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# CONFIDENTIAL

## Letter Report on German Fuels, Lubricants and Related Synthetics

### I. Aviation Gasoline

The highest quality German aviation gasoline in production at any time during the war consisted only of a mixture of selected base stocks, alkylate or hydrogenated octylenes, and lead. Many additives, such as synthetic aromatic ethers and anilines were tested and considerable information is available on this research. However, no large scale use of any of these additives has been practical.

The aviation base stocks used were essentially two in number, one a fraction of about 120°F end point obtained directly from the hydrogenation of coal or coal tar, and the other an aromatic aviation fraction of the same boiling range produced by a process similar to hydroforming. This hydroforming process (known as DHD) produces a gasoline containing about 50% aromatics.

The green German aviation fuel, corresponding most nearly to our "one hundred octane" grade, consists of about 19% iso-octane (2,2,4 trimethyl pentane quality) and 81% DHD gasoline. This blend contains a maximum of 4% aromatics. Higher aromatic contents were tested, but were found to cause valve deposits. The TEL content is 0.12% by volume (4.5 cc/gal).

The blue German aviation fuel, corresponding most nearly to our "91 octane" grade, consists solely of a coal or coal tar hydrogenation gasoline plus 0.1% volume of TEL. Its aromatic content is 10 - 15%.

≡ 4.55 cc/gal

Aviation fuels are rated primarily by a full performance curve over the range of fuel-air mixtures used in practice. A test which compares with oct 3-C measurement is apparently also made but exact specifications have not yet been learned. No evidence was found concerning new types of inhibitors or other materials that could be used to improve the quality of U.S. aviation gasoline production.

### II. Synthesis of Iso-Paraffins for Aviation Gasoline

For the manufacture of iso-paraffinic aviation gasoline components, Germany has employed several processes well known in America. Butylenes, produced either by isobutyl alcohol dehydration or by catalytic dehydrogenation of butane, are both alkylated and polymerized to octylenes, that are then hydrogenated to iso octanes.

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Of particular interest at the moment is the German research and formation on the synthesis of triptane and "Paroptan". The Ludwigshafen research group have been working intensely during the past two or more years on the synthesis, via chlorination, of the highest quality isoparaffins. They have prepared test quantities of triptane by a Grignard synthesis. They have also manufactured triptane, as a measure of success, by the combination of isobutane and 2-methyl propane. The process has been fairly well worked out and I.G. has prepared to propose a plant design to the government. A similar procedure is used to manufacture "Paroptan" from isobutane and isobutyl chloride. "Paroptan" is a 176-266°F boiling range product which apparently contains 2,2,3,3-tetramethylpentane in appreciable amounts.

The intermediate chlorides for these processes are prepared by adding Cl<sub>2</sub> to propane or isobutane in the presence of AlCl<sub>3</sub> and ultra violet light. With isobutane, the yield is said to be essentially pure 2-methyl 2-chloropropane, with propane, roughly equal quantities of 1-chloropropane and 2-chloropropane are obtained. The chlorides are reacted with isobutane, also in the presence of AlCl<sub>3</sub> and ultra violet light, employing an 8 to 1 ratio of isobutane to chloride.

These chlorination processes were never brought to plant scale employment because of the disruption by bombing of their research and other facilities. It also appears certain at this time that no plants ever were built in Germany for the synthesis of isoparaffin technology with which we are not acquainted.

### III. Lubricating Oils

Relatively little has been learned at Ludwigshafen about German lubricating oils, as they were not being manufactured at this place. A polyisobutylene known as "Oppanol" and similar to our "Paratone" is manufactured by I.G. It is used in limited amounts in some German motor oils, but I.G. themselves do not use it because of ring-sticking problems arising from its inclusion. It was tested as an ingredient of motor oil for their Army vehicles, but was not used because of poor consumption characteristics. Parafflow, a pour point depressant, is manufactured by the Germans by combining naphthalene with chlorinated paraffins. This product and its method of manufacture are already well known in America (Dow Chemical Co.).

There is evidence that the Germans are acquainted with the manufacture of synthetic lubricants containing high percentages of oxygen. For example, a patent disclosure has been found of a process for producing synthetic oil by polymerizing two mols of "polybutylene" glycol, one mol of methyl adipic acid, and one mol of isohexyl carboxylic acid.

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Another document just found describes the manufacture of a polymer of tetrahydrofuran. (Tetrahydrofuran is manufactured by first combining acetylene, formaldehyde and hydrogen to L.4 butanediol, and reacting this material over phosphoric acid to form tetrahydrofuran. Details of these reactions have already been obtained).

Polymers of ethylene have been made at Ludwigshafen and subjected to extensive motor tests. They were found to have a superior resistance to ring sticking, both alone and in mixture with other oils. Many other polymers, such as those from propylene, were tested, but none others were of interest. The bulk volume of German lubricating oils come from three sources:

- (a) Crude oil.
- (b) Polymerization of olefins obtained from cracking of paraffin wax.
- (c) Coal tar hydrogenation.

The production of lubricating oils by coal tar hydrogenation involves a new technique in hydrogenation. Whereas the common method of processing coal tar is a two stage hydrogenation, first a saturation and then a splitting step producing gasoline, the new so-called TTH process is a one stage operation over a new catalyst and produces primarily Diesel fuel and lubricating oils. Many of the details of this process have been learned.

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With respect to lubricating oil quality, a number of interesting things were learned. The I.G. laboratory at Ungstein was equipped with a one cylinder (full scale) engine that was used for testing aircraft oils for ring sticking. The engine was operated under the following conditions:

RPM 1900		
Inlet Air Temperature	104°F	
Cylinder Head Temperature	500°F	
Compression Ratio	7.5/1	
BEP	57	0428285
Inlet Oil Temperature	212°F	
Outlet Oil Temperature	220°F	

In this test engine and under the above conditions a Pennsylvania oil will prevent ring sticking for only 8 hours and Valvol for 5 hours. In contrast, the synthetic oils being produced at Leuna (a target not yet available) will permit operation for 25 hours. The Leuna oil is now reserved exclusively for use in aircraft and some tanks.

It was stated that the Leuna aircraft oil contains a phosphorus oxidation inhibitor, but does not contain anti-ring-sticking or bearing corrosion inhibitors. An effort will be made to obtain more exact information on this process and its products when the Leuna plant becomes available for inspection.

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Cold starting difficulties in German aircraft engines have been overcome by diluting a portion of the lubricating oil with kerosene in a manner similar to the scheme tested at Wright Field.

#### IV. Jet Propulsion and Rocket Fuels

##### (a) Hydrogen Peroxide (H-Stoffe) Kerosene, Gasoline, Paraffin

It is understood, that this subject will be covered in detail by a report now in preparation by Ensign E. Coraley. The item is however listed here, because a substantial amount of time and work has been spent by other members of this team to insure complete coverage. Complete information regarding the production, use, specifications and testing of 80% -  $H_2O_2$  was obtained.

##### (b) Rocket Fuels (R-Stoffe)

Testing procedures and specifications of rocket fuels were investigated:

Location: Ungstein 1 mile north of Bad Duerkheim.

Personnel: Dr. Penzig, head of laboratory

Dr. Worlienski )

Dr. Dieroth )

Dr. Mitschmann ) Assistant research personnel.

Dr. Halder (

The laboratory is one of several emergency installations equipped by I.G. when air attacks made work in Ludwigshafen impossible. The subjects covered included (in addition to regular aviation gasoline, lubricant, jet fuel, etc) the evaluation of rocket fuels. ("R-Stoffe").

The following properties of "hypergolic systems" were checked.

- (1) Ignition delay.
- (2) Burnlength.
- (3) Press. vs time diaphragm.

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The term "hypergolic system" is used to describe a system composed of a fuel and an  $O_2$  - Carrier which react immediately upon contact of each other. In the "monergolic system" the fuel and  $O_2$  - Carrier are combined in the same substance i.e.  $H_2O_2$ .

Apparently most of the work is in its initial stage but attempts were being made to develop methods of testing R-fuels in a laboratory scale and to correlate results with commercial operation. Reports covering the work done in Ungstein on rocket fuels were removed and transmitted to OIS London. Exact testing procedures are given in those reports.

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Two types of O<sub>2</sub> - Carriers are used: H<sub>2</sub>O<sub>2</sub> and 98% HNO<sub>3</sub>. A large number of fuels were tested, mostly unsaturated alcohols and acetates. A code system for these fuels was developed and the designations of most B-fuels are available.

The effects of catalysts on the different properties of hypergolic systems were also studied. The catalysts are mostly Fe Salts (FeCl<sub>2</sub>), which may be added to both the fuel and O<sub>2</sub> - carrier.

A larger installation for the study of hypergolic and non-hypergolic systems had been designed, but could not be installed at Ungstein due to allied interference. This unit was to be used to correlate the combustion characteristics of the system with the developed thrust.

Viscosity of the fuel and O<sub>2</sub> carrier is considered to be an important property - 40°C was given as maximum for cloud point. However, higher CP fuels had to be accepted lately, since the supply of the preferred stocks was interrupted by air attacks. In those cases methanol was added to keep the viscosity and cloud points low.

The latest tests that have been carried out was intended to determine the possibility of using heavy fuel oils as blending stocks with the regular B-fuel. The testing of H<sub>2</sub>O<sub>2</sub> for use as a rocket fuel was carried out and developed in similar apparatus, and is described in detail in Ensign Gormley's report on the subject.

(c) Jet Engine Fuels (H-Stoffe)

The testing and evaluation of jet fuels was also carried out at the Ungstein laboratory, a single jet combustion chamber being used to determine the "thrust" of different fuels. The types of jet engines are in use in Germany:

- (1) BMW Type: Single combustion chamber. 0428285
- (2) Junkers: Multiple combustion chamber.

Apparently the Junkers engine is the preferred unit, since it allows the use of heavier fuels. However, a simple type of fuel is now in use, which can be used by both engines. This fuel is designated as "J-II".

The following properties are considered of importance in a jet fuel by the Germans:

- (1) Boiling range 220°C Max. end point
- (2) Cloud point 45°C Max.
- (3) Low temperature
- (4) Thrust (in the Junkers engine)
- (5) Ignition delay
- (6) "Abrasion" (fuel) (in the Junkers engine)
- (7) ...

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V. Placher-Tropash

Only one witness was contacted in Indivichafen in regard to this process. The witness, Dr. Michael, had been in charge of a group working on the development of the P-T process, but it appears, that this particular group had not been successful. The research that has been carried out over the last four years covered two subjects as follows:

- (1) Synthesis over solid sintered iron catalyst, and control of reaction temperature by increased gas circulation. This process appeared to work satisfactorily in small units but it did not seem feasible when carried out on a large scale. CO decomposition and carbon deposits due to local overheating were the main difficulties.
- (2) Synthesis in liquid phase. In this process the catalyst ( $Fe_2O_3$ ) is reduced at as low a temperature as possible and dispersed in a ball mill to 2 to 5 micron particles. The catalyst is suspended in a middle fraction of the reaction product and the oil and catalyst in suspension is circulated through a cooler to control the temperature. The feed gas is dispersed by passing through a ceramic plate, leaving a foam in the reactor.

Michael mentioned that the main difficulty lay in the formation of  $FeCO$  which tends to drop out of the suspension and stick to the walls. (Note: Michael and his work were apparently not considered too highly by his superiors or collaborators)

From documents captured at Heidelberg, it is apparent, that I.G. have been quite successful in developing Fe catalysts to replace cobalt in existing FT plants. It was also mentioned that the catalyst may be regenerated. In one case a plant was designed requiring an initial catalyst charge of  $25 m^3$  with an addition of only  $5 m^3$  new catalyst in the first two years of operations. Detailed information on this process will be the subject of future investigation.

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VI. Nitrous Oxide in Aircraft Engines (G5-1)

Information on this subject was obtained from I.G. documents dated from 1941 to 1942.  $N_2O$  is used in aircraft engines for increasing power output. The following figures were given. (based on 10,000 ft. altitude condition)

(Cataler-Benda Engine)	Without $N_2O$	With $N_2O$ 100 gm/lph
Power output	690 HP	1000 HP
Specific fuel consumption	145,000 Kcal/hr.	197,000 Kcal/hr.
Combustion space temperature	375°C	540°C
Exhaust temperature	650°C	710°C

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Apparently continuous operation with  $H_2O$  addition for periods of sixty minutes was possible. A cycle test, running one hour with  $H_2O$  and followed by ten minutes normal operation, could be continued seven hours before renewal of the spark plugs became necessary. German production of  $H_2O$  for 1941 was scheduled to be around 110 tons/day. Difficulties regarding the feed of  $H_2O$  to the engine were encountered and different fuel systems were tested as follows:

- (1) High Pressure System: Liquid  $H_2O$  in  $H_2$  bottles installed in plane.
- (2) Low Pressure System: Use of a small compressor (60 lit/min to 10 ata)

In this connection, several insulating materials were tested for their suitability. It appears that the explosive properties of  $H_2O$ , particularly in a system with insulating materials of large surface/volume ratio ("foams") caused some concern to the Luftwaffe, as several unexplained explosions of planes had occurred in the air. Very extensive tests were carried out to establish these properties under firing conditions, using several types of ammunition. It was concluded that the  $H_2O$  container was no worse hazard than a regular gasoline container, but it should be noted that the  $H_2O$  could be exploded by placing a regular detonator in the liquid. It was stated verbally that explosions had occurred. This was ascribed to the explosion of  $H_2O$  containers but despite this assumption no further protective measures were taken.

VII. Diesel Fuels

Diesel fuels have been manufactured in Germany by at least three methods:

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- (a) Crude oil distillation.
- (b) Coal tar hydrogenation by a new process (GHI).
- (c) Fischer-Tropsch synthesis.

It was learned that German Diesel Fuels contain no new additives and are usually blends of the above products. The octane number of 15. The high octane numbers mentioned by the German press thesis were stated to be misleading, in that such fuels give a very low rate of pressure rise in an engine. To obviate this difficulty Fischer fuels have been blended with coal distillates, which are highly aromatic and give a high rate of pressure rise in engine operation.

The test engine used for determining the cetane number of diesel fuel is similar in many respects to the CFR engine, it is equipped with means for varying the compression ratio, and an oscillograph for determining the point of ignition and also the rate of pressure rise in the cylinder. Unknown test fuels are matched against cetane blends with the compression ratio adjusted to give an ignition delay of 180°.

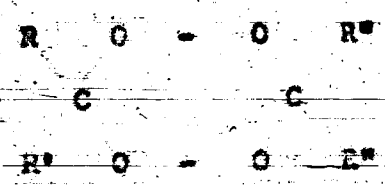
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Other pertinent specifications with respect to German Diesel Fuels is as follows:

Ave. 90% pt.	275 - 350°C
Flash point, min.	150°F
Vis. 330 @ 68°F Max.	65
Vis. 330 @ 68°F Min.	36
Water, %	.5 Max.
Ash, %	.05 Max.

Many additives for increasing octane number were tested. Peroxides have received particular attention. Ketone-peroxides of the nature of:



were viewed with favor, but, as stated, no use was made of them possibly because of the course of war which interfered with their development. Additives to prevent "precipitation" of diesel fuel components were also studied, particularly tetralin and decalin but the results were not encouraging. Another additive of interest is "graphite oxide." This is a finely divided material of approximate formula  $C_2O$ , made by a method that is not yet thoroughly understood, but which should be known shortly. It was first proposed by the German Navy as an additive to fuel oils to shorten flame length and thereby allow an increase in the heat liberation per unit volume of burning space. The effect of adding this material to Diesel fuels is as yet only speculation, but considerable attention was being given the subject and further information will be obtained.

Study also was given at this laboratory to the heating of the intake air as an aid to starting cold diesel engines. For this purpose, a briquette was manufactured consisting of 20% lignin, 30% ammonium nitrate, 30% nitrocellulose, and 20% "coal extract." The briquettes were placed in a special apparatus in the engine air intake line and were lighted with a match. Information on the test results is not complete, but apparently the development was terminated after some misunderstandings between I.S. and the German Army.

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E. Wright, Tech.

N. Reichl, Tech.

L.H. Milt,  
Lt. Comdr., USNR.

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