolic products eliminated can be recovered and marketed.

The refined mixture, known as diesel fuel "R" is clear, stable, mixes readily with all other diesel fuels, and is even less corrosive (zinc test) than petroleum gas oil. Diesel motor tests have shown that it compares advantageously with petroleum diesel fuel as to exhaust gas temperature, low CO content of these gases, and consumption per horsepower.

[redacted]

3. Preparation of the Diesel Fuel Blends. (Cont'd)

For production of a <u>low pour point diesel fuel with high centane rating</u>, distillates of paraffinic nature can be treated by liquid SO_2 followed by a butane extraction, to remove most of the waxes that cause a high pour point. This process is very similar to the Edeleanu process, but was not used extensively in Germany on account of the low yield. For example 200 kilograms of distillate from the liquefaction of brown coal, treated as above, will yield only 60 kilograms of diesel fuel of -31°F pour, 53 cetane; or 88 kilograms of diesel fuel of -5°F pour, 44 cetane.

(a) Use of Gasoline in Diesel Engines.

At various times during the war the Germans experienced a serious shortage of adequate diesel fuel. These shortages were partly due to the necessity of concentrating production efforts upon the preparation of high-test aviation gasoline. It was necessary at these times to operate diesel engines on gasoline and gasoline blends which were or could be made available locally. Regardless of the type of gasoline blend used, an addition of 5 percent of motor oil to the fuel was prescribed, to protect the fuel injection pumps and not to improve the ignitability. There is a basic difference between diesel injection pumps, lubricated and sealed by the fuel itself and gasoline injection pumps, used currently on aircraft engines, lubricated by a supply of motor oil. Naturally the situation being temporary, no change over of the injection system was made. The only difficulties mentioned in connection with the use of gasoline in diesel engines were the excessive overheating of the engine and some tendency to vapor-lock in hot weather. In certain cases additives were needed to reduce the octane rating and bring the fuel more in line with a diesel fuel. Chlorpicrin was used as one of these additives. A cetane rating of 35 was aimed at. It can be obtained either by fractionating properly the Fischer-Tropsch gasoline, or by blending a gasoline of as high as 60 octane with a high cetane diesel fuel. Naturally low aromatic gasolines such as "Ruhrbenzin" were selected in preference to higher grades.

An attempt was made to use benzol. Ignition was possible only by mixing ethyl nitrate vapour with the air used for combustion; the engine stopped as soon as this addition of vapour was cut off.

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[redacted]

3. Preparation of the Diesel Fuel Blends. (a)(Cont'd)

The ethyl nitrate was kept in a brass container in a water bath, as its boiling point is 194°C. The vapour circuit had to be absolutely tight as ethyl nitrate vapours are toxic. Approximately .3 cubic centimeters of nitrate was used per one liter cylinder. An attempt to spray liquid ethyl nitrate in very small quantity into the cylinder resulted in a serious explosion.

During the diesel fuel shortage of 1941-42 tests were conducted at the Leuna plant of I.G. Farben for the use of a 50-50 mixture of diesel fuel and Leuna gasoline produced from the hydrogenation of brown coal tar, and having a cetane rating of 35. No difficulties were noted except a slight reduction in power in trucks and locomotive diesels or in small construction engines. In large, slow-speed diesels vapor-lock difficulties developed.

4. Diesel Fuel Additives.

In Germany as well as in the United States considerable research work was carried forward to raise the "ignitability", the cetane rating, of diesel fuels. Additives were used, either without further treatment, in various proportions, or were added to the fuel in conjunction with some treatment such as "nitration", "ozonisation".

For convenience, the work done with various additives and the results obtained are summarized in table form.

Used as additive	Proportion in volume	Original Diesel fuel	CETANE RATING		Remarks
			Original	Resultant	
NITRATES & NITRITES					
Ethyl Nitrate	.5 to 1%	Petroleum Gas-Oil	45	53-59	Boils at 195°C; this is too low Vapour very toxic.
Ethyl Nitrate	1 to 5%	do	do	up to 72	Above 1% strongly corrosive in injection system

[redacted]

80518

4. Diesel Fuel Additives. (Cont'd)

Used as additive	Proportion in volume	Original Diesel fuel	CETANE RATING Original	CETANE RATING Resultant	Remarks
Amyl Nitrate	1 to 5%	Petroleum Gas-Oil	45	Up to 70	Quite corrosive in injection system
Iso Amyl Nitrite	1 to 5%	do	do	do	Much less corrosive than nitrate
Methyl nitrate		do	do	do	Not corrosive but boils at 122°F, too low
PEROXIDES					
Dimethyl-Peroxide	1 to 3 %	Petroleum Gas-Oil	45	-	Strong action but boiling point is 55°F
Ethylene-Peroxide	do	do	do	60	No special data
Acetone-Peroxide	do	do	do	do	Extremely explosive crystals - harm- only when dissolved.
Diethyl-Peroxide	do	do	do	do	Very effective
Diethyl-Peroxide	3%	Lignite Gasoline	25	31	Very effective
Diacetone Diperoxide	1 to 2%	Gasoil	45		Very effective
Diacetone Diperoxide	3%	Lignite Gasoline	25	34	
Diacetone Diperoxide	do	F.T.Kogasin No. 1	64	70	

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4. Diesel Fuel Additives. (Cont'd)

Used as additive	Proportion in volume	Original Diesel fuel	CETANE RATING		Remarks
			Original	Resultant	
Monoxy-Diethyl Peroxide	1 to 2%	-	-	-	About same action as ethylene peroxide but not quite so soluble in fuels
Dioxy-Diethyl Peroxide	Less than 1%				Appears to act satisfactorily but not soluble enough
Tetraline Peroxide	3%	Lignite Gasoline	25	39	These results are questionable
Tetraline Peroxide	do	F.T.Kogasin #1	64	89	These results are questionable
Di-Benzoyl Peroxide	do	Lignite Gasoline	25	28	These results are questionable
Di-Benzoyl Peroxide	Less than 1%	Gasoil	45	up to 54	
Acetyl Benzoyl Peroxide	2%	Lignite Gasoline	25	30	
Acetyl Benzoyl Peroxide	1.2%	Gasoil	45	55	

This tabulation shows that the number of chemicals either of the nitrate or nitrite type, or of the peroxide type, that can effectively be used as additives to diesel fuels is somewhat restricted even though many may upgrade the ignitability to a considerable extent.

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[redacted]

4. Diesel Fuel Additives. (Cont'd)

A further limitation is found in the solubility of some of these additives.

(a) Solubility of Peroxides in Various Fuels.

An important aspect of the addition of chemicals into diesel fuels is their solubility in the various types of oils at different temperatures. This in several cases, limits their use. In general it can be said that the solubility of peroxide additives increases as the percentage of un-saturated and aromatic hydrocarbons in the oil increases, while their solubility decreases proportionally to the percentage of paraffinic components.

Following tabulation gives the solubility of several peroxides at a temperature of 68°F (20°C):

Peroxides	Petroleum Gasoil	Kogasin I from Fischer-Tropsch	Lignite Gasoline	Leuna Gasoline (Hydrogenation of Lignite Tar)
DiAcetone di Peroxide	2.4%	4.2%	5.4%	4.2%
DiBenzoyl di Peroxide	1.2	.8	3.4	.8
Acetyl Benzoyl di Peroxide	2.2	8.2	15.4	-
Tetraline di Peroxide	1.8	4.8	16.1	3._
Diethyl di Peroxide	7 Vol.	6 Vol.	50:50	5 Vol.

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[redacted]

4. Diesel Fuel Additives. (Cont'd)

(b) Effect of Peroxides on Ignitability.

Further tests were conducted at the Technische Hochschule of Munich, in a test engine where the compression ratio could be modified from 10:1 to 18:1, for the purpose of determining, with several diesel fuels and various peroxide additives, how low the compression ratio could be brought, in each case, before ignition would fail to occur.

The characteristics of the tests were as follows:

Air Temperature	86°F
Cooling Water	158°F
R.P.M.	470 ± 5
Injection Angle	17° before Top Dead Center
Torque	5 Kg/m
Injection Pressure	145 Atm.
Injector	Bosch DL 120 S 5 P 6, 5 outlets.

Below are the results, indicated in "Degrees of ignition delay, measured on the indicator diagrams", for various fuels at various compression ratios. The sign = means that no measurement was available, the sign - means "ignition fails to occur".

The reference fuel in all these tests is a petroleum gas-oil from Persian crude with a cetane rating or 45.

1st Series. The fuel selected for the tests was a widely used type of brown coal tar oil referred to as "diesel fuel B" from the low-temperature distillation of lignite from Middle Germany (probably Saxony) with 2 percent of the additives indicated:

Compression Ratio	18	16	14	13	12	11	10
Reference Fuel	9	10	12	=	15	=	20/21
Diesel Fuel B without Additive	14	15/16	20	26/27	-	-	-
Diesel Fuel B With 2% of:							

[redacted]

80522

4. Diesel Fuel Additives. (b)(Cont'd)

Compression Ratio	18	16	14	13	12	11	10
Di Methyl Peroxide	9	10/11	13	=	18	=	28
Di Ethyl Peroxide	10	11/12	13/14	=	19	25	-
Di Acetone Peroxide	11	12/13	15	=	21	27	-
Monoxydi Ethyl Peroxide	12	13	15/16	=	22/23	26/27	-
Hydrogen Peroxide	12	14	17	=	25/26	28	-
Monoperparaldehyde	13	15	19	29/30	-	-	-
Acetyl Benzoyl Peroxide	13/14	15	20	26	-	-	-

Tetralin, Dibenzoyl, Dioxy-Diethyl, etc.. show practically no difference in ignition delay.

2nd Series. Same diesel fuel "B" but with only 1 percent of peroxide additives:

Compression Ratio	18	16	14	13	12	11	10
Dimethyl Peroxide	10/11	12	14/15	=	20/21	28	-
Di Ethyl Peroxide	11/12	13	17	=	24/25	-	-
Di Acetone Di Peroxide	12	13/14	17	=	25	-	-
Ethylidene Peroxide	12/13	14/15	18	=	29	-	-
Acetylbenzoyl Peroxide	14	16	20/21	27	-	-	-

These two series of tests show the effect of even small percentages of certain peroxide additives in bringing back the ignition delay of a Diesel fuel towards the ignition delay of the reference fuel of petroleum origin. In other words it can be seen how certain additives permit the use of a synthetic diesel fuel which could not be adequately consumed without these additives at the compression ration available in certain diesel engines.

The next series of tests shows the influence of peroxide additives on the stability of diesel fuels. For every compression ratio the ignition delay is shorter when peroxides were added to the fuel before its prolonged storage.

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4. Diesel Fuel Additives. ([redacted])(Cont'd)

3rd Series. A similar diesel fuel (brown coal tar) from low-temperature distillation of lignites, with 2 percent additives except as noted, and after ten months of storage.

Compression Ratio	18	16	14	12	11	10
Diesel Fuel alone	13	14	16/17	22	29/30	-
Di Aceton Di Peroxide	10	11	12/13	16	=	26
Di Ethyl Peroxide	11	12/13	14/15	18/19	23	-
Di Ethyl but only 1%	12	13	15	19	24/25	-
Acetyl Benzoyl Peroxide	12	13/14	16	21	27	-
Tetralin Peroxide	12	13/14	16	21/22	-	-
Di Benzoyl Peroxide	12	13/14	16	22	-	-

The fourth series of tests reported on the next tabulation shows that some "ignition accelerator" must be added to the diesel fuel obtained from low temperature coal tar before it can be used as diesel fuel.

4th Series. A Diesel fuel from the low-temperature distillation of coal, which does not ignite satisfactorily in the engine at compression ratio of 18:1 or below, and even at 18:1 has a 27° ignition delay, with 2 percent of various peroxide additives, or 1 percent as noted.

Compression Ratio	18	16	14	13	12
Diesel fuel without additive	27	37/38	-	-	-
Diesel fuel with:					
Diethyl Peroxide, 2%	16	18	23	30	37
Diethyl Peroxide but only 1% added	16	18	28/29	-	-
Di Acetone Peroxide, 2%	17	19/20	26	34/35	-
Di Acetone Peroxide but only 1% added	18	22	34	-	-
Mono oxy Di Ethyl Peroxide, 2%	17/18	21/22	30	-	-

4. Diesel Fuel Additives. (b)(Cont'd)

Compression Ratio	18	16	14	13	12
Acetyl Benzoyl Peroxide	18/19	22/23	31	–	–
Tetralin Peroxide	19	23	40	–	–

A final set of tests was made to see the action of the peroxide additives on a diesel fuel of petroleum origin. The same "reference fuel" is tabulated as for the first series of tests. Results show that the additives improve the ignitability of the diesel fuel beyond the quality of the reference fuel.

5th Series. Same additives in 2 percent concentration in a petroleum gas-oil (origin not known):

Compression Ratio	18	16	14	12	10	9
Reference Fuel	9	10	12	15	20/21	25
Gasoil without Additives	9/10	11	13/14	17/18	26/27	–
Gasoil with 2% of Di Ethyl Peroxide	6/7	7	9/10	11/12	16/17	22/23
Acetyl Benzoyl Peroxide	7/8	8/9	10	12/13	18	25/26
Di Aceton Di Peroxide	7/8	9	10/11	14/15	19/20	29/30
Mono OxyDiethyl Peroxide	8/9	9/10	11/12	14/15	21	29/30
Tetralin Peroxide	8/9	9/10	11/12	15	21/22	–

In addition to the better ignitability of diesel fuels containing peroxide additives, a much smoother operation and a much cleaner exhaust could be noticed.

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[redacted]

4. Diesel Fuel Additives. (Cont'd)

(c) Effect of Other Type Additives on Ignitability.

Two additives, tried at the Technische Hochschule of Munich are worth mentioning. One is "chlorpicrin" which is "trichlor nitro methane"; added in proportion up to 4 percent it increases the cetane value materially. For instance a Kogasin II, of 92 cetane, goes up to 116 cetane by nitration and to 170 with addition of chlorpicrin after nitration. The other additive is "Lupanol", a "tetra nitro methane" which in concentrations up to 3 percent has a marked influence on ignitability.

In 1942 the Technische Hochschule in Munich conducted experiments with other organic additives. It was found that the following chemicals reduce the ignitability:

Esters
Cyclic hydrocarbons (like pseudocumol, cymol)
Cyclic aldehydes (like benzoic aldehyde)
Alcohols of low-molecular weight.

The following chemicals, on the other hand, increase the ignitability:

Straight-chains aldehydes, in large proportion
(as much as 20 percent).
Alcohols of high molecular weight.

For alcohols in particular the following tabulation illustrates the results, and shows that, from n-Octyl alcohol up an appreciable increase in cetane rating can be noticed.

Alcohol Added	Porportion	CETANE RATING of Gasoil	After addition	Difference
Di Aceton-Alcohol	20%	45	36	-9
n - Propyl Alcohol	20%	46	37	-9
C_3	40%	46	28	-18
n - Hexyl Alcohol	20%	46	38	-8
C_6		do		
n - Octyl Alcohol	20%	do	47	+1
C_8	40%	do	51	+5

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[redacted]

4. **Diesel Fuel Additives, (c) (Cont'd)**

Alcohol Added	Porportion	CETANE RATING of Gasoil	After addition	Difference
n - Nonyl Alcohol	20%	46	48	+2
C_9	40%	do	49	+3
n-Decyl Alcohol	20%	do	51	+5
C_{10}	40%	do	58	+12

(d) **Effect of NITRATION on Ignitability.**

Best results with high molecular alcohols were obtained when a "nitration" treatment was given the mixture, in the following manner. First a Fischer-Tropsch Kogasin I was selected and the fractions boiling below 212°F were removed. The balance had a cetane rating of 39. This was mixed with 50 percent of various alcohols, and the mixture subjected to a nitration process by bubbling gaseous concentrated nitric acid through the liquid. The results were as follows:

Percentage of NO_2 Absorbed	Increase in Cetane
.12	0
.31	0
.67	3
1.20	7
1.58	10.5
2.08 (Saturation)	18

In most of these experiments a precipitation of pitch took place, and the oil had to be filtered after the reaction.

These fuels are not corrosive unless they are from coal origin and contain phenols.

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[redacted]

4. Diesel Fuel Additives. (Cont'd)

(e) Effect of OZONISATION on Ignitability.

The Technische Hochschule of Munich conducted a considerable number of tests in 1940-42 along the line of ozonisation of Diesel fuels for the purpose of raising the cetane rating. It was found that the length of contact of the diesel fuel with the ozone was important, and that the ignitability was raised regardless of the oil, for instance Ruhrbenzin (gasoline) was as susceptible to the ozonisation treatment as Kogasin. Taking a Ruhr gasoline of 47 cetane the following increases were noted:

After	3	hours	ozonisation,	the	cetane	was	58
"	6	"	"	"	"	"	74
"	9	"	"	"	"	"	106
"	12	"	"	"	"	"	114
"	20	"	"	"	"	"	130
"	24	"	"	"	"	"	140

Results of various experiments conducted in 1941-42 are summarized in the following tabulation:

PRODUCT, ADDITIVE and TREATMENT	CETANE RATING
Pure Fischer-Tropsch Kogasin I (Average)	64
Same Kogasin I with 10% CS_2	68
Same Kogasin I with 3% Di Acetone Di Peroxide	70
Same Kogasin I with 5% Nitro Benzol	72
Same Kogasin I with 3% Amyl Nitrite	74
Same Ozonised for 5 hours (1 liter)	82
Same Kogasin I with 3% Ethyl Nitrate	85
Same Kogasin I with 3% Tetralin Peroxide	89
Same Kogasin I with 3% Lupanol	96
Same treated in contact with nitric acid	98
Same ozonised 8 hours (1 liter)	100
Same ozonised 10 hours (1 liter)	100
Same ozonised 15 hours then extracted	106
Same extracted with methyl alcohol then ozonised 15 hours (1 liter)	134
Same extracted with methyl alcohol then ozonised 8 hours (1 liter)	148

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[redacted]

4. Diesel Fuel Additives. (e)(Cont'd)

PRODUCT, ADDITIVE and TREATMENT	CETANE RATING
Same extracted with methyl alcohol then nitrated	96
Kogasin I extracted, nitrated and ozonised (1 liter in 8 hours)	101
Kogasin I - simply ozonised at rate of 1 liter in 15 hours	113
Kogasin II - pure	92
Kogasin II - Nitrated	116
Kogasin II - Ozonised 5 hours	121
Pure cetane	100
Cetane treated with nitric acid	104
Cetane treated with nitric acid at 194°F	132
Cyclo-hexane	14
Cyclo-hexane treated with nitric acid at 130°F	26

The above tabulation is self-explanatory. A comparison of the results with those obtained by the mere addition of a chemical permits an evaluation of the effect of a treatment such as nitration, ozonisation, or a combination of the two processes.

(f) Object of German Research with Additives.

It is to be noted that the study of "diesel fuel additives", conducted in various German scientific activities was concentrated upon one single feature; an increase in ignitability. Extensive studies of the performance of these additives in various oils, their stability, their corrosive action, before and after combustion, were apparently not made. Neither have the investigators come in contact with any studies of real value about additives that would improve the entire process of combustion regardless of the ignitability. The reason seems to be that, up to this date, additives have not been considered as the proper method to improve a diesel fuel. The Germans efforts were rather to concentrate upon the preparation of the proper blends of oils, natural or synthetic, which would operate satisfactorily without the use of additives.

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[redacted]

5. The Significance of Cetane Increase.

At the Technische Hochschule of Stuttgart, considerable work was done to determine, at various temperatures, the "critical compression ratio" of a diesel engine; that is, the compression ratio below which ignition of the diesel fuel cannot be entertained. The two charts show some of the results. In Figure 1 critical compression ratios are plotted against air temperatures for fuels of various ignitabilities and for ignition accelerating vapours in the air used for combustion. Figure 2 shows the correlation between cetane ratings and critical compression ratios at normal temperature (65°C) for various additions of ethyl nitrate.

Thus it would appear that an increase in cetane rating by permitting a reduction of the "critical compression ratio" at every temperature makes it possible to build an engine that develops more power per pound or, conversely, to obtain a greater output from an engine built for a given compression ratio.

In reviewing these laboratory efforts to raise the cetane rating of oils used as diesel fuels the following questions have been justifiably asked. "How high should the cetane rating of a fuel be raised? What can be gained? What seems to be the desirable cetane limit in the light of today's knowledge? What is the diesel engine manufacturer's position with regards to extremely high cetane ratings?

The German scientists and manufacturers interviewed seem to agree on the answer summarised below. For the present high speed diesel engine 50 cetane rating is satisfactory. For the engine of tomorrow the discussion revolved around the question of "efficiency versus compression ratio".

An examination of Figure 3 shows, in the range of the Otto gasoline engine, an increase in efficiency with an <u>increase</u> in compression ratio, the latter being made possible by an increase in the "octane rating" of the fuel. A further examination shows, in the range of the diesel engine, a somewhat smaller increase in efficiency with <u>decreasing</u> compression ratio. Such decrease, as shown above, is made possible by use of a fuel having a high ignition quality.

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5. The Significance of Cetane Increase Cont'd

Therefore an increase in cetane rating, in ignitability instead of being used to further an "increase in compression ratio" is used in an entirely opposite direction, namely to make a smoother running with a "lower" compression ratio, and all the simplification in weight, material, lubrication friction losses, that such a reduction entails. The principle appears to be perfectly sound especially when friction losses are considered and will undoubtedly guide manufacturers on both sides of the ocean towards the construction of a lighter more economical engine that may eventually permit an engine intermeliate between Otto and diesel types.

6. Conclusions.

During the war it can be said that the Germans had no high quality diesel fuel as such, but blends of synthetic and natural products, each playing a definite part in the performance of the fuel. They explored the field of chemical additives but did not use them in practice. They developed certain treatments that resulted in cetane ratings of fantastic proportions. Gasolines had to be used at times when other diesel fuels were scarse. No innovations were found in the way of producing, storing or handling diesel fuels. The processes of nitration and ozonisation of diesel fuels and blends and the treatment of tar oil blends with gaseous SO_2 for purification are of major importance and may well contribute to an improvement in, or extension of American diesel fuel supplies, with their further exploration and adoption.

Prepared by:

R. J. BENDER,
Lieutenant USNR.

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APPENDIX I

THE FKFS TESTING STAND

The Technische Hochschule of Stuttgart had a department, at times 450 employees strong, for technical developments in the science of engines. It was called the "Forschungs Institut fur Kraftfahrwesen und Fahrzeugmotoren an der Technische Hochschule Stuttgart" located at Unter Turckheim near Stuttgart in a group of buildings of the Daimler Benz Factory. There a testing motor was developed, used for gasoline as well as for Diesel research, the FKFS Motor, having the following characteristics.

For diesel tests, in particular four (4) types of combustion chambers are abailable:

- Direct Injection
- Pre-combustion chamber
- Air-cell system
- Fuel-cell system

The compression ration can be varied from:

4.5:1 up to	25:1
Bore	100m/m
Stroke	130m/m
Cylinder Volume	1000 cm3 (1 liter)
Speed	Up to 2500 RPM normally, for short periods 3000 RPM corresponding to a piston speed of 42.6 feet per second

Cooling water temp	80° C
Lubricating Oil Vol.	from 3 to 6 quarts
Oil temperature	up to 100° C
Oil pressure	3 Atm.
Valve lift (both)	.15 m/m
Inlet valve opens	10° BTDC
Exhaust valve closes	12° ATDC

Injection and ignition timing controllable
Injection pressures:

Direct injection	180 Atm
Pre-comb.chamber	90 Atm
Air-cell	90 Atm
Fuel Cell	110 Atm

7

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DEUTSCHES REICH

AUSGEGEBEN AM
~~[illegible]~~
28. JANUAR 1943

REICHSPATENTAMT

PATENTSCHRIFT

№ 730853

KLASSE 12r GRUPPE 1 04

St 57006 IVd/12r

Dr. Herbert Kölbel in Moers
ist als Erfinder genannt worden.

Steinkohlen-Bergwerk „Rheinpreussen“ in Homberg, Niederrhein

Verfahren zur Reinigung von Gemischen aus Teerölen und aliphatischen Kohlenwasserstoffölen

Patentiert im Deutschen Reich vom 14. Januar 1938 an
Patenterteilung bekanntgemacht am 24. Dezember 1942

Gemäß § 2 Abs. 2 der Verordnung vom 28. April 1938 ist die Erklärung abgegeben worden, daß sich der Schutz auf das Land Österreich erstrecken soll.

Die vorliegende Erfindung bezweckt die Herstellung von Dieselkraftstoffen aus Gemischen von Teerölen, besonders Steinkohlenteeröl, mit Kohlenwasserstoffen der Paraffinreihe und betrifft ein Verfahren zur Reinigung dieser Gemische.

Es ist an sich bekannt, schwer zündende Teeröle durch Zusatz von zündwilligeren, vorwiegend aliphatischen Gasölen für den Verbrauch in Dieselmotoren nutzbar zu machen. Diese nichtraffinierten Mischungen scheiden jedoch in kurzer Zeit asphaltartige Stoffe aus, die eine motorische Verwendung und eine Lagerung unmöglich machen. Es ist bereits ein Verfahren bekannt, nach welchem solche Asphaltstoffe durch längeres Erhitzen unter Rückfluß aus Teeröl-Gasöl-Mischungen ausgeschieden werden. Die Wirkung dieser Wärmebehandlung soll dadurch erhöht werden, daß die Erhitzung des Ölgemisches in Gegenwart von Spalt- oder Hydrierungskatalysatoren oder im Beisein von Salzen des Aluminiums oder Magnesiums vorgenommen wird. Weiterhin soll die Erhitzung des Ölgemisches unter Druck von Vorteil sein.

Die nach dem angeführten Verfahren hergestellten Dieselkraftstoffe genügen jedoch nicht den Ansprüchen, die an Dieselöl für schnell laufende, empfindliche Motoren gestellt werden müssen, insbesondere besitzen derartige Dieselkraftstoffmischungen eine zu hohe Verkokungsneigung, die zu Düsenverstopfungen und zum Verkleben von Kolbenringen führt.

Die Erfindung vermeidet diese Nachteile und erzielt einen einwandfreien Dieselkraftstoff durch Reinigung von Gemischen aus Teerölen und vorwiegend aliphatischen Kohlenwasserstoffölen der Siedelage 180 bis 360°, indem die Gemische mit gasförmigem Schwefeldioxyd bei gewöhnlichem Druck behandelt und von den hierbei ausgeschiedenen

Stoffen abgetrennt werden. Durch diese Behandlung werden der größte Teil der phenolischen Anteile sowie Asphaltstoffe, Pech und Harze abgeschieden und abgetrennt. Die Anwendung von Wärme ist hierbei nicht unbedingt erforderlich. Das Schwefeldioxydgas wird zur Raffination weiterer Gemische wieder verwandt. Das so gereinigte Ölgemisch kann auf die übliche Weise durch Waschen mit Wasser oder Lauge, gegebenenfalls auch mit Bleicherde, weiter behandelt werden. Man erhält so einen hellen, lagerbeständigen Dieselkraftstoff, der frei ist von Asphalten, Harzen und phenolischen Ölen und der nur eine geringe Verkokungsneigung zeigt. Es ist ein wesentliches Merkmal des Verfahrens der Erfindung, daß das zur Raffination verwendete Schwefeldioxyd chemisch nicht mit dem Ölgemisch reagiert, so daß auf diese Weise nur ein ganz geringer Verlust an Raffinationsmitteln eintritt. Man kann so mit geringen Mengen an Raffinationsmitteln große Mengen dieser Ölgemische, z. B. durch Umpumpen des Gases, reinigen. Bezüglich der Wirkungsweise wird angenommen, daß die Paraffinkohlenwasserstoffe die als Dieselkraftstoff erwünschten Bestandteile der Teeröle — als eine Art selektives Lösungsmittel — in Lösung halten, während die unerwünschten Inhaltsstoffe unter der Einwirkung von Schwefeldioxyd als unlöslich ausgeschieden werden.

Nach einem weiteren Erfindungsmerkmal ist es für die Ausführung des Verfahrens von großem Vorteil, bei der Kohlenoxydhydrierung entstehende Paraffinkohlenwasserstofföle der Siedelage 180 und 360° zu verwenden. Diese Kohlenwasserstofföle zeichnen sich durch ihren hohen Wasserstoffgehalt bzw. durch ihre geringe Dichte aus und übertreffen in diesen Eigenschaften jedes natürliche Erdöl der gleichen Siedegrenzen. Auf Grund des hohen Wasserstoffgehaltes besitzen diese Kohlenwasserstofföle für die unerwünschten Inhaltsstoffe des Teeröles nur ein sehr geringes Lösungsvermögen, so daß die Ausscheidung dieser Stoffe mittels Schwefeldioxyds besonders leicht und schnell vor sich geht. Außerdem bietet die in Frage stehende Kohlenwasserstoffölfraktion des Benzinsyntheserohproduktes bekanntlich ganz erhebliche motorische Vorzüge, die sich in restloser Verbrennung und hoher Zündwilligkeit auswirken.

Es ist zwar bekannt, zwecks Herstellung von Dieselölen Teeröle mit Kohlenwasserstoffölen der Kohlenoxydhydrierung zu vermischen. Ganz abgesehen davon, daß derartige Mischungen infolge von Ausscheidungen und Düsenverstopfung praktisch gänzlich unbrauchbar sind, bezieht sich die Erfindung nicht auf die Zumischung dieser Kohlenwasserstofföle an sich, sondern auf ihre besondere Wirkung als selektives Lösungsmittel im Verein mit dem Schwefeldioxyd. Dieses selektive Lösungsvermögen ist begründet in dem eigenartigen Aufbau dieser Kohlenwasserstofföle, deren Wirkung auf Teeröle im Verein mit gasförmigem Schwefeldioxyd nicht bekannt war und überraschend ist.

Es sind zahlreiche Verfahren bekannt, nach denen Mineralöle und Teeröle mit flüssigem Schwefeldioxyd unter Druck behandelt werden. Bei diesen Verfahren handelt es sich jedoch um Extraktionen in der Flüssigphase. Demgegenüber unterscheidet sich die Arbeitsweise der Erfindung grundsätzlich nach Zweck und Ausführung. Weiter ist bekannt, Öle, die durch spaltende Hydrierung von Kohlen, Teeren und Mineralölen erhalten werden, mit sauren Gasen zu behandeln, um diese von festen Teilchen zu befreien. Diese Arbeitsweise ist jedoch ausdrücklich auf die Entfernung fester Teilchen beschränkt. Das Verfahren nach der Erfindung bezweckt jedoch die Reinigung von Teeröl-Paraffinkohlenwasserstoff-Gemischen, die frei von festen Bestandteilen sind; es wird daher von dem erwähnten bekannten Verfahren nicht berührt, zumal die erwähnte Wirkung des erfindungsgemäßen Verfahrens nicht zu erwarten war. Man hat auch versucht, Mineralöle, wie Petroleum und Paraffinöle, mit gasförmigem Schwefeldioxyd zu reinigen, jedoch nicht Gemische von Teerölen mit Paraffinkohlenwasserstoffen, die durch die oben geschilderten Löslichkeitsverhältnisse sich in bezug auf die Ausscheidung von Asphalt-, Harz- und Pechstoffen gänzlich anders verhalten. Das geht daraus hervor, daß sich durch getrennte Behandlung von Teeröl einerseits und Paraffinkohlenwasserstoffen andererseits mit Schwefeldioxydgasen keine Reinigungswirkung erzielen läßt.

Man hat auch schon Dieselöle verschiedener Herkunft durch Behandlung mit ozonhaltigen Gasen zu reinigen versucht; ganz abgesehen davon, daß man hierbei die Mitwirkung aliphatischer Kohlenwasserstofföle nicht erkannte, zeigen Vergleichsversuche, daß die Reinigungswirkung von ozonhaltigen Gasen auf ein Gemisch von Teeröl und aliphatischen Kohlenwasserstoffölen sehr viel schlechter ist als die erfindungsgemäße Arbeitsweise mit Hilfe von Schwefeldioxyd.

Der mit dem Verfahren nach der Erfindung gegenüber dem Bekannten erzielte technische Fortschritt besteht in der Herstellung von Dieselkraftstoffen aus Gemischen von Teerölen mit aliphatischen Kohlenwasserstoffölen, die frei sind von Asphalt, Harz, Pech und Harzbildnern, arm an phenolischen

Ölen, und die eine gute Lagerfähigkeit aufweisen. Die Anwendung von Schwefeldioxyd bietet den weiteren Vorteil des geringsten Aufwandes an Raffinationsmitteln, da dieses ohne Aufarbeitung immer wieder verwandt werden kann. Die so gewonnenen Dieselkraftstoffe haben eine rauch- und rußlose Verbrennung sowie ein kohlenoxydarmes Auspuffgas über einen weiten motorischen Belastungsbereich. Infolge der geringen Verkokungsneigung ist die Gefahr der Düsenverstopfung und Kolbenringverkrustung weitgehend herabgemindert gegenüber gleichartigen Dieselkraftstoffen, die nach den erwähnten bekannten Verfahren hergestellt sind.

Beispiel

Ein Steinkohlenteeröldestillat aus der Hochtemperaturverkokung (180 bis 320°, Dichte 0,95 bis 1,05 bei 15°) wird mit einem nach der Benzinsynthese aus Kohlenoxyd und Wasserstoff hergestellten Kohlenwasserstofföl der gleichen Siedelage (Dichte 0,77 bei 15°) gemischt. Die Mischung hat eine Dichte von 0,862 bei 15°; sie wird bei Zimmertemperatur etwa 10 Minuten mit fein verteiltem gasförmigem Schwefeldioxyd behandelt. Aus dem Ölgemisch werden etwa 4 bis 10% braune, lackartige, phenolhaltige Asphaltstoffe ausgeschieden, von denen das Öl leicht abzutrennen ist. Das Ölgemisch hat eine bedeutende Farbenaufhellung erfahren, der Phenolgehalt ist von 2,9 auf 1,2 Volumprozent gesunken, die Verkokungsneigung (nach Hagemann und Hammerich, Öl und Kohle, 12, 379, 380, 1936) ist von 0,320 auf 0,064% Benzinunlösliches zurückgegangen. Das auf die beschriebene Weise behandelte Ölgemisch wird mit verdünnter Natronlauge und Wasser nachgewaschen und einer 1%igen Bleicherdebehandlung unterzogen.

Die mit Schwefeldioxydbehandlung erzielte Wirkung geht aus den chemischen und physikalischen Daten des Ölgemisches vor und nach der Behandlung hervor:

	Vor der Behandlung	Nach der Behandlung mit SO_2
Dichte bei 15°	0,862	0,855
Phenolgehalt in Volumprozent	2,9	1,2
Verkokungsneigung:		
Benzinunlösliches	0,320	0,064
Hartasphalt	0,108	0,030
Koks	0,212	0,034
Farbe	schwarzbraun undurchsichtig	gelb, klar durchsichtig

PATENTANSPRÜCHE:

1. Verfahren zur Reinigung von aus Teerölen der Siedelage 180 bis 360° und vorwiegend aliphatischen Kohlenwasserstoffölen gleicher Siedelage bestehenden Gemischen, dadurch gekennzeichnet, daß die Gemische mit gasförmigem Schwefeldioxyd bei gewöhnlichem Druck behandelt und von den hierbei ausgeschiedenen Stoffen abgetrennt werden.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß man von Gemischen ausgeht, die außer Teeröl aliphatische Kohlenwasserstofföle enthalten, die durch Kohlenoxydhydrierung gewonnen werden.

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[illegible]

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Forschungsinstitut für Kraftfahrwesen u. Fahrzeugmotoren Techn. Hochschule Stuttgart	**Betriebsanleitung für den Kraftstoffprüfrotor.**	Bild 1

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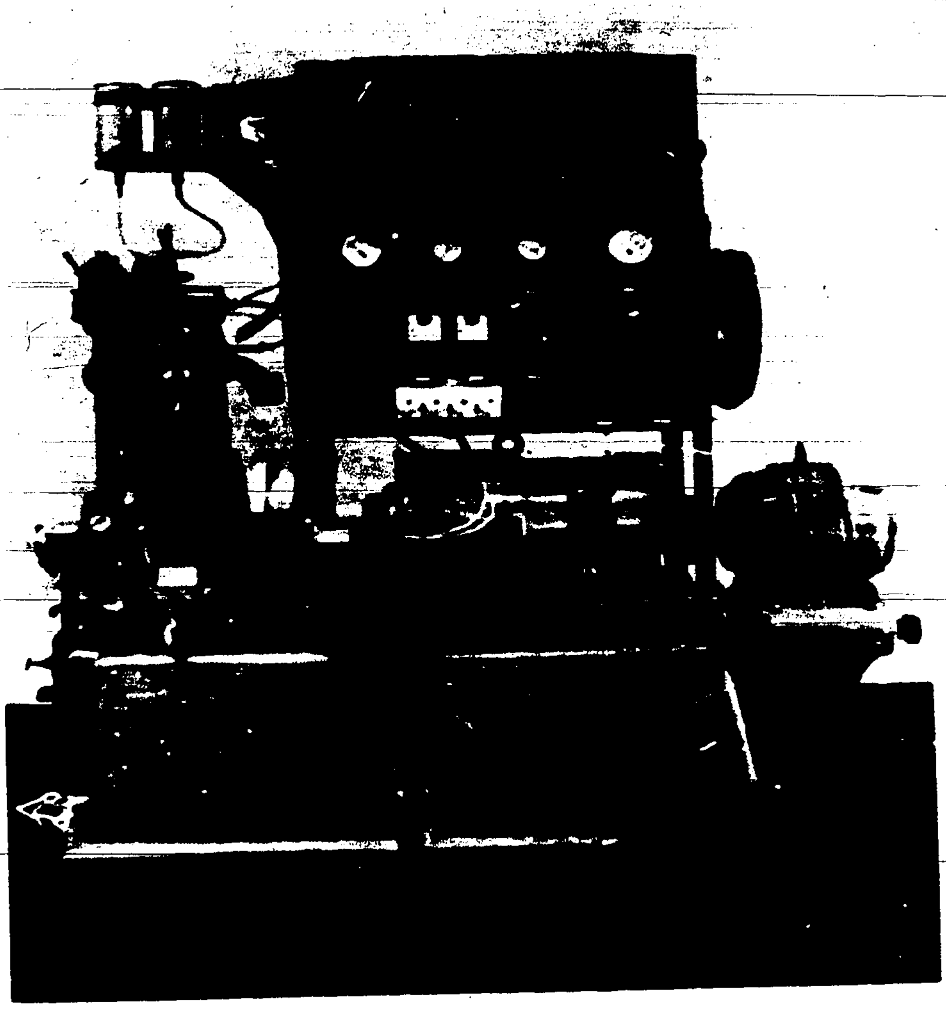

Bild 1

FKFS-Kraftstoffprüfstand.

Bearbeiter Gross Prüfer	Tag Tag	Ersatz für	Ersetzt durch	

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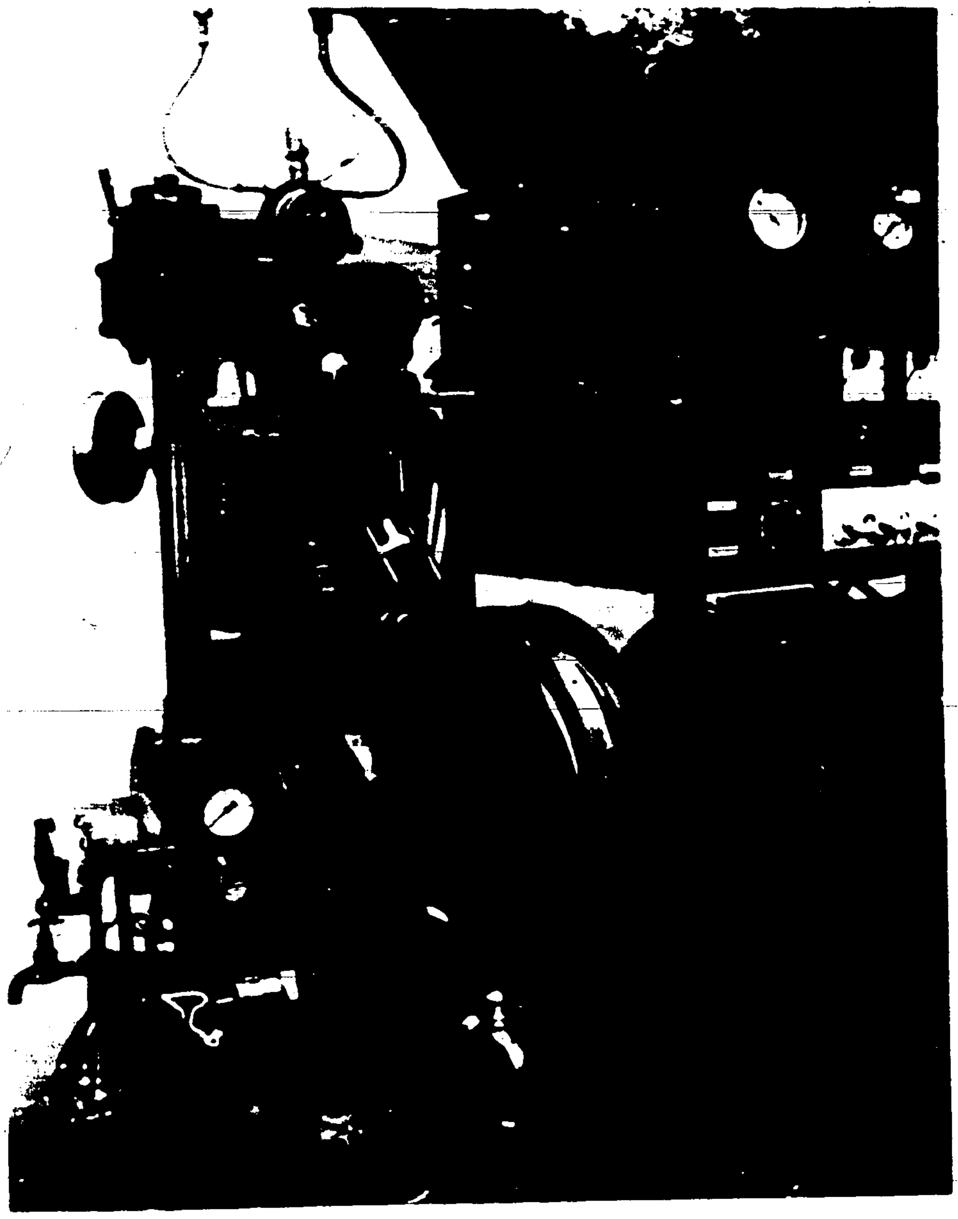

Bild 2

FKFS Kraftstoff-Prüfmotor.

FKFS Forschungsinstitut für Kraftfahrwesen u. Fahrzeugmotoren Techn. Hochschule Stuttgart	Betriebsanleitung für den Kraftstoffprüfmotor.	Bild 3

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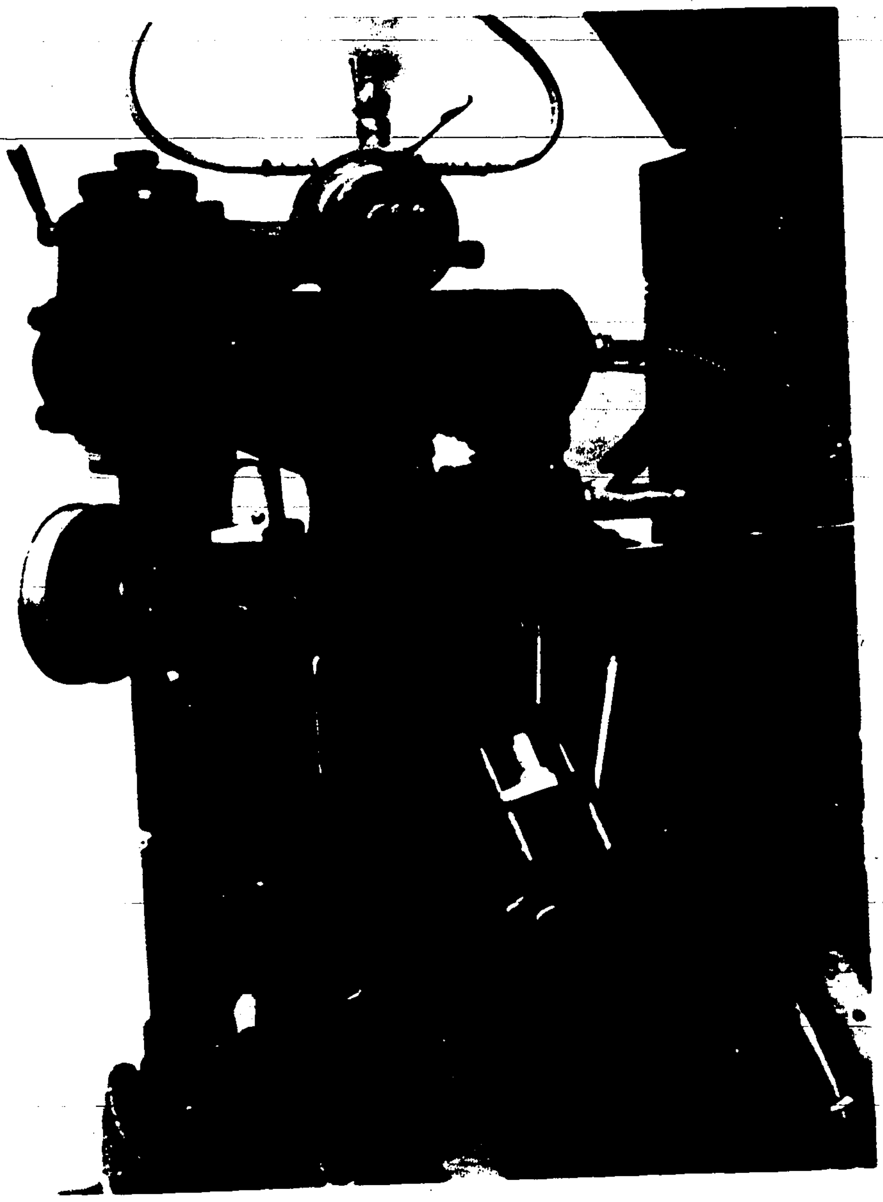

Bild 3
Zylinderaufbau.

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Bearbeiter [illegible]	Tag	Ersatz für	Ersetzt durch
Prüfer	Tag		

Unbefugte Verwendung ist strafbar und schadenersatzpflichtig

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Bild 4

Kühleranordnung.

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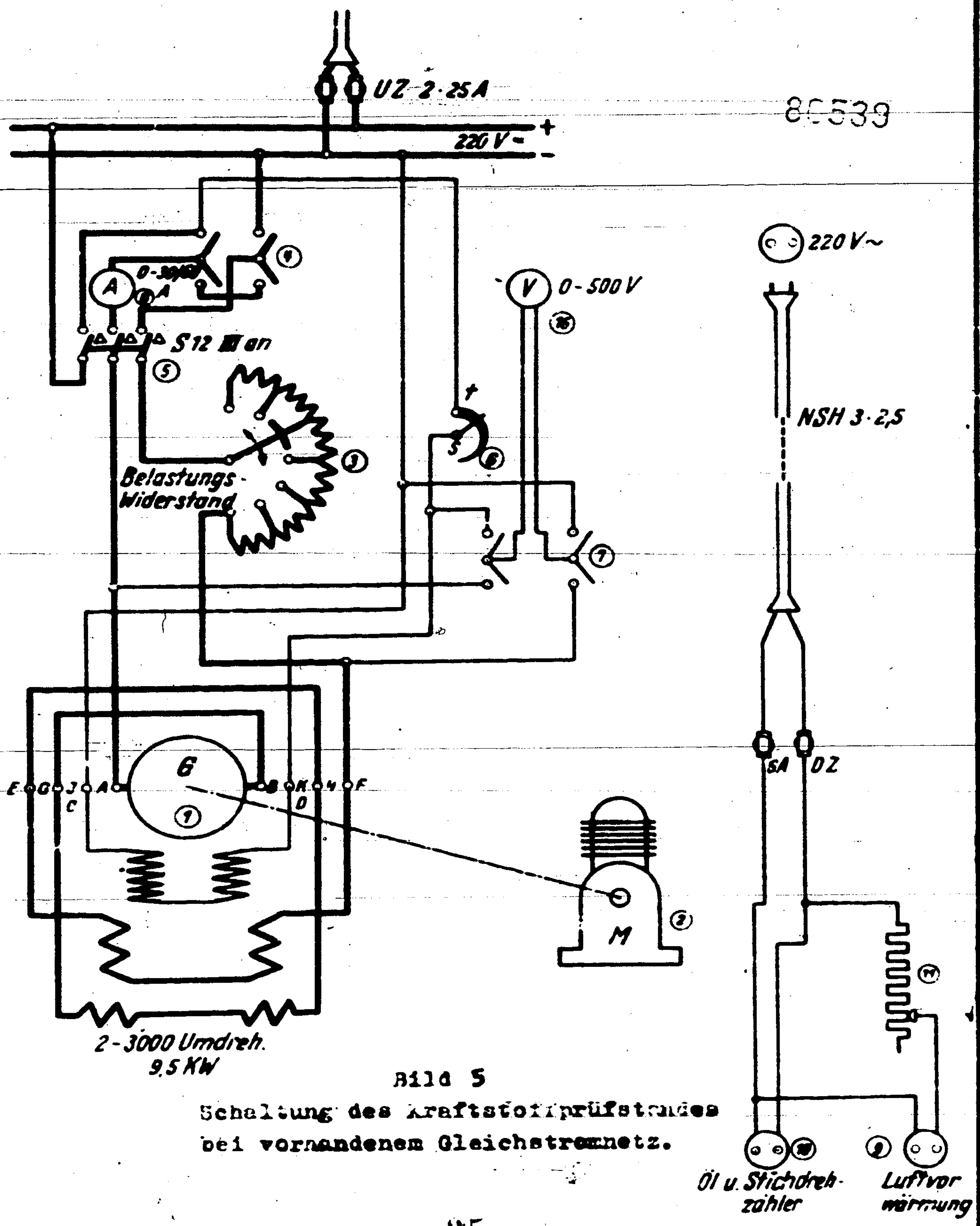

Bild 5

Schaltung des Kraftstoffprüfstandes bei vorhandenem Gleichstromnetz.

[illegible] 101.8	Tag Tag	[illegible]	[illegible]	

Betriebsanleitung für d'n Kraftstoffprüfmotor.

Bild 6

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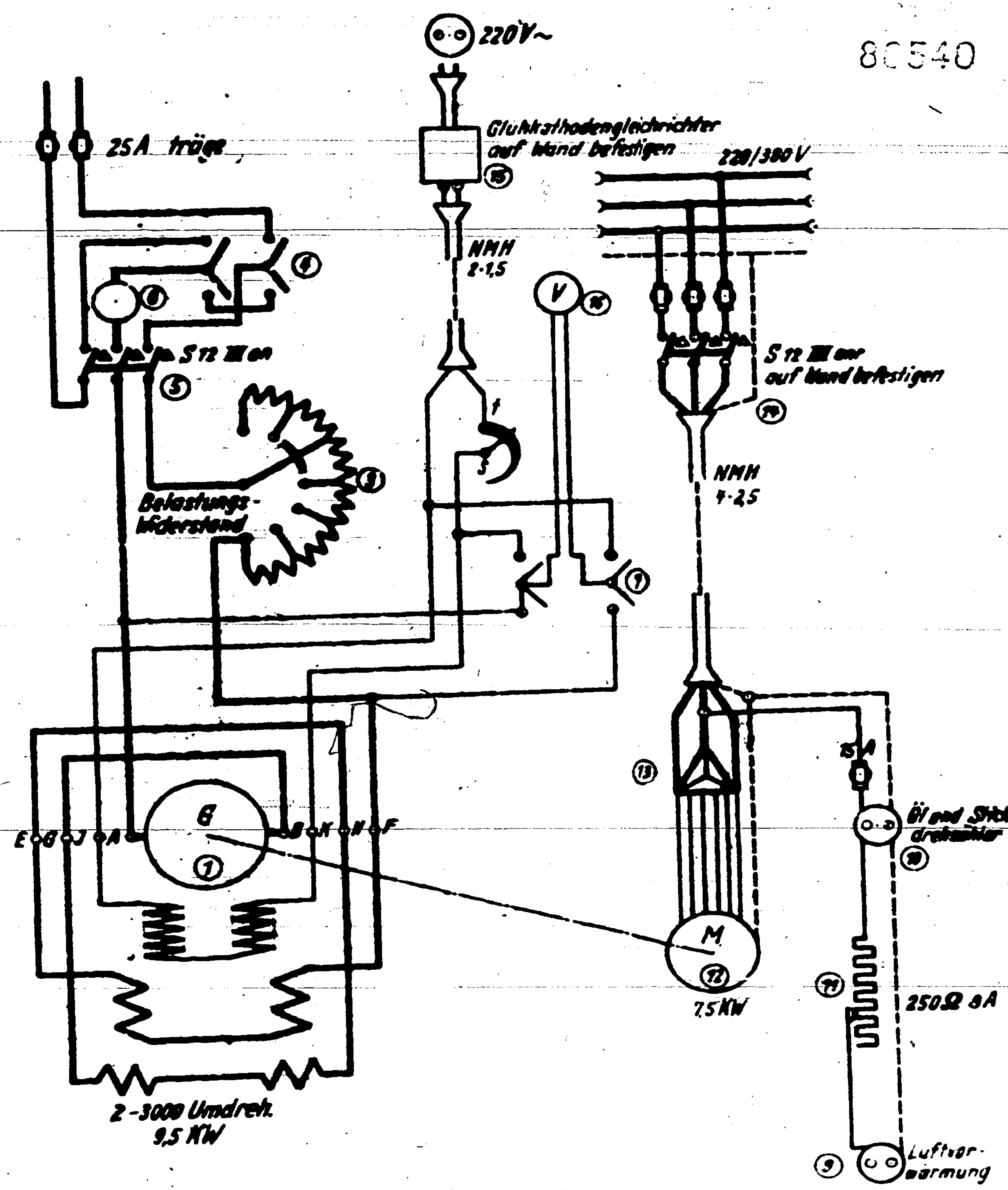

Bild 6

Schaltung des Brennstoffprüfstandes bei vorhandenem Drehstromnetz.

Bearbeiter Gréas
Prüfer
Tag
Tag

[redacted]

FORSCHUNGSINSTITUT FÜR KRAFTFAHRWESEN U. FAHRZEUGMOTOREN TECHN. HOCHSCHULE STUTTGART	Betriebsanleitung für den Kraftstoffprüfactor.	Bild 7

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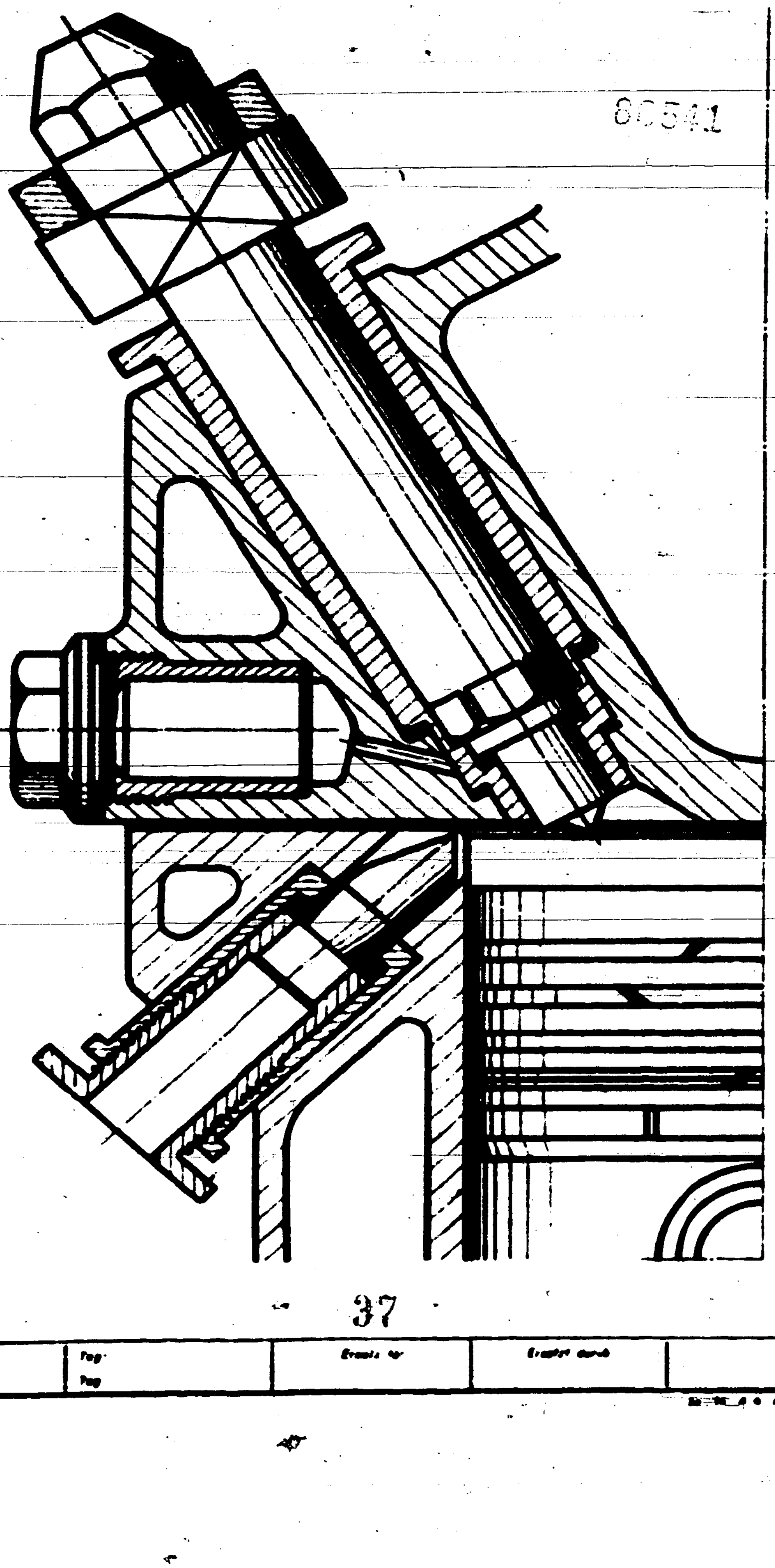
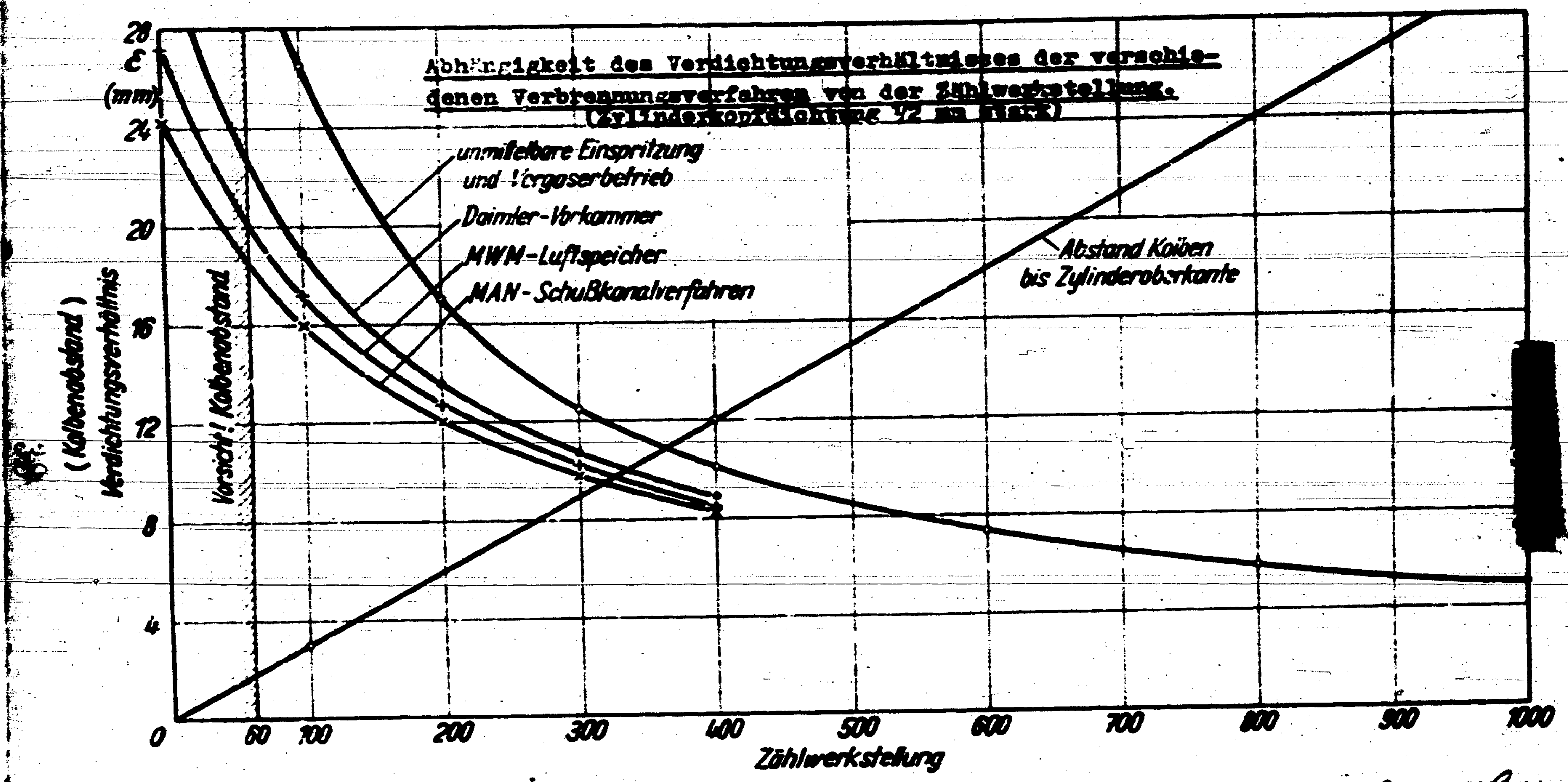


Bild 7
Quarzfenster-Einbau.

Bearbeiter Gross	Tag	Ersatz für	Ersetzt durch	
Geprüft	Tag			


Abhängigkeit des Verdichtungsverhältnisses der verschiedenen Verbrennungsverfahren von der Zählwerkstellung.
(Zylinderkopfdichtung 1/2 mm stark)

20.4.44. Gross

Bild 8.

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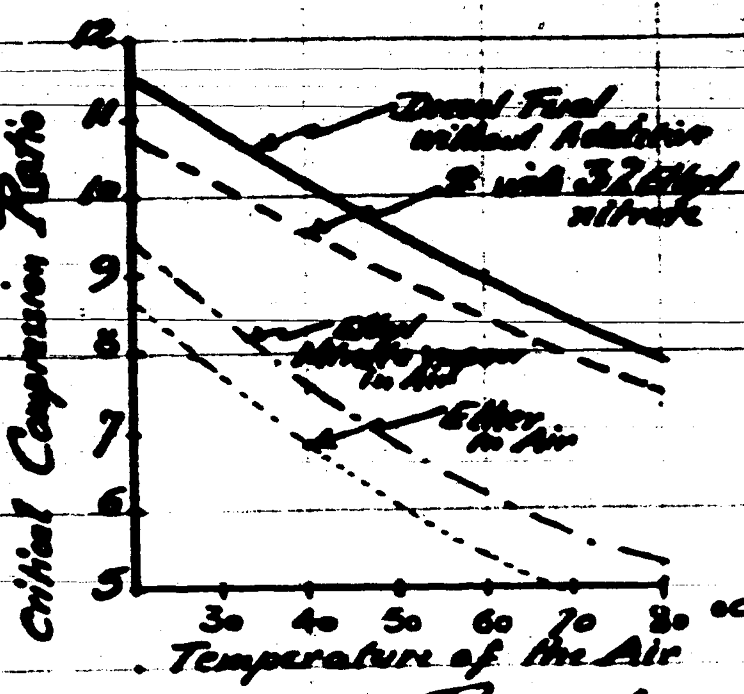

Figure 1.

Figure 3.

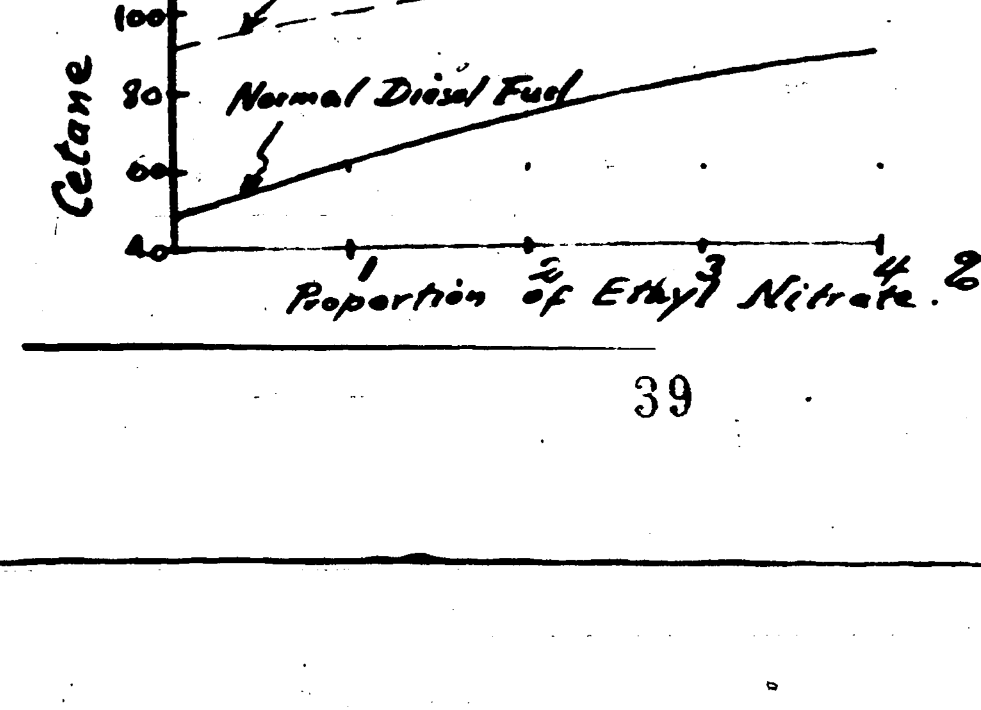

Figure 2.

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APPENDIX II

PRODUCTION IN TONS PER MONTH
For
JANUARY 1944 AND JANUARY 1945
OF
VARIOUS GERMAN DIESEL FUELS

Method of Production and Originization	1944	1945
1. Hydrojenators plants		
Leima	23900	2000
Bohlen	-	1700
Brabag Magdeleurg	3800	5300
Brabag Feits	14700	8100
Brabag Scholven	-	-
Silsenberg	-	-
Welheim	1200	-
Politz	-	-
Lutzkendorf	1800	1000
Wesseling	-	-
Ludwigshafen	-	-
Moosleierbaum	-	-
Bruso	12200	-
Blechhammer	600	-
Ileydebreck	-	-
Total	58200	18100
2. Fischer Tropsch Synshesis		
Ruhrchemie	1200	-
Victor Rauxel	-	-
Rheinpreussen	1200	-
Krupp Wanne Eickel	-	240
Essener Benzin	1500	600
Schwarzheide	2700	2000
Lutzkendorf	400	-
Schaffgotsch	600	200
Hoesch Benzin	800	-
Total	8400	3040

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[redacted]

APPENDI[redacted]D

3. Distillation of Crowncoal tar

Riebeck Weban	900	1200
Riebeck Hessel	–	810
Onhaltische Kohlenwerka		
Kopsen	1500	1500
Dea Rositz	2700	2000
Kosag Zolzan	1600	1500
Hefrag Wolfersheim	–	–
Leopold Bosdorf	–	100
Leopold Etteritz	–	–
ASV Espenhain	–	4000
ASV Hirschfelde	–	–
Total	6700	11,100

4. Refining of Natural crude oil.

Rhenania Hamburg	[illegible]
Rhenania Florisdorf	650
Deutsche Vacuum at	800
Deutsche Oslebshausen	
Deutsche Wedel	–
Deutsche Kagram	–
Deutsche Kolin	1200
Deutsche Dzieditz	–
Deutsche Gasoline at	
" Dollbergen	–
" Emmerich	–
Dea Korneuburg	1700
Dea Wilhelmsburg	–
Dea Heide	2000
Wintershall LutzRenDorf	–
" Salzbergen	400
Nova Schewchat	5100
Deurag Nery Misburg	–
Grassburg	400
I.G. Oppan	–
Sengewald	60
Trzebinia	2100
Idaweiche	150
Pechelbronn	–
Loban	6500
Vosendorf	1800
Pardulitz	1650
Oderfurt	1200
Kolin	–
Total	25,710

[redacted]

APPENCIX II CONT'D

5. Small installations stills started in 1944 in well-protected valleys.

Bogerhof Extertalbahm	880
BrunKenson near Ohlfeld	880
Messinghausen near Ohlfeld	1000
Messinghausen near Brilon	1000
Muhlenheim near Brilon	1000
Muhlental near Halberstadt	1250
Turmitz near St. Polten	1000
Weitenegg near Krems	1500
Olte Post near Pirma	450
Stotzendorf near Vienna	900
HausKirchen near Zistersdorf	2000
Bockatal	750
Total	11,610

Total Known productions	73,300T	69,570T

During the month of January 1944 known productions of other fuels, given as a comparison was:

Aviation Gasoline -	From Hydrojenators	141,500T
	From Synshens	7,300T.
	Total	148,800
Motor Gasoline	From Hydrojenators	57,100T.
	From SynShens	12,550
	From Lynite Tar	1,650T.
	Total	71,300

Gasoline production from Natural Petroleum Crude consitituted however an important item estimated convsrvatively for January 1944, at: 150,00T

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U·S·NAVAL·TECHNICAL·MISSION·IN·EUROPE

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TECHNICAL REPORT No. 217-45

THE PRODUCTION OF SYNTHETIC FUELS BY THE HYDROGENATION OF SOLID AND LIQUID CARBONACEOUS MATERIALS

August 1945

U·S·NAVAL·TECHNICAL·MISSION·IN·EUROPE

U. S. NAVAL TECHNICAL MISSION IN EUROPE
c/o Fleet Post Office
New York, N.Y.

File: A9-16(3)(10/Hn)

80548

Serial: 1437

13 October 1945

[redacted]

From: Chief, U.S. Naval Technical Mission in Europe.
To : Chief of Naval Operations (OP-16-PT).

Subject: U.S. Naval Technical Mission in Europe Technical Report No. 217-45, The Production of Synthetic Fuels by the Hydrogenation of Solid and Liquid Carbonaceous Materials - Forwarding of.

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L. V. HONSINGER
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TECHNICAL REPORT No. 217-45

THE PRODUCTION OF SYNTHETIC FUELS BY THE HYDROGENATION OF SOLID AND LIQUID CARBONACEOUS MATERIALS

SUMMARY

This report describes the various principal methods of producing synthetic fuels by high pressure hydrogenation as practiced in Germany. The various techniques of operation, designs of equipment, and characteristics of the products are described, and whenever possible, the relative merits and best uses of the different items are discussed. No attempt has been made to make an economic survey of the industry, since the subject is greatly confused by German finance and slave labor. However, this report does analyze the important features so that there is a technical basis for evaluation of the various phases in the light of existing local conditions. The data in this report were all obtained either by interrogation of personnel, examination of documents collected from the various plants, or by visual observation.

August 1945

U. S. NAVAL TECHNICAL MISSION IN EUROPE.

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Appendix (cont'd.)

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THE PRODUCTION OF SYNTHETIC FUELS BY THE HYDROGENATION OF SOLID AND LIQUID CARBONACEOUS MATERIALS

1. Introduction.

The production of synthetic fuels by the hydrogenation of coal and tar under conditions of high temperature and pressure is a comparatively new industry even though the initial experiments were completed by Dr. Bergius before the start of World War I. For a long time, the process of converting solid fuels of low hydrogen content to liquid ones with a high hydrogen content appeared to be of mere scientific interest because of the high investment and operating costs of the necessary plant. In 1933 when Germany started in rapidly to prepare for war, it became imperative to improve the processes, and so an enormous amount of effort was expended in experimental development of better methods for coal hydrogenation. The results of this work were successful in developing techniques for treating coal and tar so that over three million tons of fuel were produced in 1942 by these methods. The cost of gasoline produced by hydrogenation was high (about 15 cents per gallon)(1) but, for a country that had practically no petroleum this was not exorbitant. In order to better understand the changes in practice, it is of interest to briefly trace the development of hydrogenation in Germany.

In 1911, Dr. Friederich Berguis started his first experiments in treating coal with hydrogen under pressure. By 1913 the work had reached the point where he took out his first patents on the subject. The research continued for a number of years, on a small scale, until 1924 when I.G. Farbenindustrie started work at Ludwigshafen on the hydrogenation of tar. Dr. Berguis continued his work until about 1930. He will probably be remembered as the "Father of Coal Hydrogenation", but it was the I.G. Farbinindustrie that developed the industrial applications.

After a brief period of research work at Ludwigshafen G. started the construction of a plant at Leuna in 1926

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1. Introduction (cont'd.)

to produce 100,000 tons per year of gasoline from lignite, and in April, 1927 the first gasoline was produced. The through-puts of coal were low and the efficiencies poor, but these were gradually improved by new design of equipment and better understanding of the process(2). In 1933 a new high activity pelleted tungsten sulfide catalyst was developed that increased the gasoline yield. The following year another catalyst tungsten sulfide on activated clay was developed, which in combination with the first one, was used throughout the war in most of the plants, and produced high quality gasoline.

Between 1935 and 1941 about ten large hydrogenation plants were created in mid-Germany, the Ruhr, and eastern Germany to hydrogenate coals and tars. Research work had shown the beneficial effect of high pressure on the decomposition of coal, and so most of the new coal plants were built to operate at 700 atmospheres pressure. The research work in this period was largely devoted to methods of increasing production by changes in operating technique and/or equipment, as well as to methods for increasing the octane number of the gasoline. With the start of the war the accent was on production, and every effort was made to obtain the maximum quantity of fuel from a given plant. Most plants hydrogenated quantities of tars in addition to coal, since the specific output of gasoline was greater from tar.

Although the hydrogenation plants were owned by several large companies, the integration of the industry was such that most of them followed the I.G. process, and exchanged information with the I.G. research center at Ludwigshafen for the material benefit of all. The result was that only minor variations in operation were found at the different plants, these having been largely caused either by differences in raw material or older design of equipment.

The following report is intended to present the chief items of interest in the German hydrogenation industry, and to describe features which have not been reported in the literature. It is not intended to be a complete record of

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1. Introduction (cont'd.).

German hydrogenation technology, but only to cover the important principles of the art so that the reader can evaluate the process.

2. Sources of Information.

The data in this report were collected by personal inspection, interrogation of personnel, and examination of the documents(3,4,5) of most of the hydrogenation plants in Germany. The plants in the Ruhr area and in middle Germany were covered on two inspection trips, while some data were obtained from operating reports(6,7) on plants in eastern Germany that were in Russian occupation territory. The following is a list of the plants visited, the principal type of material processed, and the important personnel interrogated.(8)

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Name of Company	Location	Raw Material Processed	Annual Productions	Principal Personnel Interrogated
1. Braunkohle Benzin AG	Bohlen-Rotha	Brown Coal Tar	180,000 tons Aviation Gas.	Dr. Wolf, Plant director, Dr. Schweitzer, Dir. of Hydrogenation
2. Gelsenberg Benzin AG	Gelsenkirchen-Horst	Bituminous Coal	300,000 tons Aviation Gas.	Dr. Prosst, Plant Dir., Dr. Jacob, Dir. of Hydrogenation
3. Hydrierwerke Scholven AG	Scholven-Buer	Bituminous Coal	200,000 tons Aviation Gas.	Dr. Schmidt, Dir. of Hydrogenation.
4. I.G. Farbenindustrie AG	Leuna	Lignite and Brown Coal Tar	600,000 tons aviation gas & Diesel Oil	Dr. Schneider, Dir. of plant, Mr. Cron, Eng. of Hydrogen.
5. I.G. Farbenindustrie AG	Ludwigs-Haven	Principal Research Center for Coal Hydrogenation		Dr. Simon; Dir of Exp. Hydro. Plant. Dr. Donath, Dir of Hydrog. Research
6. Wintershall AG	Lutzendorf	High Asphalt Bituminous Coal Tars and Mineral Oil Residues	5,000 tons Gasoline + 10,000 tons Dissel Oil	Plant Director; Hydrog. Director.
7. Ruhröl AG	Bottrop Welheim	Bituminous Coal Pitch	60,000 tons Aviation Gas. 120,000 tons Fuel oil	Mr. Stinnes, owner of plant; Dr. Broche Chem. director; Dr. Döring, Research director.

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Name of Company	Location	Raw Material Processed	Annual Productions	Principal Personnel Interrogated
8.Union Rheinische Braunköhle Kraftstoff AG	Wesseling	Ligaite	105,000 tons Auto Gasoline, 120,000 tons Diesel oil	Dr. von Blumenoron Dir. of Plant; Dr. Peuchert
9.Braunköhle Benzin AG	Zeitz-Tröglitz	Brown Coal Tar	100,000 tons Auto gas, 120,000 tons Diesel oil, 25,000 tons parffins, 15,000 tons lube oils	Dr. Ville, Plant Dir., Dr. Przybylka Chief Engineer; Dr. Lehman, Physcist

OTHER HYDROGENATION PLANTS

Name of Company	Location	Raw Material Processed	Annual Production
1.Hydrierwek Hermann Göring AG	Brüx	Brown Coal Tar	300,000 tons Auto gasoline, 300,000 tons aviation gas.
2.Braunköhle Benzin AG	Magdeburg	Brown Coal Tar	120,000 tons auto gas; 120,000 tons Diesel oil.
3.Oberschlesien Hydrierwerke AG	Blechhammer	Bituminous Coal	240,000 tons aviation gas; 260,000 tons fuel oil
4.Hydrierwerke Pölitz AG	Pölitz	Bituminous Coal and pitch	200,000 tons aviation gas; 150,000 DHD gasoline.

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3. General Outline of Hydrogenation.

The hydrogenation of coal was performed in two stages since it was impossible to treat coal directly with active catalysts without subsequent loss of catalyst activity due to fouling of the surface. Therefore, in order to produce high anti-knock gasoline the coal was first liquefied and the resultant low molecular weight, clean oil was destructively hydrogenated over active catalysts to produce a gasoline of good octane number.

The first stage of the process was commonly called the sump or liquid phase (see drawing No. 1). After the coal had been dried and crushed it was mixed with heavy recycle oil from the process and ground into a paste. Usually about two parts of coal were mixed with three parts of recycle oil plus small amounts of catalyst. The resultant viscous paste was raised to the operating pressure of either 300 or 700 atmospheres in large, hydraulically-operated paste pumps. Most of the plants operated the sump phase at about 700 atmospheres since both the through-put of coal and the decomposition of asphalt were higher. The paste was next mixed with recycle hydrogen and passed through heat exchangers counter-current to the outlet products from the process. The heat exchangers supplied between 50 and 90 percent (depending upon the plant) of the heat required to bring the paste-gas mixture up to temperature. The additional heat was supplied in a tubular, gas-fired preheater.

The paste left the preheater at a temperature of about 425°C and entered the bottom of a series of three or four large, unpacked converters. These converters were large steel forgings about one meter inside diameter by 18 meters long, internally insulated to maintain a relatively cool pressure shell. The hydrogenation of coal was a highly exothermic reaction, and hence sufficient heat was liberated to raise the feed to the reaction temperature of about 470-485°C in the first few meters of travel in the first converter. The temperature was controlled by injecting cold hydrogen at three or four different points in each converter. During the passage of the paste-gas mixture through the reactors, about 95 percent of the carbon in the coal was

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DRAWING No. 1

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3. General Outline of Hydrogenation (cont'd.)

converted to gaseous and liquid products, and these latter were destructively hydrogenated to lower molecular weight products. Thus the material leaving the last converter after a contact time of about one hour at approximately 475°C had a viscosity near that of water.

The oil and gas next entered a hot separator which was a large steel vessel internally insulated, where the gaseous products and the liquid plus solids were separated. In the process of separating the two phases, a large proportion of the more volatile oil constituents were stripped out and carried along in the gas stream. The hot separator, therefore, produced a crude separation of the products of the sump phase and simplified the handling of the light oil. The oil and gas vapors, after leaving the separator, were partially cooled by counter-current heat exchange with the incoming paste and gas and then given a final cooling in a water cooler. The condensed liquid was collected in a cold separator, while the gas was purified in a oil scrubber and recycled in the process. The condensed oil was expanded stepwise in either two or three stages to atmospheric pressure. The gas evolved from the first expansion was lean in higher hydrocarbons, and it was usually used for fuel. The gases from the other stages were treated to recover the C3 and C4 fractions which could be used as alkylate or bottled gas for vehicles. The oil was distilled and produced a light heads product with an end point of about 325°C called middle oil A. The residue oil was recycled for pasting of fresh coal.

The heavy slurry in the hot separator contained the solids left from the hydrogenation reaction. These solids were largely catalyst, ash, and unconverted coal, and amounted to about 20-25 percent weight of the slurry. This material was cooled to about 200°C and then expanded to atmospheric pressure through special valves that had hard alloy stems and seats to resist abrasion from the solids. The viscosity of the slurry was cut by the addition of about 25 percent of a light oil, such as middle oil A, and the diluted mixture fed to continuous centrifuges. These machines were conventional high gravity, automatic solid ejection-

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3. General Outline of Hydrogenation (cont'd.)

type centrifuges, and they produced a clarified oil containing about 5-10 percent of finely divided solids and a residue that had a solid content of 35-40 percent. The oil was recycled for pasting purposes while the thick residue was coked in a steam distillation unit to recover about 75 percent of the oil. This latter oil was also used for pasting, while the dry residue was either discarded or mixed with coal and burned.

The middle oil A which was the chief product of the sump phase, contained too much oxygen, nitrogen and sulfur compounds to be used directly for gasoline. Hence, it was necessary to reduce these compounds and add more hydrogen in order to make satisfactory fuels. This part of the process was called the gas phase and was usually conducted in two stages when aviation gasoline was desired. The oxygen and nitrogen compounds existed in the sump phase oil mostly as phenols and nitrogen bases, respectively. As they were poisons for the active catalyst employed in the gasoline production stage, it was necessary to remove them. This was accomplished in a catalytic process called the prehydrogenation stage. This operation was conducted at 300 atmospheres and 400°C over pelleted tungsten sulfide (catalyst 5058) in a plant that was much like the sump phase. These converters, however, were equipped with trays to hold the catalyst. Between each two catalyst beds was a system of baffles which served to mix the hot oil and gas vapors with cold hydrogen introduced to control the temperature. Usually three or four converters connected in series were used in this stage and a contact time of about 1-1/3 hours was sufficient to hydrogenate the aromatics to naphthenes and to reduce the oxygen, nitrogen, and sulfur compounds to hydrocarbons with the formation of water, ammonia, and hydrogen sulfide, respectively.

The temperature was purposely held low in this stage to avoid excessive cracking, since the function of the prehydrogenation step was only to saturate the oil with hydrogen and to destroy compounds which would poison the gasoline production catalyst. The products of the 5058 stage were distilled giving a small gasoline cut which could

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3. General Outline of Hydrogenation (cont'd.)

either be blended with alkylate or processed in the next stage. If desired, diesel oil could be removed as a fraction boiling over 200°C. Usually, however, most of the diesel oil was left in the middle oil B fraction boiling over 150°C and was processed in the next stage to make aviation gasoline.

The middle oil B, which consisted mostly of naphthenes and normal paraffins, was treated in the gasoline production stage over a catalyst consisting of tungsten sulfide and activated clay (catalyst 6434). The equipment for the process was similar to that used in the 5058 stage, but the temperature was a little higher, about 425°C. The oil throughput was a little greater so that the contact time averaged about one hour. The function of the 6434 catalyst was to crack open the naphthenic rings and to isomerize normal paraffins to iso-paraffins. At the same time a reduction in the average molecular weight of the oil occurred so that a huge fraction of the oil boiling over 200°C was converted into gasoline. The liquid product from the gasoline stage was distilled to give aviation gasoline that had an unleaded octane number of 70 to 75. The addition of 0.12 vol% of lead tetaethyl increased this value to between 90 and 95. The heavier oil left after the removal of the gasoline fraction was recycled together with fresh middle oil B to the 6434 stage.

As mentioned in the introduction, a considerable fraction of the German gasoline supply was produced by the hydrogenation of tar and pitch. These materials were easier to handle because they were already in a liquid state, and hence the mechanical problems attendent on the solids removal were much simplified. Furthermore, the hydrogen contents were greater in these materials than in coal, thus both the hydrogen consumption and the operating difficulties caused by coking were greatly reduced.

Tars and pitch were handled in a two stap process in much the same manner as the coal. The crude tar was given an initial distillation to remove the gasoline and middle oil. The latter treated either directly over 6434 catalyst,

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3. General Outline of Hydrogenation (cont'd.)

if the phenol and nitrogen contents were low or given a prehydrogenation treatment as was done with sump phase oil from coal if they were too high. The heavy distillation residue was processed in the sump phase under conditions very similar to those employed with coal, although the through-puts were a little greater. The treatment of the sump phase middle oil was usually carried out directly over 6434 catalyst, as the phenol and nitrogen contents of the oil were low. The yields and quality of the gasoline so produced were inferior to that produced where a prehydrogenation stage was used, but a considerable saving in investment was realized by the elimination of one high pressure operation.

A new process to produce lubricating oils by hydrogenation was developed in 1936 by the I.G. Farbenindustrie and first put into plant operation at Zeitz in 1939. The low temperature hydrogenation process (known as T.T.H.) treated brown coal tar over an active catalyst such as 5058 in the sump phase at 390-410°C and 300 atmospheres pressure. Very little cracking occurred, but instead a refining of the oil took place through the elimination of oxygen, nitrogen, and sulfur. Brown coal tar has a high paraffin content, and the purpose of the T.T.H. process was to preserve the paraffins, while hydrogenating the aromatics to naphthenes. Therefore, if the temperature was allowed to rise, the yields of lube oils and paraffin wax decreased, and greater quantities of diesel oil and gasoline were produced. The diesel oil manufactured by the process had a cetane number of about 50 and the lube oils had a V.I. of 60-80.

Another new process which attracted quite a lot of attention in the literature, but which actually played a very minor part in the German fuel program, was the Pott-Broche process for the extraction of bituminous coal. Only one unit had been built and the output from this unit was largely coked to make electrode carbon. In practice the bituminous coal was extracted at about 100-150 atmospheres pressure and 420°C in the liquid phase using a tetralin-cresol mixture. The product was filtered to remove solids, the solvent distilled off and recycled, and the asphalt-type residue processed in the sump phase like pitch. The opinion

3. General Outline of Hydrogenation (cont'd.)

of the operators of this process was that it was better adapted for making special products such as coatings and insulation, than for fuels.

The various steps of the coal hydrogenation processes are discussed in greater detail in sections 4 to 9 enclusive, and in section 10 comparisons of the products and operation of the different methods are presented.

4. Description of Sump Phase Operations.

(a) Processing of Brown Coal.

The German brown coal or lignite occured in large thick beds, which averaged 200 to 300 feet in depth. On account of the thickness and proximity of these beds to the surface, strip mining methods were employed. The brown coal as mined resembled dirt in appearance, since it had a deep chocolate color. The coal preparation, which included drying, grinding, and paste mixing, are discussed in detail in U.S. Naval Technical Mission in Europe Report entitled "Production of Hydrogen and Synthesis Gas from Solid and Gaseous Fuels"(9), and hence only the principal points will be described here.

The raw lignite contained on the average 50 percent moisture content before use. The brown coal when dry was very susceptible to spontaneous combustion in air, and consequently, elaborate precautions were taken to keep an inert atmosphere of carbon dioxide or nitrogen over the coal at all times during the drying, grinding, and pasting. The pulverizing of the coal was accomplished by mixing heavy recycle oil from the centrifuges with dried coal in ball or mixing mills and wet grinding until the coal had been properly comminuted and a homogeneous suspension of coal in oil, known as paste, produced. For best results the oil had a viscosity of 100-150 centistokes at 85°C., and sufficient coal was added to give a paste that had a viscosity of 1500-2000 centistokes at 85°C. Although the viscosities were measured at 85°C., the actual operating temperature of the mills was usually about 120°C, since this reduced the vis-

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4. Description of Sump Phase Operations (a)(cont'd.)

cosity of the oil and permitted most of the free water in the coal to be vaporized.

The concentration of coal in the resultant paste depended upon several variables such as the type of coal and the quality of the pasting oil. The Wesseling plant, which processed Rhine lignite(10), could only handle 36 percent coal in the feed on account of the "gelation" properties, whereas Leuna which treated middle German lignite, operated with 40-42 percent coal in the paste. The average weight of the coal paste was 1.1 tons per cubic meter.

During the grinding of the coal in the oil, catalysts were added and thoroughly mixed in the paste. Iron and sulfur were the more common catalytic elements used for brown coal hydrogenation, and since most coals contained 3 to 6 percent sulfur, it was usually only necessary to add iron. This was accomplished by the addition of 4-6 percent, based on the weight of coal, of "Bayermasse" or "Roterz" (impure iron oxides produced during the purification of alumina ores.). With the Rhine coal, which was very low in sulfur (0.75 percent), it was necessary to add about 1.25 percent of elementary sulfur to the paste, but in other plants this was not necessary(10). Molybdenum and/or zinc had previously been used for catalysts, but iron and sulfur were nearly as active and had the advantage of being much cheaper.

The coal was ground so that about 40 percent was finer than 250 mesh (English measure) and essentially all of it was under 200 mesh before it left the mill. The paste was fed to the large high pressure paste presses in a recycle system which kept the feed moving throughout the entire manifold, and assured a continuous supply of hot uniform composition paste to each of the several pumps connected in parallel. The paste presses were large, double-acting, hydraulically driven piston pumps, which had capacities varying from 10 to 25 cubic meters per hour maximum, depending upon the different sizes employed at the various plants. In general, the larger capacity pumps were newer; the smaller sizes being old machines still kept in service. In order

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4. **Description of Sump Phase Operations (a)(cont'd.)**

to better resist the abrasive action of the coal paste, the plungers were hardened to about 400 Brinnel, and the value seats were made of specially hardened alloy steel. The packing material was usually metallic rings of either white metal or lead-calcium alloy, and a lantern ring was located in the packing section so that between 80 and 200 liters per hour of flushing oil could be injected to keep paste out of the stuffing box. By the use of flushing oil the packings had a life of about six months under normal operating conditions.

The paste leaving the presses at either 300 or 700 atmospheres depending upon the method of operation, as will be described later, was joined with recycle gas and entered the first heat exchanger in the coal stall. All of the coal hydrogenation plants were constructed on the basis of individual coal stalls or chambers, and each chamber contained two heat exchangers, one preheated, three or four converters, and a hot separator. These pieces of apparatus were mounted in a tall concrete structure which helped to protect the operators by isolating the equipment and localizing fires that might occur from mechanical failures. The size of the various plants depended upon the number of stalls which they operated, since the output of any one stall did not vary greatly among the various plants. Large plants, such as Leuna, operated nine (9) sump phase stalls, whereas the smaller installations usually consisted of two to four units.

The heat exchangers were large forgings of chrome-nickel molybdenum steel 500 or 600 millimeters inside diameter by 18 meters long; the two sizes differed only in the number of tubes and consequent available heat transfer areas. Inside of the steel forging was a diatomite or brick lining about 65 millimeters thick which insulated the pressure wall from the hot contents. A thin stainless steel tube (0.5mm) was located inside of the insulation, and this liner contained the fluid products and resisted the corrosive attacks of high temperature hydrogen and sulfur. The tube bundle with baffles was placed inside of the liner, and connected to the heads through conical adapters. The tubes were made of galvanized N5 steel (chrome-vanadium

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4. Description of Sump Phase Operations (a)(cont'd.)

alloy) and measured 23 by 14 millimeters by 16.5 meters long. The 500 millimeter heat exhanger usually held 151 of these tubes and had a heat transfer area of 145 square meters, whereas the 600 millimeter exchanger had 199 tubes and 190 square meters of surface. The closures were made by the compression of aluminum gaskets in the conventional manner, by bolts on each flanged head. The assembly and construction details are shown in drawing no C-1 in Appendix C.

In operation the paste and gas entered at the bottom of the first heat exchanger at about 60 to 80°C, and flowed up around the outside of the tubes, counter-current to the outlet products inside of the tubes. The paste leaving the first exchanger had been heated up to about 200°C, and it then was further heated in a similar manner in the second unit to about 320°C. (Refer to drawing No. 2 for flows in the sump phase). The heat transfer coefficients varied greatly, as would be expected with materials that fouled and corroded the equipment, and hence the average values were difficult to determine. For equipment in good condition, the overall heat transfer coefficient varied from 200 to 250 kilocalories per hour per square meter per degree centrigrade (40-50 BTU per hour per square foot per degree Fahrenheit). After the surface had become fouled from caking or coking of solids, the values might drop to 50-100, at which time it was usually necessary to take the equipment out of service(11,29,30).

After leaving the second heat exchanger, the feed entered a gas-fired preheater where its temperature was raised to about 410-430°C. The preheater was a rectangular furnace about 7 meters long by 4 meters wide by 14 meters high, divided into sections to hold the preheater tubes. Drawing Nos. C-1 and C-2 in Appendix C shows one of the more common types of gas-fired heaters, in which hair pin tubes were located in vertial rectangular sections at one end, and the combustion chamber was at the other end. Fuel gas was burned in the combustion chamber, and the hot gases mixed with hot recycle gas and passed through the sections housing the preheater tubes counter-current to the flow of material being heated. The gas leaving the last tube

DRAWING No. 2

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4. Description of Sump Phase Operations (a)(cont'd.)

section was picked up by recycle blowers and returned to the mixing chamber. This high circulatory system, using two blowers of 50,000 cubic meters per hour each (measured at 1 atm. and 450°C) helped to prevent local overheating and increased the themal efficiency. The heating value of the fuel gas employed was about 2000 kilo calories per cubic meter, and between 3000-4000 cubic meters per hour were required.(12)

The hair pin tubes were constructed of N8 or N10 steel, which were chrome, vanadium, molybdenum, tungsten alloys of high tensile and creep strengths. The tubes themselves were 171 by 120 millimeters in diameter, and about 14 meters long. The number of tubes required varied greatly from plant to plant, the range being from 6 to 20 hairpins. In any case the principle of operation was the same, and the furnace was proportioned to accomodate the number of tubes required. On the outside of the tubes, perpendicular to the central axis, were welded a series of steel fins 300 millimeters square, four millimeters thick, and spaced 14 millimeters apart. These fins added heating surface, and thus raised the heat transfer rate which nevertheless was very low. The heat transfer coefficient averaged 6-8 kilo calories per hour per square meter per degree centigrade.

After leaving the preheater, the hot paste-gas mixture entered the first of a series of three or four converters. The older designs used three vessels, whereas the more modern practice was to use four, and hence this report will discuss the four converter coal stall. Three very common sizes of converters were used, either singly or in combination with each other; however, the only important differences, between them were the overall dimensions, since the internal construction was essentially the same. The details of the construction are shown on drawing no. C-4 in Appendix C. Two of the converters were 800 and 1000 millimeters inside diameters, respectively, by 18 meters long, while the third was 1200 millimeters by 12 meters long. The pressure bodies were forgings of N2 (chrome-molybdenum) steel, heat treated to improve the mechanical strength. The inside surface was insulated with two layers of diatomite brick and

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4. Description of Sump Phase Operations (a)(cont'd.)

asbestos cement so that the thickness of the insulation was about 65 millimeters. A thin V2A (stainless) steel liner, about 0.5 millimeters thick, was placed inside the insulation and connected with the top and bottom heads through concial adapters. The stainless steel liner was used to contain the reactants, since it was resistant to sulfur and hydrogen corrosion. The closures were of the straight compression type, as in the case of the heat exchangers using aluminum gaskets, since copper would have been corroded by the sulfur and ammonia. In the top head were three or four small inlet connections for introducing cold hydrogen at different points in the converter to control the reaction. A large inlet and outlet connection were located in the center of the bottom and top heads, respectively, and the external piping was connected by means of standard lens ring type points.

The hydrogenation of coal is an extremely complicated chemical process, and since coal is not a homogeneous substance, but is composed of many high molecular weight organic compounds, it is impossible to state exactly what occured during the reaction period. An average analysis of brown coal on a dry basis was 62 percent carbon, 5 percent hydrogen, 1 percent nitrogen, 5 percent sulfur, 18 percent oxygen, and 9 percent ash. The relatively high ratio of hydrogen to carbon, plus the high oxygen content, made the lignites reasonably easy materials to hydrogenate. On the other hand the high oxygen content caused a loss of valuable carbon which was eliminated as carbon dioxide, and also a hydrogen consumption to produce water. The brown coal apparently contained a large fraction of paraffin base substances with carboxylic acid groups, as well as condensed aromatic and naphthenic rings with oxygen, nitrogen, and sulfur included in the rings and in scattered connecting bridges. Under the action of heat and high hydrogen pressure, the large molecules were depolymerized with the loss of a large percentage of the oxygen as carbon oxides from the carboxylic acid groups, and as water from ether type linkages. Similarly part of the nitrogen and sulfur were eliminated as ammonia and hydrogen sulfide, respectively, while a fraction of the nitrogen remained in bases such as

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4. Description of Sump Phase Operations (a)(cont'd.)

aniline, and the oxygen and sulfur in phenols and thiophenols, respectively. A considerable amount of cracking and hydrogenation of the depolymerized coal oil resulted in the hydrogen content being markedly increased and the average molecular weight of the oil being lowered. During, the reaction, part of the carbon in the coal was also converted into gaseous products ranging from methane to butane. Obviously, some of these reactions occurred simultaneously, while others went in series, but the principal overall effect was to convert most of the coal into a lower molecular weight oil having a hydrogen content higher than that of the original coal, and at the same time to form a considerable fraction of gaseous materials.

In the processing of brown coal a pressure of 300 atmospheres was sufficient to handle the middle German coals, such as Leuna used, but 700 atmospheres was needed to properly convert the more refractory Rhine lignites.(10) These latter coals were poor in hydrogen and rich in oxygen, and by experiment were found to require the higher pressure. The overall conversion of the carbon in the coal to gaseous and liquid products was between 95 and 99 percent, but the oil yield was low because of the high oxygen content. It took approximately 2.1 tons of lignite ton produce one ton of middle oil, so that the production per stall was not as great as when treating older coals or tars.

The hot paste and gas mixture leaving the preheater was joined by additional fresh hydrogen, heated in a separate set of "U" bends in the preheater, and then the combined feed entered the bottom of the first converter. The production of hydrogen for the process is described in detail in U. S. Navy Technical Mission in Europe Report entitled "Production of Hydrogen and Synthesis Gas from Solid and Gaseous Fuels"(9). Inside the converter the flow of gas carried a quantity of solids and heavy oil up the center of the vessel to the top, where the gas and part of the liquid products left the converter, and entered the base of the second reactor. Some of the solids and heavy oil, having a higher density than the average fluid contents, sank down the sides until they either reached

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4. Description of Sump Phase Operations (a)(cont'd.)

the bottom or were again trapped in the gas and carried toward the top. In this manner the contents of the converter were continuously circulated, thus providing better heat transfer and temperature control, as well as permitting the materials that needed hydrogenation most to remain the longest in the reaction zone. The first one or two converters were usually larger in diameter than the latter ones, since this permitted better circulation during the intial stages of the hydrogenation. For 300 atmosphere operation the 1200 millimeter diemeter by 12 meter long converter was usually used first, while at 700 atmospheres the size was usually 1000 millimeters by 18 meters. The last converters in the series were usually 800 millimeters by 18 meters long.

The hydrogenation of coal was a highly exothermic reaction, and the feed was quickly heated up to the reaction temperature of 470-480°C within the first few meters of travel. The average through-put of paste was 1.1 to 1.3 tons per cubic meter of reaction space per hour, and for a four converter coal stall with 27 cubic meters reaction volume, this corresponded to 30-35 tons per hour. The corresponding gas flow was about 25 to 30,000 cubic meters of gas with a hydrogen content of about 80%. In order to control the temperature during the reaction due to the heat liberation of about 400 kilo calories per kilogram of coal, an additional 10-15,000 cubic meters of cold hydrogen were introduced through the connections on the top heads, into the converters at three or four levels. The turbulent cycle in the converters helped the heat transfer, and by adjusting the amount of hydrogen added, it was possible to control the temperature and prevent local overheating. The amount of gas circulated was several times that theoretically required, since only 1500 cubic meters of hydrogen were consumed in the production of one ton of middle oil.

The temperature was usually controlled by the asphalt content of the coal liquefaction products, since a high asphalt oil required a high temperature to give satisfactory conversions to lighter oils. The gas formation, partic-

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4. **Description of Sump Phase Operations (a)(cont'd.)**

ularly the methane, was greater as the temperature increased, so that it was desirable to operate it the lowest temperature consistent with a satisfactory reaction rate and conversion. Brown coals were usually low in asphalt, and hence high conversions and little trouble from this material were experienced.

One of the most troublesome problems with lignite was the formation of little solid balls of calcium carbonate which settled to the bottom of the converters and caused stoppages. These globules were called "caviar" or account of their resemblance to the real product, and means had to be supplied for their removal.(13,14) Usually the formation was most troublesome in the first converter where the coal was undergoing the initial decomposition. By means of a line tapping into the base of the first converter, a small amount of sludge, such as 100-200 liters per hour, could be withdrawn and treated in the solids removal unit. Usually only the first converter needed this simple sludge withdrawal line, but the plant at Wesseling had more difficulty with the Rhine brown coal, and more elaborate methods were needed to cope with the "caviar" problem. For more complete details on "caviar" refer to U.S. Naval Technical Mission in Europe Technical Report No. 87-45, pages 52-58.(15)

After passing through the converters in series, the gaseous and liquid products, together with a small amount of unconverted coal, ash, and catalyst, entered a large high pressure vessel called the hot separator. This apparatus performed a very important function besides merely separating the gases from the heavy oil and solids. Operating at a temperature of about 450°C, practically all of the water and a large fraction of the more volatile oil constituents were stripped from the solids containing heavy oil. This separation of a light overhead oil from the heavy oil was, of course, not as sharp as would be obtained by a distillation of the total product, but the fractionation of such a heavy oil containing solids would have presented formidable difficulties. Approximately 80 percent of the oil boiling up to 350°C was stripped from the heavy slurry by this process.

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4. **Description of Sump Phase Operations (a)(cont'd.)**

The hot separator was a vessel of N1 (chrome-molybdenum) steel 800 millimeters inside diameter by 9 meters long. (See drawings nos. C-5 and C-6 in Appendix C. for details of construction) As in the converters and heat exchangers it was necessary to insulate the walls and use a stainless steel liner to hold the fluid contents. In the top head were inlet and outlet connections for the converter products, and gas plus oil vapors, respectively, as well as connections for a thermocouple well and liquid level regulator pipes. The lower head contained the outlet for the heavy oil plus solids. The inlet pipe was brought in and down one side of the vessel instead of being centered, since this apparantly gave better separation of the gas and liquid products. The volume of the separator up to the feed downpipe was approximately 1.5 cubic meters. In operation the liquid level was held reasonably constant by an automatically-operated liquid level controller.

There were several minor variations in design of the separator; the chief differences being in the inlet pipe and the bottom cone. One of the more common models employed a steep conical bottom connector to prevent solids from adhering to the wall of the liner, thus aiding in the removal of the solids from the separator. Cooling coils were inserted in both the top and bottom sections, and part of the fresh hydrogen for the process was given a little preheat here. By control of the quantity of cooling hydrogen, it was possible to regulate the amount of oil stripped out of the product, and hence the solids concentration and viscosity of the residual oil could be adjusted. In normal operation the solids content in the slurry was held between 20 and 25 percent.

The gas and oil vapors leaving the top of the separator passed down inside of the tubes of the second or hot heat exchanger countercurrent to the warmed paste and gas feed. With an inlet temperature of 430-450°C., the products were cooled to about 275°C, and then entered an intermediate separator to collect the condensed oil. This vessel was a forging of the same size and shape as the hot separator, but the internal apparatus was much simpler, since only

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4. Description of Sump Phase Operations (a)(cont'd.).

clean light materials were handled. The bottom head had a rather flat conical adapter, and there were no cooling coils employed. The condensed oil volume was controlled by a liquid level regulator connected to the apparatus.

The gaseous products leaving the intermediate separator next passed to the top of the first or cold heat exchanger. Frequently, it was necessary to add water to the gas stream at this point to prevent inorganic salts, such as ammonium carbonate and sulfide from condensing and causing crusts or stoppages. About 1000 liters per hour of water were usually sufficient, but with certain coals, such as Rheine brown, it was necessary to use so much as 2100 liters.(15) The products were cooled in passing through the heat exchanger to between 175-200°C.

Further cooling was provided in trombone water coolers, which consisted of between 4 and 6 sets of 6 tubes each operating in parallel. The pipes were 58 millimeters inside diameter by about 16 meters long, so that the total surface was 80 to 120 square meters. Frequently, part or all of the previously mentioned water was injected at the inlet to the cooler, the difference depending upon plant operation.

The products leaving the cooler at about 70°C entered another large vessel known as the cold separator. This apparatus was a cylindrical forging usually 800 millimeters inside diameter by 6 to 9 meters long. See drawing no. C-7 in Appendix C., for details of construction. The ends were partly swedged so that the size of the openings into the vessel were about one-half of the inside diameter, and removable closures were used on each end. In operation the longitudinal axis was inclined at about 5 to 10° from the horizontal in order to provide a larger gas-liquid interface, and thus reduce the entrainment of froth in the outlet gas. The lower head had two connections, the upper one for the gas and liquid inlet, and the lower one for the liquid outlet. On the inside of the vessel there were two thin tubes connecting with the inlet and outlet parts on the head, and these tubes were curved so that the inlet stream impinged on the upper surface of the separator, while the liquid outlet

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4. Description of Sump Phase Operations (a)(cont'd.)

line naturally dipped down toward the bottom. On the upper head there was a gas outlet connection, and this head also carried an internal pipe to take gas out of the top of the chamber. The separator was equipped with a liquid level control to automatically regualte the fluid volume.

The non-condensable gases, still at high pressure, entered the suction ring of the recycle gas system. This suction ring connected the outlet sides of several coal stalls and helped to simplify the gas purification and recirculation system by equalizing the pressures and reducing the number of control instruments. The hydrogen content of the outlet gas had been reduced to about 60 percent, and it was necessary to partially purify it before using it again in the sump phase. An oil scrubbing system operating at the system pressure, was used to selectively remove part of the methane and higher hydrocarbons and thus maintain the purity of the recycle gas. The principal parts of the purification system consisted of absorption towers, solvent circulating pumps, and power recovery engines with necessary gas-liquid separators. The towers were steel forgings that varied in size from 1000 millimeters by 12 meters to 1300 millimeters by 15 meters long. They were usually packed with Raschig rings and adapted for gas inlet and liquid outlet connections at the base and gas outlet and solvent inlet at the top. The usual hourly through-puts were about 75 cubic meters of solvent to 50,000 cubic meters of gas for the larger size tower, although the liquid to gas ratio was adjusted to give an outlet hydrogen purity of 70-75 percent.

The solvent, containing dissolved hydrocarbons and hydrogen, was next expanded to about 50 atmospheres in expansion engines, and the power recovered was used to circulate part of the solvent within the process. The gas separated at this pressure was lean in higher hydrocarbons, and was used for cracking or fuel purposes. The liquid was then blown down to atmosphereic pressure, and this gas, which contained an important propane-butane fraction, was treated to recover these materials as is described in Section 6. The regenerated solvent was then recirculated to the towers.

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4. Description of Sump Phase Operations (a)(cont'd.).

As previously explained, the gas outlet streams from several coal stalls were connected, and this header fed impure gas to a series of washers all operating in parallel; the number of units of course varied with the quantity of gas to be treated. The gas outlet streams from the washers were also connected into a manifold that served several booster compressors. These were single stage machines that handled between 50-80,000 cubic meters per hour at differential pressures from 50-80 atmospheres. The outlet gas from the circulating compressors was mixed with fresh paste and started another cycle through the apparatus.

The light liquid products in the intermediate separator and the cold separator were expanded stepwise in two or three stages to atmospheric pressure. When a two step system was used, the intermediate pressure was usually 50 atmospheres, and the flashed gas, being quite lean, was used for fuel. The gas from the atmospheric pressure expansion was treated to remove C_3-C_4, as described in Section VI, while the liquid was distilled to yield a heads fraction of 325° E.P. called middle oil A, and a heavier residue oil that was recycled for pasting of coal. The middle oil A was treated in the gas phase, as described in Section V, to make gasoline and diesel oil, and this middle oil constituted the primary product from the sump phase. The distillation procedures and gas treatments are both covered in more complete detail in Section VI on Products Separation.

The heavy oil and solids that were left in the bottom of the hot separator were cooled by counter-current heat exchange with part of the fresh hydrogen make-up gas and finally by water to about 200°C. The slurry was then blown down to atmospheric pressure through special valves operated by the liquid level controller. These valves had replaceable stem faces and seats of tungsten carbide, to resist the abrasions of the solids. See drawing no. C-8 in appendix C for the details of construction of the expansion valve. A large expansion chamber was used after the seat to reduce the pressure drop across the valve and increase the life of the seat. In operation the valves were opened wide for a few moments and then shut, for if they had been used to

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4. **Description of Sump Phase Operations (a)(cont'd.).**

throttle, the seats would have been cut out in one to two hours. By operating the valves in pairs, each one working singly for about 15 minutes, the average working life was about 500-600 hours. The replacing of the seats and stems was not difficult, for a valve could be reconditioned in about 15 minutes while the twin was operating.

The gas evolved from the sludge was usually used for fuel, and the slurry after dilution with oil was centrifuged to recovery the pasting oil for the next cycle. The solids containing residue from the centrifuges was caked to recover additional pasting oil. These operations are covered more completely in Section VII, on Solids Removal and Oil Recovery.

(b) **Processing of Bituminous Coals.**

The bituminous coal fields in Germany were located in two principal areas, the Ruhr and Silesia; and in both of these districts the Germans had large coal hydrogenation plants for the production of motor fuels. Bituminous coals differed in composition from the previously discussed lignites, since they were much older geologically, and had lost a major portion of the oxygen as well as part of the hydrogen so that the hydrogen-carbon ratio was lower than that of lignite. The condensed ring structure of the coal gave the resultant oils higher aromatic and naphthenic contents than those from lignite. An average analysis of bituminous coal, on a dry basis was 5 percent ash, 78 percent carbon, 5 percent hydrogen, 1 percent nitrogen, 3 percent sulfur, and 8 percent oxygen. In general the Ruhr coals were a little older than the Silesian and had a slightly lower hydrogen to carbon ratio, but this difference did not seem to affect the coal through-put greatly.

The mechanical operation of the sump phase for bituminous coal hydrogenation differed in a few respects from that employed with lignites. However, since the same types and sizes of equipment were used, and since most of the major features were similar, only the points of difference will be described in this section. There were two systems

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4. **Description of Sump Phase Operations (b)(cont'd.).**

of operation which varied chiefly in the manner in which the feed paste was heated. The first or older method, as practised at Gelsenberg and Scholven used only one heat exchanger, but had two preheaters. Bituminous coal paste of the desired concentration could not be used in a heat exchanger, as was done with brown coal, on account of the swelling and fouling of the tubes, and hence it was necessary to heat the paste plus a small stream of gas in a gas-fired preheater section. The major portion of the hydrogen stream passed through the heat exchanger counter-current to the outlet products, as in the case of brown coal, and was then united with the hot paste. This mixture of gas and paste, was then heated in a second preheater section up to 425°C. before entering the converters.

This system was obviously less thermally efficient than the standard brown coal process, and this was aggrevated by the extremely low heat transfer coefficient of about 6 kilo calories per square meter per hour per degree Centigrade which was obtained in the gas-fired preheater. Therefore, research was conducted to try to adapt the brown coal technique to bituminous coal.(16,17,18) It was found that coal pastes of about 35 percent concentration operated satisfactorily in the heat exchangers with heat transfer coefficients similar to those obtained with brown coal paste.(17) Therefore, a new method of operation was developed in which the total coal paste was made up into two batches. A thin coal paste of 36 percent fresh coal was preheated together with about 90 percent of the recycle hydrogen in a series of three heat exchangers. A thick coal paste containing about 48 percent coal was heated with 10 percent recycle hydrogen in a gas-fired preheater, and then the two streams were combined. The composite mixture was heated to 425°C. in a preheater in exactly the same manner as was done with brown coal. The ratio of thin paste to thick was usually about 1.1 to 1.2 and the combined paste contained about 41 percent coal. This second method of operation, as practiced at Pölitz and Oberschlesien, reduced the heat requirements by nearly 50 percent, and at the same time it greatly lowered the pressure drop through the unit.

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4. Description of Sump Phase Operations (b)(cont'd.)

The asphalt contents of bituminous coals were considerably higher than those of lignites, and since these materials were very refractory toward hydrogenation, it was necessary to operate the sump phase converters at 485°C. In most of the plants the operating pressure was 700 atmospheres,(19) since the higher hydrogen pressure had a very pronounced effect on the asphalt decomposition. The catalysts used were 1.5-5 percent of "Bayermasse" or "Roterz", 1.3 percent iron sulfate, and 0.3 percent sodium sulfide, all based on the weight of coal. These materials were mixed with the coal and ground in a mill in the same manner as was done with lignite.

Each coal stall usually contained four 1000 millimeter diameter by 18 meter long converters giving a total reaction volume of 36 cubic meters. The coal paste through-puts averaged between 33 and 37 tons per hour, which gave a contact time of very nearly one hour. The gas volumes were 30,000 cubic meters per hour circulated with the paste, and 20,000 for temperature control in the converters. The hydrogen consumption per ton of middle oil produced averaged about 1600 cubic meters, while the conversion factor for middle oil from coal was 0.6 tons per ton. The conversion of bituminous coal was quite high, about 95 percent of the carbon being transformed into gaseous and liquid products.

At Scholven the hydrogenation plant operated at 300 atmospheres pressure, since a more active catalyst was used. A mixture of tin oxalate and ammonium chloride, 0.06 and 1.0 percent, respectively, based on the weight of coal was added to the paste. This catalyst gave the less favorable conversion of 90 percent of the coal at through-puts comparable to those used in other plants. There were, however, mechanical difficulties in operation, since the chloride was quite corrosive.(20) The two points where the maximum corrosion occurred were in the preheater tubes, and in the coolers where water started to condense and gave an acid solution of chloride salts. On account of the corrosion difficulties, the tin-chlorine system was not popular in Germany, and Scholven was the only plant so operated.

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4. Description of Sump Phase Operations (b)(cont'd.)

Bituminous coal middle oils were richer in aromatics and naphthenic compounds than those obtained from brown coal, and the gasoline made from them had good octane ratings. The description of the further processing of these middle oils to produce fuels is described in Section V.

(c) Processing of Tars and Pitches.

The hydrogenation of coal tars and pitch played an extremely important part in the German fuel program for the war. There were at least six large plants which processed only tars and pitches from the numerous coke ovens, and in addition to these, nearly every coal hydrogenation plant used some tar mixed with the paste to increase its production. Low temperature tar from brown coal was the principle raw material, and this tar contained about 81 percent carbon, 11 percent hydrogen, 1.5 percent sulfur, 0.5 percent nitrogen, and 6.0 percent oxygen. The phenol content was about 10-15 percent.

The crude tar as received, contained about 2 percent water and 1 percent of fine dirt. These materials were separated in centrifuges, since it was necessary to remove the water to prevent crusting and overheating of the tar in the still preheater. The latter was caused by sudden vaporization of the water with subsequent stagnation and carbonizing of the tar. The dirt was removed to protect the sump phase catalyst from being fouled and its activity reduced. After removal of the dirt and water, the purified tar was distilled, giving a middle oil plus gasoline fraction boiling below 320°C, and a heavy residue. This latter material, which amounted to about 55 percent of the tar, was treated in the sump phase; to produce additional middle oil.

The catalyst most frequently employed for tar hydrogenation was iron sulfide on coke breeze such as that obtained from coke ovens or Winkler generators. About 0.5 - 1.0 percent of this powder was made into a paste of about 40 percent concentration using freshly stripped tar residue oil for a vehicle. This paste was mixed with about one hundred

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4. Description of Sump Phase Operations (c)(cont'd.)

times its volume of heavy slurry from the hot separator at the entrace to the heat exchangers and pumped with the fresh tar through the unit. The catalyst concentration therefore was about 4-5 percent of the tar feed.

The operation of the sump phase with tar was nearly the same as with brown coal, the chief difference being the greatly reduced solids removal problem. (See drawing no. 3) A small bleed, corresponding to approximately the quantity of fresh catalyst paste, was withdrawn from the hot separator and centrifuged to recover the oil. A hot recycle oil pump, located in the system, recirculated slurry from the hot separator back to the inlet of the preheater and thus increase the turbulence in the converters.

In general the hydrogenation of tars and pitches could be classified into two chief types of operation. The brown coal tars which were low in asphalt (2-5 percent) required less drastic condition than did the pitches and cracking residues which were high in asphalt. For materials in the first category a reaction temperature of about 450-460°C and a pressure of 300 atmospheres were employed. The through-put of fresh tar averaged about 0.5 tons per cubic meter of reaction volume per hour, and for each ton of tar, approximately 1000 cubic meters of gas were circulated. The heat of reaction was much less, averaging about 120 kilo calories per kilogram of middle oil produced, and hence the temperature control in the converters was much easier. Since coal tar had a higher hydrogen content and lower molecular weight than coal, greater yields of oil could be obtained than with coal. About 30 percent more middle oil was produced in a given unit (that used coal tar) and the hydrogen consumption was approximity 250 cubic meters per ton of middle oil, or about 15 percent of that required for coal. In general the brown coal tars were easily handled in the sump phase, and they were a desirable raw material for gasoline production.

The hydrogenation of high asphalt tars and cracking residues was conducted at Lutzkendorf, where a pressure of 700 atmospheres and a temperature of 500°C. was required to

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DRAWING No. 3

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4. Description of Sump Phase Operations (c)(cont'd.).

give satisfactory conversion. On account of the refractory nature of the material being processed, the through-put was low. It averaged about 0.35 to 0.40 tons per cubic meter per hour. A very high hydrogen partial pressure (92 percent) was maintained in the gas in order too accellerate the asphalt decomposition, but outside of the more drastic conditions required, the rest of the operation was the same as with brown coal tar.

The hydrogenation of pitch, as typified by the operation at Welheim (See drawing no. 4) was conducted at 480°C and 700 atmospheres pressure. The feed consisted of 60 percent fresh pitch with a 70°C melting point plus 40 percent heavy recycle oil from the process. The feed rate averaged 25 cubic meters per hour of liquid, and 45,000 cubic meters of gas were used per stall of four converters having a total reaction volume of 36 cubic meters. The hydrogen consumption was considerably greater than in plants processing brown coal tar, since pitch was a material relatively poor in hydrogen. On the average, 700-800 cubic meters of hydrogen were required to convert one ton of pitch to middle oil and fuel oil. The overhead oil collected in the cold separator was distilled to give a middle oil fraction for processing in the gas phase, while the residue was sold for fuel oil. This last operation was quite different from that practised in plants treating coal tars, since there the distillation residue was recycled. The high asphalt content of the pitch, and its low susceptibility to hydrogenation made further treatment of the heavy oil less attractive than in the case of tar. With a market for fuel oil, this provided a convenient way of keeping the asphalt content in the system from becoming too great. The gasoline produced from pitch had a good octane rating on account of its high aromatic content. The preparation of gasoline from pitch middle oil is described in Section V.

5. Description of Gas Phase Operation.

As previously mentioned, the purpose of the gas phase was to take the liquified coal or middle oil from the sump

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DRAWING No. 4

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5. Description of Gas Phase Operation (cont'd.)

phase and, by a combination of hydrogenation and cracking, convert it into gasoline. At first this operation was conducted in one step over a molybdenum-magnesium-zinc catalyst (No. 3510) at temperatures around 460°C. This catalyst, however, produced too much gas and its activity was rather low, so that the through-put of oil was small. In 1933, after laboratory tests at Ludwigshaven, the I.G. plant at Leuna first tried pelleted tungsten disulfide catalyst (No. 5058) in the place of 3510.(21) This new material was about three times as active as the first catalyst, and hence it was possible to operate at a lower temperature and obtain a superior product with better yields. The tungsten sulfide was very active in hydrogenating aromatics to naphthenes as well as reducing phenols, nitrogen bases, and sulfur compounds to hydrocarbons. However, the high proportion of naphthenes and paraffins in the gasoline produced by this method gave a low octane number of about 60. By the addition of lead this could be made into motor gasoline, but not aviation grade. The diesel oil on the other hand was of fair quality, the cetane number falling between 35 and 50.

Since the German emphasis was upon aviation grade gasoline, a search was made for a catalyst that could convert naphthenes and normal paraffins into isoparaffins. In 1937, Leuna started to use a tungsten sulfide-activated clay catalyst (No. 6434) to convert the product from the 5058 stage into aviation gasoline. The unleaded gasoline produced by this material had an octane number of 70 to 75, which by the addition of tetraethyl lead, could be easily raised to aviation grade. This latter catalyst could not treat middle oil from the coal sump phase directly, since the phenols and nitrogenous bases in the oil poisoned and drastically reduced its activity. Therefore, it was necessary to pretreat the sump phase oil with 5058 catalyst to remove the oxygen and nitrogen compounds before using the 6434 catalyst. This resulted in a two stage gas phase operation which continued with only minor changes throughout the war. However, when only auto gasoline or diesel oil were required, a one step process using 5058 catalyst was employed. Obviously, many variations of these processes could be used, depending

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5. Description of Gas Phase Operation (cont'd.)

upon the particular demands, but the use of 6434 to make aviation gasoline, and of 5058 to make diesel oil and motor gasoline became the basis of the German synthetic fuel program for coal hydrogenation.

(a) Prehydrogenation Stage.

The feed for the prehydrogenation was usually middle oil from the sump phase hydrogenation of brown or bituminous coals and tars. To this was added a recycle middle oil from the distillation of the product. A typical analysis of a bituminous coal middle oil was: specific gravity 0.956 at 20° C.; aniline point -12.5° C.; phenol content 17%; and distillation range 145-322° C.

The oil was pumped up to the operating pressure of 300 atmospheres in large pumps quite similar to those used for handling coal paste. The maintenance on these oil pumps was less, however, on account of the absence of solids and the consequent reduction in abrasion of the pistons and packings. Hydrogen was next added to the oil from the pressure header which contained recycle plus make-up hydrogen.(9) About 1500 cubic meters of gas containing between 70 and 80 percent hydrogen were circulated for each cubic meter of oil feed.

Referring to drawing no. 5, which shows a typical flow for the gas phase, it will be seen that the oil and gas mixture entered the bottom of the first of two heat exchangers. These pieces of equipment were built exactly like the ones used for the sump phase, and operated in the same manner with the inlet material on the outside of the tubes flowing upwards and the outlet products on the tube side flowing down. The sizes varied with the plant, but two of the most common were the 500 millimeter diameter with 151 tubes, and the 600 millimeter diameter with 199 tubes. These two exchangers were both 18 meters long and had heat transfer surfaces of approximately 145 and 190 square meters, respectively. A new design of the 600 millimeter heat exchanger had been made in which there were 241 tubes having a total surface area of 228 square meters. This later ap-

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DRAWING No. 5

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5. **Description of Gas Phase Operation (a)(cont'd.)**

paratus had probably been planned for new gas phase installations since its use was not in evidence in the plants visited.

With a feed rate of approximately 20 cubic meters of oil plus 20,000 cubic meters of gas per hour entering the cold heat exchanger at near room temperature, the heat transfer warmed the feed to about 180° C. In the second or hot exchanger the feed was further heated to about 300° C. The overall heat transfer coefficients were usually about 250-300 kilo calories per hour square meter degree centigrade (51-61 BTU per hour per square foot degree Fahrenheit), although at times under favorable circumstances the values went as high as 400-500 metric units.

As in the sump phase, it was necessary to give the feed a little additional heating in order to warm it to the point where the heat of reaction was sufficient to carry the temperature up to the reaction zone. In the sump phase, gas-fired tubular preheaters were used exclusively. In the gas phase, gas-fired preheaters similar to those employed in the sump phase were used in some installations, while in others electrical heat was used. The former type has been described in section IV, but the latter equipment was employed only in the gas phase operation.

The preheater consisted of four to six 120 by 90 millimeter tubes of N8 steel, approximately 15 meters long, encased in a thin steel cylindrical shell. (See drawing no. C-9 in Appendix C). Instead of using heating elements, the tubes themselves were the electrical resistors, thus increasing the thermal efficiency. Steel lugs were welded on the outside of the tubes, and electrical connections were made to them through bus bars backed up with steel plates. The tubes were supported by ring clamps insulated from each other and from the steel shell at the top end. Rock wool insulation was packed around the tubes inside of the shell to reduce the heat losses. The transformers used to reduce the electric current operated on a primary voltage of 6000-7000 volts, and usually one was required for each pair of hair pin bends or four straight lengths. The hot side of

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the secondary winding of the transformer was connected to the binding post connecting the tops of the two inside lengths of tubing, while the negative or grounded side of the transformer was connected to binding posts at the top of each outside length. Thus the electrical current flowed through one complete "U" bend, heating up the tube by reason of the I^2R loss in the steel. For obvious reasons, a low potential of about 70 volts and a high ampere current were employed in this type of apparatus. In general the electrical type of heater was satisfactory when its limitations were not exceeded.

One of the big advantages of the electrical type of preheater was that the heat input could be quite accurately measured, and thus better control could be obtained. The electrical type was also somewhat less expensive to build, and where the power load was not too high, the operating costs were reasonably favorable. However, there were several rather serious disadvantages connected with the electrical preheater. If the material being heated inside the tube started to carbonize, polymerize, or cake on the walls in any way such that the heat transfer was reduced, then the wall temperature of the tube increased, since the electrical input remained constant. The higher wall temperature increased the local electrical resistance, so that the greatest amount of heat was being liberated in the section where the heat transfer was the lowest, and this still further raised the local pipe temperature. If the contents in the tube continued to cake or coat, as was usually the case when the local temperatures became excessive, then the preheater tube would become heated to such a point that it would rupture and possibly cause a serious fire. For this reason, the electrical preheater could be used only on clean materials such as distilled oils, but even then gas-fired preheaters were often used.

Another liability, although not as great as the first, was caused by the increase in electrical resistance of the steel with temperature. Thus the greatest heat density in the tube was at the outlet end, whereas the reverse situation would have been more desirable on account of carbonization. This defect was partially overcome by heating the total length in short sections, as has been previously des-