

C O N F I D E N T I A L

GERMAN PETROLEUM INDUSTRY
HAMBURG DISTRICT

REPORT No. 1

RHENANIA-OSSAG MINERALOLWERKE

HAMBURG

Reported By

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on behalf of the

BRITISH MINISTRY OF FUEL & POWER

AND THE

U.S. TECHNICAL INDUSTRIAL INTELLIGENCE COMMITTEE

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COMBINED INTELLIGENCE OBJECTIVES SUB-COMMITTEE

G-2 Division, S. H. A. E. F. (Rear) APO. 413

I N T R O D U C T I O N

Rhenania-Ossag, Mineralölwerke

Shell-Haus, Hamburg.

Black List Item 30/3.01

This target is the Head Office of Rhenania-Ossag, and it was here that most of the technical staff were interrogated.

The notes comprising this report are divided into the following sections:-

1. General.
2. Aircraft Engine Oils & Appendix
3. Synthetic Lubricating Oils.
4. Voltol.
5. Basic Oils & Additives.
6. Motor Oils.
7. Gear Oils.
8. Greases.
9. Cutting Oils and Rust Preventatives.
10. Hydraulic Oils.
11. Marine Engine Oils. Torpedo Oils.
12. Regeneration of used oils.
13. "Emulsion" Lubricants.
14. Extracts.
15. Asphaltic Bitumen.
16. Research (Amsterdam) and Hamburg.

Sections Nos. 1 to 13 are contributed by Mr. C.H. Barton, Sections Nos. 14 & 15 by Mr. D. Morten & Section No. 16 by Mr. Vladimir Haensel.

Sections Nos. 1 to 15 deal principally with the utilisation and performance of petroleum products and are based on interrogation of the technical personnel of the following organisations:-

Rhenania-Ossag.

Dr. Lütke-meier	-	Technical Director
Prof. Zerbe	-	Research Director
Dr. Ziegs		
Dr. Seeles		

Rhenania-Ossag (Ctd.)

Dipl. Ing. Beuerlein.
Herr. Rössig.

Rhenania-Ossag Laboratory, Tiessau.

Dr. Reichel, Manager. See Report No. 6

Chemische Physikalische Versuchsanstalt der Kriegsmarine
Dänisch Nienhof, Nr. Kiel.

See Report No. 11

Deutsche Vacuum Oel A/G. Oslebshausen, Nr. Bremen.

Dr. Goetz, Managing Director. See Report No. 4
Herr. H. Harms - Engineer.
" Kuchta - Chemist.

Section No. 16 deals with Research, principally with reference to the work carried out at Amsterdam under the direction of Prof. Zerbe.

SECTION 1. General

Dr. Lütke-meier said that during the war, oil companies with British and U.S. connections such as the Shell and Standard companies, were regarded with suspicion by the German Government who restricted the amount of technical information made available to them and, furthermore, left a minimum of development and research in the hands of the oil companies. The investigational work of Rhenania-Ossag during the war was therefore restricted to matters related to their own production and marketing problems, in particular the development of the synthetic lub. oil manufacture from paraffin wax, extreme pressure additives, and the working out of substitute materials for grease manufacture, lub. oil blends, etc. to replace fats and other components in short supply.

Rhenania-Ossag's knowledge of developments in gasoline, kerosine and Diesel fuels during the war was almost non-existent, since all their production of these fuels was passed to one of the Government organisations such as Z.B. (Zentral Büro für Mineraleöl) or WIFO to be blended for use by the armed forces etc. There was no Petroleum Pool Board as in the U.K. No coal oil, brown coal, alcohol or other non-petroleum fuels were passed to the oil companies for blending with petroleum and Rhenania's knowledge of developments in the non-petroleum fields was apparently very slight.

Although no outstanding developments appear to have taken place in petroleum technology, applications, and testing, the detailed information acquired from Rhenania and the Vacuum etc. provides some picture of the operations and conditions of the mineral oil industry of Germany in war time and gives the answers to many of the questions propounded by the Applications sub-Committee of Group 30 as well as to some of those debated by the U.K. Enemy Oils Committee. The conclusion, reached from the examination of captured oil samples, that the Germans maintained to the end the quality of the oils supplied to the Wehrmacht, was supported by the data made available by the oil industry. At the same time it was found that the quality of the oil products supplied for civilian use deteriorated as the war progressed, particularly during the last year of hostilities when the effect of the

bombing of refineries and transportation became very marked.

Dr. Lütke-meier and his staff and colleagues were very co-operative throughout and seemed anxious to place at our disposal all their available information, including files, reports and Government specifications for oil products. A comprehensive collection of the latter documents was obtained from Rhenania, in addition to those acquired from the Deutsche Vacuum Co.

SECTION 2. Aircraft Engine Oils.

At the start of the war the two main oils of the Luftwaffe were AeroShell Mittel (A.S.M.) and Intava or Rotring 100. Both oils are approximately 100 secs. Saybolt at 210°F (about 180°E at 50°C). The former oil was a blend of 15% Endvoltol with 85% Edeleanised Venezuelan distillate and the latter a solvent refined (DuoSol) residue from American or German paraffinic crudes. When stocks of imported Venezuelan oil (including some at Rotterdam) had been exhausted in 1940, Reitbrook oil was Edeleanised and, later, other types of asphaltic ("A") oils from Austria, e.g. Zistersdorf crude were similarly treated for making A.S.M.

~~Distillates from indigenous paraffin base ("P") crudes were also extracted in the SO₂ plant and were dewaxed for use in A.S.M. The proportion of A.S.M. compared with Rotring or Intava oil, used by the Luftwaffe gradually decreased from 1941-2 onwards as engines were developed to give higher outputs and the tendency to piston ring-sticking increased. Eventually A.S.M. was used only in certain bomber engines and in the Junkers Jumo (aero) Diesel engine in which this oil is very satisfactory as regards ring-sticking.~~

As the synthetic lub. oil production increased on Aero oils these oils were used for blending with mineral oil (Appendix A). The synthetic oil (made to 45°E at 50°C) was not used alone, but was blended with an equal weight of solvent refined "P" type oil. This scheme had the merit of raising the V.I. of the solvent refined mineral oils and also of improving the oxidation stability of the synthetic oils.

Although 80 (Grauring) and 120 (Grünring) oils appear in captured lists of Luftwaffe oils, no information on these grades was obtained from the oil companies. Presumably these grades, which had a limited use, were blended by one of the official organisations, such as WIFO.

No viscosity index raisers, such as Oppanol (=Paratone) were used in German aero oils owing to the possible depolymerisation of such materials in service. No additives other than I.G's R and S were used in aero oils. These materials are non-metallic compounds and 0.2% wt. was added to Intava or Rotring (mineral and

synthetic) oils. The composition of these additives which were understood to be oxidation and ring-sticking inhibitors, was unknown to Rhenania, but the latter found them to have little effect on oil performance as regards ring sticking.

It was confirmed that oil frothing troubles had occurred in military aircraft and work had been done towards the development of a laboratory frothing test, on the lines of those used in the U.S.A. and U.K. No anti-frothing additives for aero oils had apparently been developed in Germany.

Appendix (Aero Engine Oils).

Aero Engine Lubricants & Their Components.

The two principal oils used by the Luftwaffe are referred to as S.3 and V.2 in R.L.M. Specification GL/AMII of March 1943. Both oils are approximately 100 secs. Saybolt at 210°F.

V.2. is AeroShell Mittel (A.S.M.) made by Rhenania-Ossag and consists essentially of about 15% Voltol and 85% SO₂-extracted asphaltic distillate although paraffinous distillates, SO₂-treated and dewaxed, were also incorporated. The detailed specification of A.S.M. is TL147-500 of March 1943.

S.3 is a hydrocarbon oil and was developed from Rotring or Intava 100 oils which were, at the outset of the war, 100% solvent-refined, paraffin or mixed base mineral oils made at the Deutsche Vacuum Ges. DuoSol plant at Oslebshausen Bremen. With the coming into production of "synthetic" oils about 1942, the mineral lubricant became a 50/50 blend of high viscosity (36° - 50° E/50°C) solvent refined mineral oil. The Deutsche Vacuum Co. continued, however, to supply to the Luftwaffe Rotring D consisting of 100% DuoSol-refined mineral oil and Intava also a solvent-refined oil. The synthetic oil took the place of Bright Stock and permitted the inclusion of the low viscosity, solvent refined, long residuum mineral oils.

Specification details of the components of S.3 are given in RLM GL/A.MII of June 1944. The low

viscosity components (Dünnöle) are solvent refined mineral oils, whilst the high viscosity oils (Dicköle) which are blended with equal weights of the former, are synthetic oils. Of the low viscosity oils, SS607 was made by Rhenania-Ossag by SO₂ extraction of asphaltic distillates ('A'crudes, such as Reitbrook) SS707 was made by Deutsche Vacuum (Bremen) by DuoSol treatment of paraffin-type crudes (Nienhagen etc.) and 807 was Nerag's furfural treated oil (formerly propane deasphaltised residue and later a distillate - evidently asphaltic, judging by increased density of the corrected figure shown.) The synthetic oils SS 906, 1006 and 1106 were respectively I.G. (Leuna) Rhenania-Ossag (Harburg), and Pölitz products. The final blends of S3 oils were assigned numbers derived from those of the components. Thus an S3 oil made from Rhenania-Ossag's low and high viscosity oils SS 607 and 1006 was known as SS 1060, and a blend of Deutsche Vacuum's SS 707 with Leuna synthetic oil SS 906 was denoted by SS 970.

The finished blends were made up both by the refiners, such as Rhenania-Ossag and Deutsche Vacuum, or by the Government controlled blending and storage organisations, such as WIFO who received the components from the refineries. In all cases, about 0.2% of an I.G. anti-oxidant and anti-ring sticking additive was incorporated in the final blend.

The specification for finished S.3 oils, R.L.M. GL.A.MII of March 1943 gives two sets of limits for this grade in order to allow for the variations due to the different components. The finished S.3 blends were tested for ring-sticking in the BMW 132 single cylinder aero engine specimens of which were available at the major oil companies' laboratories etc. S.3 was required to have at least as good a ring-sticking performance as the standard oil, Rotring D (see detailed specifications such as TL 147-561 of 1.4.43. for SS 960).

No oxidation test is included in the specifications for aero-engine oils, but an evaporation test at 250°C, Conradson carbon, refractive index maximum and V.I. are laid down for the components as well as for the finished oils.

SECTION 3. Synthetic Lub. Oils.

The Rhenania plant was erected at Harburg between 1940 and 1942 and produced oil from 1942-June 1944 when it was moved to Osterode (Hartz mountains) for erection underground. The new installation was not carried out.

The production of finished oil rose to a maximum of 700 tons per month. The wax feed stock was taken from the Harburg dewaxing plants which handled "P" oil distillates. Up to 25% oil could be included in the wax but the yield improved as the oil content was reduced as the proportion of lighter wax was increased. A yield of about 50% finished oil was obtained on the wax + oil feed. The polymerisation with $AlCl_3$ was carried out with a trace of water present. Polymerisation was done at $20^{\circ}C$, with a finishing period at $60 - 80^{\circ}C$ to reduce the bromine value of the final product to 2. In the final vacuum distillation 4% light oil was taken over. This fraction was used for making compressor oils but the bulk of the production was reserved for Aero oils as was the case with the other synthetic oil plants in Germany (at Pöhlitz, Leuna, Schkopau, Ruhr-Chemie etc.)

(For properties of synthetic oils see Appendix on Aero Engine Oils Section 2).

A sample of the first synthetic oil production from Rhenania-Ossag, Harburg, was obtained from Shell-Haus and was placed with the other samples for despatch to C.I.O.S. London.

SECTION 4. Voltol.

The pre-war Voltol plant at Freital, Dresden, continued throughout the war on a production of 200 - 250 tons/month. Endvoltol was the main product made, as in pre-war days, from 33-1/3rd% wt. rape oil and 66-2/3rds% wt. mineral oil distillate. No other fatty oils, such as soya oil, were used.

The main use of Voltol (Endvoltol) was in A.S.M. aero oil, but some was used for army motor oils until the shortage of edible fats in 1943 put a stop to this application.

Some special Voltol made from 25% wt. rape and ~~75% wt. mineral oil to a viscosity of 20°E at 100°C~~ was exported to France for blending with the low viscosity lubricants prepared from colophony by cracking in presence of catalysts (Zn.salts). By this arrangement a saving of rape oil was brought about, since blown rape had previously been blended with the oils from colophony.

"Halbvoltol" made from straight rape oil to a viscosity of about 15°E at 100°C was incorporated (3%) in hydraulic oils for the Luftwaffe.

No Voltol was made by the chemical catalyst (e.g. BF₃) process in Germany during the war, according to Dr.Lutkemeier's information and no Voltol plant was erected in Hamburg or any other place. All the Voltol and Elektrion products were supplied by the plants at Dresden and Ghent.

SECTION 5. Basic Oils & Additives.

It is evident that the quality of the oils for the armed services was maintained to the end, but the quality of many of the oils supplied for civilian use underwent a marked deterioration from 1943 onwards. (See section on motor oils).

In the case of greases and compounded oils much work was done in finding and applying substitutes for the fats normally incorporated. Montan wax and its derivatives, naphthenic acids and synthetic fats, i.e. oxidised paraffins, were largely used as "ersatz" materials.

The steam cylinder oil position became difficult early in the war, apparently for two reasons:

(1) the fact that the Government omitted to acquire adequate stocks of American cylinder oil residues, and (2) the shortage of dewaxing equipment in Germany for treating residual oils. By the end of 1939 stocks of Pennsylvanian and similar cylinder oils had been exhausted, and substitutes had to be made from high viscosity asphaltic distillates. Eventually dewaxed solvent refined residues became available in limited quantities for superheat steam cylinders from the plants of Wintershall A.G. at Lutkendorf and Nerag at Misburg. The steam cylinder supply position was also aided by the use of "emulsion lubricants".

The supply of high V.I. lubricants particularly for aero engine oils and for the Army's motor oils was enhanced by the manufacture of high viscosity synthetic hydrocarbon oils which made good the shortage of Bright Stocks. The general principles involved in the preparation of these oils were known and applied in the U.S.A. and Netherlands East Indies before the war, but the Germans appear to have developed the processes especially in the direction of using light hydrocarbons, such as ethylene, as starting materials. The synthetic lubricants made for aero oils were all of the high viscosity type (45°E at 50°C) equivalent to a heavy Bright Stock. (See Appendix on Aero Oils).

In the case of additives, the anti-oxidants (R & S) used in non-compounded aero oils were made by I.G. No other additives were used in engine oils, except Oppanol Gemisch B15, the V.I. raiser, also made by I.G., which was used by the Army in gear oils as well

as in engine oils. Extreme Pressure additives based on fatty oils were abandoned about 1942 owing to the fat shortage, and satisfactory substitutes made from petroleum or organic chemicals were evolved by the Shell and Vacuum oil companies.

SECTION 6. Motor Oils.

The Army originally had an "Einheitsoel" with unchanged viscosity for winter and summer use for all types of automotive engine. The oil had a viscosity of 8°E at 50°C and a V.I. of about 90. For North Africa, "Sondermotoren Oel "T" (tropical) with a viscosity of 12°E/50°C and V.I. 80 - 90 was used. Oppanol (Gemisch Bl5 ex I.G.) was permitted in these oils, but no other additives have been used at any time.

The first Russian winter campaign (1941) showed that an Einheitsoel was unsatisfactory and a winter and summer grade were introduced (Specifications RLM-GL/A-MII of June 1944 also TL6032 and 6033 of 15.7.44).

To obtain the flat viscosity-temperature curves Oppanol was first used, but the Army decided that this component produced gummy piston deposits (a conclusion not supported by the Shell and Vacuum Oil Co's experiments) and Oppanol was banned from the winter grade although its use continued in summer grade oil. 10 - 20% of synthetic oil 5°E/50°C from cracked Fischer-Tropsch "liquid" waxes (made by Ruhr-Chemie) was included in the winter oil to improve the V.I. Voltol was also permitted as a component of engine oils until 1943 when the shortage of rape oil brought its use in this direction to an end.

For civilian use the quality of motor oils gradually deteriorated until the last few months of hostilities when unrefined topped crudes of low asphalt content, filtered to reduce the ash content, and blended with 10 - 20% spindle oil to give viscosities of 6°E and 8°E at 50°C for winter and summer respectively, were in use.

No H.D. type additives appear to have been developed in Germany for use in high speed Diesel or other internal combustion engines.

SECTION 7. Gear Oils.

The Wehrmacht started the war using normal type mild E.P. oils with viscosities in the range 15 - 24°E at 50°C and passing at a test load of 240 kg. in the 4-ball apparatus. The exigencies of the Russian winter, however, drove them to reduce the viscosity of the oil to 6°E at 50°C. For a time an oil of 4°E at 50°C was actually used but was abandoned owing to leakage losses. By the use of Oppanol (Gemisch B15) it became possible to raise the viscosity from 6° to 8°E without impairing low temperature (-40°C) fluidity (Spec. RLM GL/A-MII June 1944). The failure of Oppanol supplies about 1943-4 again made a reduction in viscosity to 6°E at 50°C necessary.

Shortage of fats led in 1942 to failure of supplies of sulphurized fatty oils, and lead naphthenate plus free sulphur came into use. Other successful E.P. compounds which were used by the Wehrmacht were:

- (1) a sulphur compound made by treating a cracked wax olefin mixture (boiling 150° - 300°C) with Sulphur monochloride. The final product has a sulphur content of 17 - 20% and is satisfactorily non-corrosive. 10% by weight is used to meet the Army's E.P. requirements in the 4-ball test.
- (2) a substance, known as Etrol made by the Vacuum Company. This appears to be a nitro compound together with free sulphur and some fatty oil.

SECTION 8. Greases.

The manufacture of greases was carried out at Grasbrook until November 1944.

Supplies of fatty oils became difficult from about 1942 onwards and the principal grease making materials became tallow, synthetic fats (oxidised paraffins) and refined and unrefined Montan wax.

Two lithium stearate greases, made at about 200°C were developed for military purposes:-

- (1) A low temperature grease for aircraft, instruments etc., containing 12% soap in an Edeleanised gasoil (2°E at 20°C) with a flash point of 130°C. This grease was cooled in trays and worked in a 3-roll mill after reaching atmospheric temperature. The drop point was 170°C and the A.S.T.M. unworked penetration 230. A low temperature torque was required but no oxidation or working stability. (Specification TL 147-750 June 1944).

In the later stages of the war, owing to lack of Edel. oil, a straight asphaltic gasoil with a pour point of -65°C was incorporated.

- (2) Another lithium grease with a similar soap content was made from a spindle oil of 4°E at 20°C for the Army for low temperature winter operation. This grease was successfully tried out in airscrew hubs but did not get into service before the war ended.

The Army's "Einheitsfett", for vehicle tracks etc., was made by Grasbrook with the sodium soaps of Montan Wax ST (refined) to a drop point of 130°C. This grease is water insoluble.

The principal grease supplied by Grasbrook to the Navy was the same as Aerofett blau, a lime-tallow grease made with a spindle oil (4°E at 20°C). (Specification TL.147-735 June 1944).

A new type of thickened oil (K3) has been prepared by mixing a specially made fine silica gel (9%) with an oil low in aromatics (Dr. Zerbe's Patent). The maximum production of the special silica gel (ex

(2) DEGUSSA Basel) had reached two tons per month. contd. The "grease" was said to be "stable" over a temperature range from about -30°C (depending on the pourpoint of the oil) to higher than 200°C .

The K3 was made by Rhenania in two main grades: as a lime-base grease substitute, using a mineral oil of $4^{\circ} - 5^{\circ}\text{E}/50^{\circ}\text{C}$, and as a lubricant for heavy calenders in paper mills, using an oil base of $18^{\circ}\text{E}/50^{\circ}\text{C}$. It was found that the "grease" was unstable in presence of water which was preferentially adsorbed by the silica, water resistance increased, however, with viscosity of the base oil.

A large sample of the special silica gel was obtained for despatch to London.

SECTION 9. Cutting Oils & Rust Preventatives.

Economy in the use of soluble cutting oils was effected by the use of emulsions containing only 1½% oil instead of the usual 5% - 10%. For this purpose the proportion of emulsifying agent (sulphonated fish oil etc.) was increased slightly. Rhenania consider that the dilute emulsions gave good service performance.

Owing to shortage of supplies, no sulpho-soaps have been used recently by Rhenania-Ossag to prepare ordinary grades of soluble cutting oils. The emulsifying agents have been based upon resin and naphthenic acids. Ozokerite and unrefined Montan Wax were added to reduce foaming.

For straight (non-emulsion) oil for heavy cutting operations about 3% wt. fatty oil which had been sulphurised and chlorinated was used.

I.G. have developed a soluble cutting oil made from a synthetic gas oil by treatment with sulphur monochloride, 1% of this material dissolved in water has been successful in practice.

Anti-corrosion soluble oils for cooling systems and engine protection during storage have been supplied only to the military services.

Anti-rust compounds used by the services were petrolatum, wax and oil mixtures. (Specifications TL147 - 770 C).

SECTION 10. Hydraulic Oils.

For aircraft controls Rhenania-Ossag supplied the Luftwaffe with a -50°C pour point asphalt base mineral oil, - Edeleanu treated - and with a viscosity of 1.6 at 20°C, blended with about 3% Voltol. This oil met the synthetic rubber swelling test requirement of maximum volume increase after 24 hours of 5% and 9% at soaking temperatures of 80° and 100°C respectively.

SECTION 11. Marine Engine Oils. Torpedo Oils.

Compounded marine oils containing blown fatty oil were given up early in the war and were substituted by blends containing such materials as 1½% wt. of a sodium soap of Montan Wax to confer the necessary emulsification properties on the oil.

Torpedo oils were discussed both with Rhenania and with Dr. H. Eckarth at the C.P.V.A. (Chemische Physikalische Versuchsanstalt, at Danishch Nienhof, near Kiel (See Report No.11).

All parts of the launching and motive mechanism of torpedoes driven by I.C. engines (using alcohol or decalin as fuels) were lubricated by an oil of the following type:

11½%	wt. neatsfoot oil
3¾%	rape "
3%	blown rape "
10%	tricresylphosphate
3%	Paraflow
69%	refined mineral oil, about 4°E/50°C (in the Rhenania blends the mineral oil consisted of 29% spindle and 40% 6.5/50°C raffinate).

The tricresylphosphate was added to improve the lubricating properties (Schmierfähigkeit). The properties of the above blend were as follows:

	d20	.920 - .940
Visc. at 20°C		12° - 14°E
" " 50°C		3.1° - 3.7°
Setting Point		- 40°C

Electrically driven torpedoes were lubricated by a blend of mineral oil, fatty oil, Paraflow and 25% - 40% Clophen, a chlorinated hydrocarbon mixture with a specific gravity of 1.6, made by I.G. The blend had a specific gravity slightly over 1.0 and was intended to be "trackless" i.e. not to show the trail of the torpedo, but in practice it was not found possible to eliminate the air or gas trail of the torpedo. The oil had a setting point of -30° to -35°C and a viscosity of 6° - 7°E/50 C

A booklet of the Kriegsmarine lub. oil (Zd M) specifications was obtained from Shell Haus and another edition from the test lab. at Achim.

SECTION 12. Regeneration of Used Oils.

Regeneration of used aero engine oils was carried out by the Deutsche Vacuum in their DuoSol plants at Bremen and Collin (Czechoslovakia). The used oil, after removal of diluent and solid impurities was added in the proportion of 10% to the crude residue fed to the extraction plant. It was demonstrated that used AeroShell Mittel (A.S.M.) containing Voltol could also be recovered in this way, but A.S.M. was not actually regenerated on the large scale.

The Kriegsmarine (Navy) apparently regenerated their own used oils, but no particulars of the processes used were obtained.

—Regeneration of army and other used oils was done by small firms controlled by the Government.

SECTION 13. "Emulsion" Lubricants.

These were introduced to promote oil saving. A mineral oil containing a small percentage of emulsifying agent was supplied to the user who stirred the oil with about an equal volume of water at room temperature and then used the water-in-oil emulsion as a lubricant. Rhenania-Ossag had made a study of this type of lubricant in pre-war days and during the war supplied large quantities of emulsion lubricants for large gas engines, gas compressors, steam cylinders including locomotive, fabric bearings, mine wagon axles, shafting etc. The emulsifying agents employed were Montan Wax, an oxidised synthetic wax (supplied by Henkel as "Emulgator A") and Voltolized unrefined ozokerite, the Voltolization treatment being carried out on a solution or suspension of 5 - 10% ozokerite in oil. The Montan Wax blends were unsuitable for high temperature use as their emulsions became unstable at 70° - 80°C.

Three viscosity grades were supplied for steam cylinder lubrication and three for other purposes. The viscosity of the emulsion is greater than that of the original oil. Thus an oil of 6.5°E at 50°C produced an emulsion with an equal volume of water having a viscosity of about 25°E at 50°C.

SECTION 14. Extracts.

During the war extracts were much in demand and formed a part of normal trade, having nothing to do with WIFO, etc. Demand was such that there was no need to go out for the highest quality, and the Edeleanu extracts were actually diluted with paraffinous residue in order to increase the quantity available. They were used mainly as rubber extenders, printing ink components, waterproofing agents for paper, particularly for black-out (see Amsterdam report on this), putty substitutes, camouflage paint (only small quantities). Only in the case of the requirements for rubber extenders were there any special requirements, and for this purpose a special fraction of viscosity 18°E. at 50°C. known as F.18, was prepared.

Otherwise extracts varied in viscosity from 5 to 50 E. and were blended to meet market requirements. Rhenania also processed some of the Oslebshausen DuoSol plant extract by distillation, thus giving asphalt bottoms and a good quality distillate extract, but as from 1944 the Vacuum Oil Co. appreciated the financial advantage of this business and processed their own DuoSol extract.

SECTION 15. Asphaltic Bitumen.

Owing to the cessation of asphaltic crude imports, production dropped as soon as pre-war stocks had been worked up, as indicated by the following figures:-

<u>Harburg Refinery</u> - pre-war	300,000	tons/annum		
	1940	120,000	"	"
	1944	50,000	"	"

The total German production, which in 1940 was about 700,000 tons per annum, had dropped in 1944 to about 140,000 tons. This drop did not, however, seem to effect the German economy seriously, as there was a fairly adequate supply for industrial uses e.g. for insulating, acid-proof mastics, paper impregnation, roof, hot neck lubricants etc., and tar products were available for the limited amount of road repairs undertaken, coal tar being often employed. This is quite an interesting point, as Dr. Ziegs said that there was really very little traffic, including military, on the roads during the war, this apart from the Autobahnen.

A considerable portion of the German main roads are surfaced with stone sets, and these have stood up fairly well without maintenance. Damage to asphalt roads would mainly seem to have occurred recently, due to the heavy traffic of the retreating German and advancing Allied armies.

The usual straight grades of asphalt were made ranging from 200 pen. down to 10-15 pen. No cutbacks of any kind were made, not even creosote, as all distillates were required for more important purposes.

The crudes available for production of asphalt were Roumanian topped crude, till supplies ceased, as well as Reitbrook and Brigetta (Hannover). Zisternsdoff paraffin base crude was used for the production of blown bitumen.

Some difficulty in making bitumen derivatives occurred owing to the differences between German and imported (e.g. Venezuelan) crudes. For example in preparing blown bitumens from German and

Austrian asphaltic residues it was necessary to give a preliminary blowing at 100 - 120 C, followed by fluxing with a waxy fuel residue and then by a second blowing treatment.

The low acid value of indigenous bitumens, as well as the necessity for using substitute emulsifiers, caused difficulties in the preparation of emulsions. Colophony and related wood products were widely used for the emulsification of bitumen.

Owing to the shortage of solvents, bitumastic paints were partly replaced by emulsions made with clays, and the use of similar mixtures for paper impregnation was also developed during the war. On the whole, however, it did not appear that any new technical applications of asphalt products had been developed.

Though there had been an idea of improving the earth roads in Russia by some cheap process such as soil stabilisation, the Government attitude was firmly in favour of well-known methods and they had no time for substitute processes of unproved value. A small soil stabilisation trial was carried out near Magdeburg using 4-5% of heavy Zisternsdorf fuel, which contains between 4 and 6% of wax. This was added to fine Loess, which was pasted with water and mixed in a pug mill to a pumpable slurry. The resultant material was dried out in layers on the road before rolling, and some attempt was made to establish control of the process by water swelling and cone penetration tests. Dr. Ziegs could not say whether asphalt application work had in fact been done outside his knowledge by the German Government, as the latter were extraordinarily secretive and had never sought Rhenania's co-operation, though he understood they were using bitumenised paper for cartridge cases and for waterproofing some type of plastic land mine, but had not sought the Products Department's co-operation in this matter.

It was noted that the concrete Autobahnen were generally in extremely good condition and only on occasional sections was there any destruction of the surface in the neighbourhood of the joint. In mining districts, where subsidence was likely, asphalt was used instead of concrete owing to the latter's tendency to crack and fissure.

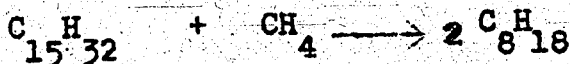
SECTION 16. Research (Amsterdam).

Professor Zerbe, one of the research directors of Rhenania Ossag, was also one of the German appointed directors of the B.P.M. laboratories at Amsterdam. He was interrogated primarily on the work done at Amsterdam during the German occupation, and on research at Hamburg. The Dutch BPM director at Amsterdam, Dr. Caviet, and his staff, stated that successful efforts had been made to keep secret from the Germans the results of their work on their own oil research problems. Therefore the information to which Professor Zerbe had access is mainly that which was instigated at Amsterdam by the Germans themselves. A considerable amount of information on the work done, which was turned over to the Germans, was available at Hamburg, and a list of documents removed is attached at the end of this report.

The following topics were discussed:-

1. Methanization.

The work on methanization, that is the addition of methane to all sorts of hydrocarbons, was done originally by Drs. Slatineanu and Sexauer and co-workers of the Concordia Company in Oberhausen, Rheinland. It was proposed that this work be continued at Amsterdam. The amount of work done by Slatineanu is very considerable. The basic idea was that methane becomes highly active at high temperatures, and high pressures, such as 400°C and 2000 atms and should react with hydrocarbons. An example of such a reaction is the following:



In a few of the early experiments, Slatineanu did obtain a yield of liquid product amounting to more than 100%, indicating that methane had apparently reacted. He then proceeded to try to duplicate such results, but was not successful. From there on he carried out a large number of experiments using all sorts of catalysts, temperatures and pressure conditions, using not only methane, but also hydrogen-methane mixtures as well as nitrogen. The experiments appear to have been of a very haphazard nature. After Slatineanu had failed to show the interaction of methane with hydrocarbons, Sexauer took over and proceeded to check Slatineanu's work in a more scientific manner. His conclusions were that methane did not enter into the reaction. Despite the fact that the results were negative, both Slatineanu and Sexauer have

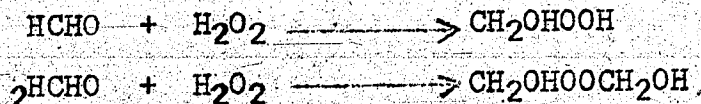
obtained, incidental to the methane reaction, some interesting data on the cracking of hydrocarbons at high pressures. The results, obtained in apparatus varying in size from small autoclaves to one having a volume of 700 liters and capable of operating at 2000 atmospheres, should be studied in detail to increase our knowledge of the behaviour of hydrocarbons under severe conditions of temperature and pressure.

2. Propane Peroxide.

The work on the incomplete oxidation of propane with oxygen was started at the beginning of the War. The date of the first Dutch patent application is April 10, 1940. The work had been continued throughout the war. When the process had been developed to a sufficient extent, the I.G. became interested in building a larger plant for the production of hydrogen peroxide which is the important product of the propane peroxide process. Such plans, however, did not materialize.

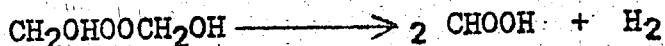
The propane peroxide process is carried out as follows in pilot plant operation:-

12.7 cu.m./hr. of 95% pure propane (containing no propylene) is mixed with 4.8 cu.m./hr. of oxygen. The reaction mixture enters a spherical reaction vessel made of V₂A steel (stainless steel), the inlet point being so arranged that the entering gas mixture does not flow along the walls, but assumes a rotating motion inside of the spherical reactor. The gas mixture is fired by means of a sparkplug, and a temperature of 465°C is maintained in the vessel by varying the amount of oxygen supplied. Once the reaction has started, further firing by means of the sparkplug is not necessary. The optimum contact time is 5 seconds. The reaction vessel is apparently not insulated and the inner wall temperature is maintained at a point slightly above the dew point of the reaction products. These products are primarily water, hydrogen peroxide and oxyalkylperoxides. The oxyalkylperoxides are formed presumably by the interaction of aldehydes (primarily formaldehyde) with hydrogen peroxide:-



The gaseous reaction product is first cooled to a temperature above the dew point of the water formed and then to 35°C. Considerable amounts of aldehydes (acetaldehyde) remain in the gas phase at this temperature and the liquid product which separates out contains a higher concentration of hydrogen peroxide than it would if the entire product were cooled to a lower temperature. The liquid product leaving the first cooler is cooled to 0°C. and is stored. Approximately 1.5 liters of the "peroxide liquid" is formed per hour, the "peroxide liquid" having an active oxygen content of 18 m.g. per cc. Approximately 10 mg. per cc. is due to the hydrogen peroxide content and 8 mg. to the oxyalkylperoxide.

In order to separate a solution of hydrogen peroxide, the organic peroxides are decomposed selectively into formic acid and hydrogen, while hydrogen peroxide remains practically unchanged:-



The mixture is subjected to azeotropic distillation with steam to give 30% hydrogen peroxide and formic acid. Some acetic acid is also formed.

The non-condensable gas coming from the first cooler amounts to 16.3 cu.m./hr. *and has the following composition:-

CO ₂	0.6%
O ₂	3.2
CO	3.0
H ₂	0.1
C ₃ H ₆	8.8
C ₃ H ₈	84.3
	<hr/>
	100.0

This gas is washed with sulfuric acid to remove propylene and returned to the reaction chamber.

* This value is too high - more propane and propylene found in exit gas than available at the inlet.

Calculations have been made on yields. Based on once through operation, 100 cu.m. of propane would yield 5.2 kg. of 30% hydrogen peroxide, and 2.5 kg. of a mixture of formic acid and acetic acid. No calculations have been made on recycle yield.

The process does not operate well on air-propane mixtures, however, no experiments under pressure using air-propane mixtures have been made.

3. Mirasol Process.

No details have been obtained on this process dealing with extraction of oils using antimony trichloride as a solvent. The process is carried out at the melting point of antimony trichloride (about 80°C.) and is characterized by the fact that once-through operation gives as good results as multiple extraction with phenol, furfural, sulfur dioxide, etc. The ratio of solvent to solute is 1 to 1. The losses of antimony trichloride are about 0.01% in a single operation. The details are available in the monthly reports found in Hamburg.

4. Continuous Grease Plant.

The basis for this process is the continuous maintenance of the ratio of water, soap and oil at a constant value. Pressure is required to speed up the saponification and to maintain the water in the system; therefore, the process has to be run under pressure. The saponification is carried out at 180°C., using 8-10 atms pressure. The saponification requires more water than is to be left in the grease; therefore, water has to be released continuously from the process in the form of vapor.

The process is carried out in two (sometimes three stages), with good agitation. In the first stage, the saponification of the fat takes place, oil is added

(some is present at the start to facilitate saponification) and the mass is stirred. It then proceeds to the second stage (under pressure) and cooled to 80°C., where it is again stirred. This is followed by a slow removal of the finished grease.

The autoclaves are small, the reactor volume being 80 liters per 3,000 kg./month production. The operation is truly continuous and needs no supervision for periods of 24 hours.

The whole trick is to set conditions and concentrations so that the quality of the grease remains constant.

5. German Patent Applications of Rhenania-Ossag (under secrecy orders.)

(a) Preparation of Lubricating Oils using Sublimed Aluminum Chloride:

The feature of this application (filed in 1941) is the use of vapor AlCl₃ in preparing lubricating oils from olefins. The process is carried out by subliming AlCl₃ in a separate vessel and allowing the vapor, in the form of a fog, to impinge upon the agitated olefin mixture so that the AlCl₃ is absorbed at the surface in a very finely divided form. The reaction taking place, as well as the quality of the oil and the yield, remain the same, but the aluminium chloride consumption and reaction time are reduced considerably. Thus, instead of using 4% AlCl₃ and 7 hours time to reach zero bromine number according to the old method, the new method requires 3% AlCl₃ and 15 minutes to reach zero bromine number.

A modification of this process lies in using a part of the raw polymer formed as a carrier for AlCl₃. This is done by removing a part of the raw polymer and adding to it, in the same vapor form, mere AlCl₃. The paste produced is pumped into the polymerizing vessel where it is contacted with a fresh olefin mixture. In the preparation of the paste, complexes are formed, and the amount of paste used is such that, in the polymerization step, the net amount of AlCl₃ is 3% based on the olefins to be polymerized. The reaction time is 80 minutes compared to 15 minutes using the alternative

process, and 7 hours using powdered $AlCl_3$ as a catalyst. The advantage of this modification, despite the required reaction time of 80 minutes, is that every polymerizing reactor does not need to be equipped with an $AlCl_3$ sublimator, since the paste can be prepared on a continuous scale.

(b) Preparation of High Quality Lube Oils.

The feature of this process is the stopping of the polymerization reaction of olefins with aluminum chloride prior to the completion of the reaction, removing the unreacted olefins by distillation and subjecting these olefins to a second polymerization treatment. Thus, instead of allowing the bromine number to drop from 120 to zero, it is decreased to only 60, followed by removal, distillation etc. The oil from the first stage may have a viscosity index of 140, while that from the second stage may have a value of 98. Thus, the whole idea is to produce two or three grades of oil; the first grade can be blended with natural (refined) oil to give the proper viscosity index of 100. The poorer grade products from the succeeding stages are blended to give a motor oil of a lower viscosity index. A greater variety of products, along with the fact that a part of the oil made has a better quality than can be obtained otherwise, are the features of the process. An additional feature is that the sludge produced during the incomplete polymerization in the first stage is utilized in the succeeding stages and no more fresh aluminum chloride is added in the later stages.

(c) Pretreatment of Olefin Mixtures prior to polymerization to Lube Oils:

The feature of this process is the pretreating of olefin mixture prior to polymerization the treatment being carried out in the vapor phase at $300^{\circ}C$. In the presence of granular fuller's earth or zinc chloride. The advantage of such a process is that the lube oils produced in the subsequent polymerization step have a lower carbon residue content. Thus, untreated olefins may produce a lube oil having a carbon residue of 0.26, while treated stocks give a lube oil having a carbon residue of only 0.05. The treatment presumably removes some of the aromatic constituents which are formed during the cracking of the gatsch, particularly when the gatsch contains Diesel oil.

(d) Process for separating Naphthenic and Paraffinic fractions:

The feature of this process is the fractionation of high boiling oils in the presence of bitumen or azeotrope forming materials to obtain a separation of paraffinic and naphthenic fractions. For example, a Rumanian oil boiling above 300°C . was vacuum distilled to give six fractions with pour points of -7, -9, -5, -5, -5, $^{\circ}\text{C}$., while in the presence of 30% soft Rumanian bitumen, the six fractions obtained had pour points of -35, -30, -21, -15, -15, -9°C . The materials used for "Azeotropic" distillation do not distill over but remain as residue. There appears to be no mistake about the results obtained; in other words, it could be reasoned that a small part of the bitumen did distill over and acted as pour point depressor. However, this was not the case, since the bottoms were tested for paraffin content and the results obtained showed that an actual separation has been obtained. The process is very recent, and just a short time ago, it was applied to a 900 barrels distillation unit with good results.

(e) Extreme Pressure Lubricants:

- (1) The process consists of treating a mixture of olefins with sulphur chloride, or a mixture of sulphur chloride and sulphur, or sulphur and chlorine, to produce dopes for extreme pressure lubricants. The reaction is carried out at $25-85^{\circ}\text{C}$. with 60% by wt. of S_2Cl_2 for three hours with stirring. The mixture has to be cooled to maintain it at that temperature, and HCl is removed by blowing air through the mixture.

The viscous product obtained contains about 12% S and 9% Cl, the amount of S and Cl varying with the molecular weight of the olefin charged. The use of S and Cl_2 instead of S_2Cl_2 is less desirable in view of lower yields. Under these conditions, both S and Cl_2 are added to the olefins at 120°C . An increase in the extreme pressure lubricating properties can be attained by previously saturating the S_2Cl_2 with S. The following results were obtained by the use of such a dope:

Four-ball machine test.

Mineral Oil	alone			120 kg.
"	"	0.5%	by wt. of dope	300 kg.
"	"	1.0	" "	340 kg.
"	"	3.0	" "	360 kg.
"	"	5.0	" "	500 kg.

The use of this dope does not produce corrosion when the concentration is not in excess of 1%. The extreme pressure lubricating properties of this material can be further enhanced by the addition of such materials as fatty acids salts and naphthenic acid salts.

- (2) The feature of this process involves ~~simultaneous polymerization and sulfochlorination~~ of olefins to produce high flash point extreme pressure lubricants. For that purpose, aluminum chloride was present along with S Cl in concentration of 0.5-3%.
- (3) The feature of this process is the saturation of the olefin mixture with sulphur prior to the treatment with sulphur chloride.
- (4) The feature of this process consists of first vacuum distilling neutralized sludge resulting from the sulphuric acid treatment of lube oils, followed by saturating the overhead fraction with sulphur. It was found that such an overhead fraction could dissolve 2-3% sulphur and thus give good, non-corrosive, extreme pressure lubricants. On the other hand, ordinary petroleum distillates could not dissolve more than 0.5% sulphur (in the cold.)

(f) Plasticizers.

The Rhenania-Ossag Company was supplying the rubber companies with 2000-3000 tons per month of plasticizers. The amount used in the manufacture of such items as rubber heels was 10% while 20% was used in the manufacture of tires. A number of patent applications were filed together with the "Metallgesell-

schaft" (Frankfurt-a.M.) and the following were placed under secrecy orders:-

- (1) The feature of this process is the use of finely divided clay, which has been previously used in the refining of lube oil, in the following manner: The clay is treated with gasoline to remove lube oil from it, but to retain on the clay the aromatic constituents. The clay is then mixed with synthetic rubber, thus providing both a filler and a plasticizer at the same time.
- (2) The use of aluminum chloride sludges as plasticizers for synthetic rubber.
- (3) The use of condensation products of oil extracts and formaldehyde as plasticizers.
- (4) The use of extracted bitumen as a synthetic rubber plasticizer. The asphaltenes are removed by extraction and only the maltenes are utilized.

(g) Greases.

One of the interesting developments of the Rhenania-Ossag Company is the silica gel-oil grease.* The grease is made up by compounding 9% specially prepared silica gel (Deutsche Gold und Silber Scheidung Anstalt-Degussa, Frankfurt a.M.) with 91% by weight of a heavy machine oil (10°E @ 50°C.) The oil has to be free of polar substances. Considerable concentration of aromatics in the oil is to be avoided, the best raw material is a well refined oil. The grease is compounded on rollers in the cold. The product obtained cannot be distinguished from normal greases, and is intended for use in hot bearings, but not for use in high speed bearings where the suspension is broken up and the silica gel is actually centrifuged out. The grease has no melting point and is stable up to the point where the oil begins to crack. Also, the grease does not freeze until the pour point of the oil is reached. No information is available on the method used by Degussa in preparing the silica gel (actually an aerogel). The application of this grease has gone so far as to try it as a protective ointment for sunburn, but no conclusive results have been obtained on the harm of the silica gel to the skin. The use of this grease for such purposes does appear to be

somewhat farfetched.

* A sample of the silica gel has been obtained at the new Rhenania-Ossag Laboratories at Wedel (Möller Optical Works).

(2) The use of mineral oils compounded with aluminum stearate or naphthenate to give greases is the subject of one patent application.

(h) Miscellaneous:

- (1) One patent application deals with the use of lube oil or bitumen emulsions during the actual copolymerization of butadiene and styrene in making synthetic rubber.
- (2) One patent application deals with the use of distillation products of sulfuric acid sludges and their condensation with formaldehyde to give resins.
- (3) One patent application deals with the use of montan wax-like materials as additives to prevent the separation of lube oil residues in engines. Another application specifies the use of "Voltol" in 3% concentration for the same purpose.
- (4) T r e a t i n g .

The use of bauxite instead of fuller's earth for treating oils is said to save on the cost of treating. The granular bauxite is regenerated after ten volumes of oil have been treated over one volume of bauxite. The regeneration is carried out using direct air injection, the temperature rising to 900-1000°C. Five regenerations can be used without decreasing the treating characteristics.

(Signed) V. HAENSEL.

AMSTERDAM DOCUMENTS REMOVED FROM HAMBURG.

1. Physical-chemical properties of hydrocarbons boiling above 20°C (2 copies)
2. A Study of the Structure of unsaturated hydrocarbons using Peracetic acid
3. The preparation of Paraffin Emulsions
4. The Preparation of paper sizings
5. Paper sizing with "Lubex"
6. A list of Researches carried out at Amsterdam
7. Abstracts of Researches on the control of plant diseases

8. Notes on studies on oxidation mechanism
9. Activation of methane by high pressure (3 copies)
10. Propane peroxide preparation (Summary)
11. " " " (Report)
12. Propane peroxide (Dutch copy)
13. Chlorination of paraffin for plant sprays (2 copies)
14. " " " " " " (Dutch copy)
15. Preparation of paraffin emulsions for the paper industry (2 copies)
16. Deparaffination of lubricating oils
17. ~~The preparation of non-corrosive fats~~
18. Properties of fats as a function of method of preparation (Dutch copy)
19. Raman spectra in oil analysis (2 reports)
20. Extreme pressure lubricants

21. Inspection of high boiling oils by absorption analysis
(2 copies)
22. Report on synthetic oil
23. The improvement of oxidation susceptibility of
synthetic bright stocks
24. Ring analysis of hydrocarbon mixtures, in two parts
(2 copies)
25. Deparaffination of lubricating oils
26. A review of control of plant diseases
27. Analysis of cracked distillates, separation of mono-
and di-olefines

28. Constitution of lubricating oils
29. Voltolization
30. Effect of conditions of polymerization on synthesis
31. Solvent extraction of cracked distillates
32. Synthesis of hydrocarbons
33. Raman spectra in hydrocarbon analysis (Dutch copy)
34. UOP characterization factor (Dutch copy)
35. Continuous Grease production
36. Isolation of propane peroxide
37. " " " " (Dutch copy)

38. Oxidation (Dutch copy)
39. Propane peroxide
40. " "
41. Propane peroxide, flow diagram

42. List of reports at Amsterdam

43. Analysis of solid paraffins
44. Hydrocarbons available at Amsterdam
45. Organization chart of the Amsterdam Laboratory
46. Work distribution of the Amsterdam Laboratory
47. Patent applications under secrecy orders, relating to lubricating oils (2 copies)
48. Patent applications under secrecy orders, relating to rubber-oil industry
49. Progress report Amsterdam, 1941
50. 10 monthly reports of Amsterdam, April 1943
~~April 1944~~
51. Production of propane peroxide
52. Dutch patent applications
Nos. 52521, 53470, 55114, 52522, and unnumbered
26th January 1944 (granted; 15th January 1944)
53. Catalytic oxidation studies at Amsterdam
54. List of researches at Amsterdam
55. Progress report on researches at Amsterdam
56. List of reports and patent applications at Amsterdam
57. Status of work at Amsterdam in May 1940
58. Code for Amsterdam organization divisions
59. Partial list of reports removed to Amersfoort, Holland
60. Refining of Persian oils
61. Refining of oils by treatment with $Sb Cl_3$.
62. Correspondence on propane peroxide
63. Fractionation of oils - patent application
64. Corrosion of distillation equipment.