

4. COSTS

As all German refinery equipment was conventional and, in fact, judged by modern UK and US standards, rather old-fashioned, no attempt has been made to collect details of operating costs. Both from the desire to conserve oil and in view of the cheapness and availability of coal, it was very common to use coal, not only for steam and power purposes, but in many cases for the oil processes themselves, an interesting example being the firing of the solvent recovery furnaces of the Duosol plant at Oslebshausen with coal.

5. DISTRIBUTION OF PETROLEUM PRODUCTS

During the war, distribution from the refineries for military purposes was made in the first place to Government-operated depots known as WIFO (Wirtschaftliche Forschungsgesellschaft) installations where motor spirit, aviation spirit and lubricating oils were stored; here leading and blending operations were carried out on the products to meet the official specifications.

The Germans had no inland pipe-line distribution system corresponding to that constructed in this country during the war, and the main distribution of oil products was carried out using existing road, rail and water transport facilities.

An interesting result of the distribution through the WIFO organisation was that no tetra-ethyl lead deposition trouble due to long storage of leaded fuels was encountered as the supplies from these installations to airfields, base depots, etc., took place only a short interval after the leaded blends were completed. Some

evidence of this trouble commencing was found when high-performance fuels of high aromatic content were introduced.

Civilian and industrial supplies, on the other hand, were controlled by the Zentral Büro für Mineralöl, which was a distributing organisation corresponding very closely to the British Petroleum Board, marketing a limited number of petroleum products standardised to meet pool specifications.

Most of the WIFO blending and storage installations had been designed and constructed before the war and were located at strategic sites throughout Germany. In general, these installations were self-contained and consisted of buried or partly buried storage tanks, underground blending and loading pump-houses, lead-blending plants and adequate facilities for bulk loading and for filling aviation spirit, motor spirit and lubricating oils into jerricans and drums. A typical installation of this type was that located at Achim, near Bremen, which had been specially designed to supply the German Navy with the full range of petroleum products. It was built almost entirely underground and included a large number of well-dispersed underground tanks, some of which were as large as 20,000te capacity, giving a total storage of over 250,000 tonnes. All these installations were camouflaged and were adequately serviced with special road and rail facilities.

Summarising, it may be said that the industry devoted its attention to converting German crude oil into the maximum possible production of lubricating oil. Its success may be judged from the fact that it was responsible for between 90 and 95% of the total lubricating oil production during the war.

G—Lubricating Oil Production

1. GENERAL

The preceding section on petroleum refining dealt with the production of natural petroleum lubricants, from which it will have been seen that no new developments in manufacturing processes had been made by the Germans during the war.

As Germany was short of natural petroleum and had produced the bulk of her fuels by synthetic processes based on coal, it was expected that new developments would have occurred in the field of synthetic lubricating oils.

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

Table III in the summary of this report (page 6) shows the sources and methods of manufacture used for the production of the synthetic grades, and more details on the methods of manufacture form the substance of this section.

The synthetic lubricating oils produced fall into two main classes.

Hydrocarbons

These are mainly polymers of olefins made either from a single pure hydrocarbon such as ethylene or from a mixture of olefins such as a specially prepared distillate containing olefins from, say, C_6 , C_{10} . As will be seen later it is also practicable to condense chlorinated paraffins and aromatics to give a lubricating oil

of a more aromatic nature than is obtained from the olefin polymerisation.

Non-Hydrocarbons

The German developments were found to be almost entirely in the field of esters.

As it was the desire of several German industries to enter this field, it seemed that development might take place in different ways according to the raw materials most readily available, and this was found to be the case. IG were found to have played a very large part in this development, but Ruhrchemie, who might also have been expected to contribute largely, in view of the olefins available from their Fischer-Tropsch plants, had made little progress in translating the results of their developments to large-scale production.

2. HYDROCARBONS

i. IG DEVELOPMENTS

a. Research and Development

IG had carried out extensive research work between 1929 and 1936 on the subject of the relation of VI to constitution and the mechanism of formation of olefin polymers. From this work on well-defined chemically homogeneous hydrocarbons, a picture of the structural conditions necessary for producing a good viscosity-temperature behaviour was built up. This work was an indispensable aid to IG in the technical development of the two manufacturing-scale synthetic lubricating oil processes the polymerisation of wax cracking products and ethylene polymerisation—both of which are described below.

b. Process used at the Norddeutsche Mineralöl Raffinerie at Stettin-Pölitz

(1) *General.*—This process is based on the production of olefins by wax cracking.

The wax used must be of a straight-chain structure and must be cracked in the vapour phase with no liquid present. To obtain structures with the double bond at the end of the molecule, the cracking time must be short at high temperatures (forming at least 95% olefins), followed by quenching to prevent isomerisation of the olefin and migration of the double bond. Wax from the atmospheric pressure Fischer-Tropsch process (controlled to a maximum melting-point of 80°C and therefore without the heaviest ends) was a suitable cracking stock. Wax from the medium pressure synthesis was unsuitable, due to the presence of branched-chain paraffins. The wax obtained from brown coal tar distillation was suitable for production of the required type of olefin.

Petroleum wax, as such, could not be easily handled by this process, but could be converted to a suitable product by a combination cracking-hydrogenation step which yielded a mixture of 50% diesel oil and 50% straight-chain paraffin wax. The hydrogenation was carried out at 200ats and 400°C with a tungsten sulphide catalyst, this process being in use at Ludwigshafen, where 1,000te/month slack wax from Hanover crude containing 60% paraffin was processed.

The plant at Stettin-Pölitz cracked a mixed wax containing Fischer-Tropsch wax, brown coal tar wax, and a special petroleum wax prepared at Ludwigshafen.

(2) *Wax cracking.*—The wax was preheated to a temperature of 450–470°C and completely vaporised. It was then passed through a cracking tube bank directly heated by flue-gas, the outlet temperature being controlled at 490–510°C at atmospheric pressure, the average residence time being 25 seconds. 5% steam may be injected into the cracking bank.

The cracked product was quenched in a steam heat-exchanger to 260°C, all the condensate at this temperature being recycled back to the cracking section, the vapours passing to a fractionator, where the desired olefin fraction (35–300°C), was removed as bottoms. The light overhead from the fractionation, representing 26–28% by weight of the wax charged, was made up as follows:—

Methane-ethane-propane	45–40
Ethylene	19–20
Propylene	18–20
Butylene	18–20

The yield of the desired liquid olefin fraction, 35–300°C boiling range, was 70–72% by weight. This product was 95–97% unsaturated with an iodine number of 150 and the conversion on the original wax was 35% per pass.

(3) *Polymerisation.*—This was carried out in water-jacketed agitators of 15–20te capacity. The aluminium chloride was first mixed with light recycle oil from the process and then part of the olefin feed added. After heating initially to 70–80°C to start the reaction, the reaction temperature (which was dependent on the product required) was controlled by the rate of addition of the olefin feed. The time of reaction was 15–22hr and the product was finished by heating the batch to 100–110°C for a further 2hr to polymerise the lower polymers formed in the early part of the reaction. Two grades of oil have been manufactured by this method:—

SS1103	Viscosity normally 3°E at 100°C
SS1106 6°E at 100°C

Operating conditions for the reactors for these products were as follows:—

	SS1103	SS1106
Reaction temperature °C	70	(Low as possible; winter 40, summer 50)
Catalyst consumption (% of finished oil)	7–8	14–16

(4) *Separation and refining of Polymer.*—The AlCl_3 sludge was separated at 80–100°C by ordinary centrifuges, no methanol being needed for separation. The AlCl_3 addition product thus separated was in liquid form.

The lubricating oil portion was treated with water at room temperature to decompose traces of aluminium chloride, then treated with lime and fuller's earth, filtered and distilled under vacuum with steam. Part of the light ends were recirculated for suspension of aluminium chloride in the polymerisation reaction and the remainder used as diesel oil. This oil could also be hydrogenated and then treated with SO_2 and Cl_2 in the Mersol synthesis.

The aluminium chloride addition product from the centrifuges was decomposed with water, treated with lime and fuller's earth and used as steam cylinder oil after stripping of low-boiling hydrocarbons for flash-point specification. This steam cylinder oil was considered to be better than the corresponding product from ethylene, because it was obtained at a lower polymerisation temperature and was less unsaturated.

(5) *Yields.*—The ultimate yields, based on the wax charged to the cracking unit, were approximately as follows:—

	Type of operation	
	SS1103	SS1106
Gas from cracking	.. 27–30% wt	27–30% wt
Diesel oil	.. 7.0	5.6
Finished lubricating oil	.. 49.5–52.5	49.0–52.5
Steam cylinder oil	.. 8.4	11.2
Unaccounted	.. 8.6–2.1	7.0–0.7
	100	100

(6) *Properties of Products.*—Typical inspections of the products, where available, are given in Table LXVIII.

Production.—The plant commenced operation in 1941; the capacity being 1,400te/month lubricating oil, corresponding to about 3,000te/month pure wax. The average production of the plant during the war was about:—

1,000te/month	SS1106
200	Diesel oil
250	Steam cylinder oil

c. Ethylene Process used at Leuna and Schkopau

(1) *General.*—The success of this process depends very largely on the freedom from impurities of the ethylene used, although the effect of the composition of the catalyst and operating conditions also play a considerable part. The ethylene required can be produced from a variety of raw materials, such as cracked gas, thermal rupture of ethane, hydrogenation of acetylene, dehydration of ethyl alcohol and separation from coke oven or town gas.

The Leuna plant was based on the production of ethylene by the thermal cracking of ethane, that at Schkopau on the hydrogenation of acetylene.

Two further plants at Heydebreck and Moosbierbaum were both to be based on the thermal cracking of ethane.

(2) *Thermal cracking of ethane.*—The ethane used was 94% pure; it contained 2% of propane and 4% methane. The gas must be absolutely free from hydrogen.

TABLE LXVIII
NORDDEUTSCHE MINERALÖL RAFFINERIE STETTIN-PÖLITZ

	SS1103	SS1106	Specn. for SS1106	Steam cylinder oil
Sp.gr at 20°C	—	0.866	0.870	0.879
Viscosity at 50°C	cs	332-348	277	520
" " 100°C	cs	21.2	44.4-45.2	38.2min
VI	115-124	113-115	107min	108
Flash point	°C	220min	312	280min
Fire point	°C	—	350	330min
Setting point	°C	—30max	—29	—25max
Neutralisation no.	mgKOH/gm	—	0	0.06max
Saponification no.	mgKOH/gm	0.1	0.1	0.2max
Conradson carbon	%	0.2max	0.2	0.25max
Ash	%	Trace	Trace	0.01max
Noack evaporation loss 250°C	%	—	2.3	5.5max
Pour point	°C	±10°C	IBP °C	150min
Cetane no.	72-73	Sulphur	..	0

In this process ethane (3 vols) and oxygen (1 vol) were preheated separately at atmospheric pressure to 600-650°C and 400°C respectively. The gases were mixed and passed through a cracking furnace, the cracking conditions being 880°C at 300-400mm Hg pressure. The cracked gases were quenched by a water-cooled heat-exchanger to 150°C and then by direct injection of water. A small amount of nitrogen (up to 20% of the ethane) was added to the ethane cracking furnace as a control of cracking.

The cracked gas produced was 1.7 times the volume of the initial ethane and its composition was as follows:—

C ₂ H ₄	31%	CO ₂	1.5%
C ₂ H ₆	17%	C ₃ H ₈	1%
CO	11%	N ₂	2.5%
H ₂	27%	O ₂	1%
CH ₄	8%		

The products were next washed with NaOH in order to remove organic acids and formaldehyde.

Acetylene removal.—This was removed by hydrogenation over a nickel-chromium catalyst at a temperature of about 205°C at atmospheric pressure, the linear velocity being stated to be 10-12cm/sec. The hydrogen required for the hydrogenation was already present in the cracked gas and any oxygen present was hydrogenated to water.

After hydrogenation the gas was compressed to 16.5-18.5ats for further purification.

Oil absorption.—The gas was passed counter-current to a middle oil (from coal hydrogenation) for absorption of benzene and higher hydrocarbons. The rich oil was stripped with steam in the usual way.

Activated charcoal absorption.—The gas was then passed through towers containing activated charcoal to remove the last traces of benzene, the charcoal being regenerated by steaming and cooling with nitrogen. The effectiveness of the absorption was checked by cooling a gas sample down to -60°C and noting whether there was any condensation.

CO₂ removal.—The bulk of the CO₂ was removed by counter-current washing with "Alkazid" solution which was regenerated by heating and steam stripping at atmospheric pressure. The exit gas contained 0.1-0.5% CO₂.

Four counter-current towers in series using caustic soda were used for the complete removal of CO₂; the caustic solution was not regenerated. To check the complete removal of CO₂ a sample of exit gas was continuously bubbled through a barium hydroxide solution.

Linde low-temperature fractionation.—This plant was designed to separate the gas into four fractions. After drying over silica gel the gas was pre-cooled and fed to the first tower under pressure. This tower produced methane and permanent gases as overhead product and ethylene and heavier hydrocarbons as bottoms.

The second tower gave ethylene and ethane as overheads and the residue of propylene and heavier hydrocarbons was passed to fuel gas. The ethylene and ethane overhead fraction passed to a third tower giving ethylene as overhead and ethane as bottoms. The ethylene was compressed to 85-100ats for storage; the ethane, representing about 26.5% of the feed, was recycled to the ethane cracking furnace.

(3) **Hydrogenation of carbide acetylene.**—The lubricating oil plant at Schkopau was built as a semi-works plant to utilise the excess acetylene from the large synthetic rubber plant, Buna Werke A.G. Excess acetylene from the rubber plant was hydrogenated to ethylene using 0.01% palladium oxide catalyst supported on silica gel. The reaction took place at 200-250°C at atmospheric pressure, the yield of ethylene being reported as 72% of theoretical. After water washing, the gas was fractionated in the Linde plant to yield 99% pure ethylene.

(4) **Purity of ethylene.**—The ethylene should be of the highest possible degree of purity and should contain absolutely no oxygen or sulphur compounds. The purer the ethylene the better the quality and yield of the final products and the more rapid the process of polymerisation.

The ethylene concentration should be as high as possible and above 95%. A higher content of inert gases such as nitrogen, methane or ethane is undesirable. Up to a total content of 5%, however, the quality of the polymerised products was not influenced. The influence of the various contaminating gases is given below. All figures are in percentage by volume or in mg/m³. The volumes are calculated at 15°C and 735mm Hg.

Propylene and butylene.—Harmless below 0.5%.

Butadiene and other diolefins.—Harmless below 0.1%.

Carbon dioxide.—This was one of the most dangerous contaminants. Quantities which could just be detected by Ba(OH)₂ solution were sufficient to cause a complete breakdown of polymerisation. For this reason the ethylene must be continually tested by passing through Ba(OH)₂ solution. The latter must not become cloudy, even after 4 weeks.

TABLE LXIX
IG (LEUNA) PRODUCTS

Product	V120	SS903	SS906	R oil	RR oil
Type of product	Light spindle oil	Aviation engine oil	Aviation bright stock	Cylinder oil type	Very heavy
Sp.gr at 20°C	—	0.850–0.860	0.860	ca0.9	0.96
Viscosity at 100°C	20 at 20°C	285	700	—	—
" " 210°C	—	27	44	30	190
VI	—	108min	108	105	70
Pour point	–80	–22	–13	–35	—
Open flash	—	225	224	—	—
Neutralisation no.	—	0.2max	0.06	—	—
Saponification no.	—	0.5max	0.3	—	—
Conradson carbon	—	0.2max	0.2	0.15	5.0
Ash	—	0.01max	nil	—	—
Remarks	Boiling range 240–410°C	—	—	—	Iodine value > 100

Carbon monoxide.—This was not quite so dangerous as CO₂. Up to a content of 0.005% it was still tolerable, although undesirable. A CO content below 0.001% (Linde hæmoglobin test) was required. Quantities from 0.001 to 0.005% had a noticeable effect on quality. The smaller the CO content, the lower the specific gravity and the higher the VI of the final product.

Carbonyl sulphide (COS).—This compound was harmless below 5mg/m³.

Oxygen.—This affects the reaction above 0.1%.

Oxygen-containing products (e.g. alcohols, aldehydes, ketones, ethers, etc.).—These were not nearly so objectionable as CO₂.

Ammonia, amines.—These affect the process. The limiting values had not yet been determined.

Sulphur compounds such as H₂S and mercaptans.—Amount should be below 15mg/m³.

Phosphorus and arsenic compounds.—Their effect was approximately the same as that of the sulphur compounds. The limiting values had not been exactly determined.

Water vapour.—More than 300mg/m³ gave inferior products. Below 250mg/m³ normal polymers were obtained.

The problem of water content was especially important with ethylene since, when the latter was separated in the Linde plant, not all the water was removed, since ethylene forms very stable hydrates with water. Thus the experimental values for the water content (determined by means of finely divided P₂O₅ on glass wool) is many times the calculated value. The ethylene, compressed to 100–200ats, was dried in towers filled with coarse lumps of calcium chloride.

(5) *Composition of the catalyst.*—The AlCl₃ was made at Ludwigshafen and Schkopau by passing CO + Cl₂ over bauxite. The average amount of unsublimable residue in the AlCl₃ should not exceed 2.5% by weight; higher residues caused a fall in VI. The FeCl₃ and TiCl₄ contents of the technical AlCl₃ were also important; SiCl₄ and MgCl₂ had no effect. The FeCl₃ content had a decisive effect on the pour point of the finished product. Under precisely similar conditions of reaction, the following products were obtained, using catalysts with varying iron content:—

Type of AlCl ₃	Viscosity °E at 100°C	VI	Pour point
AlCl ₃ iron free ..	3.83	121	–14°C
" + 0.6% Fe ..	4.39	119	–20°C
" + 2.0% Fe ..	4.03	118	–35°C

An iron content of 2.5–3.5% by weight was required; higher iron contents had a bad effect on the VI. It was also found that this iron content must not be produced merely by mixing AlCl₃ with FeCl₃, but that the iron must either be present as oxide in the bauxite or be added to it. The formation of FeCl₃ must be simultaneous with that of AlCl₃ and they must be sublimed together. This matter of iron content was of great importance when it was desired to produce light oils, i.e. viscosity below 4°E at 100°C. For the synthesis of highly viscous oils of from 5 to 7°E at 100°C, the question was of considerable less importance.

(6) *Polymerisation of ethylene.*—The process was carried out as a batch process in autoclaves, the procedure being as follows:—

- A slurry of AlCl₃ (5–7% wt of the finished lubricating oil) and recycle light oil was made in the autoclave and kept in suspension by stirrers. This slurry occupied 15–25% of the volume of the vessel.
- The reactor was swept out with ethylene, and the purge line isolated.
- Ethylene was added to give a pressure of 30ats.
- The autoclave was heated to 65°C by circulation of hot water in the jacket. Reaction set in immediately, the temperature rose to about 180–210°C, and the pressure to about 35ats. The compound formed by this reaction represented the catalyst for the subsequent polymerisation of ethylene.
- The reaction was quenched at this stage by circulation of cold water in the jacket. This procedure, from the first addition of ethylene, required about 15min.
- When the temperature had been reduced to 110–120°C ethylene at 60ats pressure was introduced and the temperature was held constant by jacket cooling. The polymerisation caused a pressure drop in the reactor until the reactor was full of liquid. At this point the temperatures at the top and bottom of the autoclave were the same and the pressure in the autoclave rose to the ethylene line pressure.
- When the autoclave was full of liquid, the ethylene supply line was closed, the pressure in the reactor was blown down by means of a gas release at the top of the reactor, and the contents were ready for processing. The blow-down gas contained a large proportion of ethylene and after purification it was returned to storage for re-use.

It was alleged to contain about 1% C_2-C_8 paraffins which had to be removed before returning to the synthesis plant.

(7) *Working of the crude polymer.*—The contents of the reactor were blown to a batch separation vessel where, if the oil and catalyst layers did not readily separate, a small amount of methanol was added to effect separation. The mixture was then centrifuged, giving a crude oil, still containing a little catalyst complex, and the bulk of the sludge ($AlCl_3$ -complex). The oil was treated with about 2% of methanol and lime after which it was filter-pressed prior to distillation. In the distillation, three cuts were made, yielding recycle oil, V120 and SS906.

By decomposing the $AlCl_3$ sludge with an aqueous $AlCl_3$ solution (obtained from previous treatments) a highly unsaturated oil was obtained (viscosity 5.0–5.5°E at 100°C; VI ca. 80–85° pour point ca. –20 to –25°C; Conradson carbon ca. 0.6–0.7 and iodine value over 100). After treatment with 6% $AlCl_3$ for 3 hours at 120–150°C, the oil was refined and topped, the residue being known as R oil.

By decomposing the second $AlCl_3$ sludge with water, a highly unsaturated oil known as RR oil was obtained. This oil had drying properties, and was used under the name of Karboresin R as a paint vehicle and as a plasticiser in Buna processing.

Products and properties.—Table LXIX gives the approximate inspection data of the products from this process and an indication of the use to which each one was put.

Yields: (a) *Leuna.*—The maximum working capacity of the plant was 1,200te/month ethylene, but on the average only 1,000te were processed. A breakdown of the production is given below:—

740te	SS906
80 „	R oil
70 „	V120 (the high boiling fractions of the light ends from the distillation—flash point 120°C)
30 „	Ethylene which has not been converted to lubricating oil. This consists of low boiling liquid hydrocarbons like pentane, hexane, etc.
80 „	Working losses
1,000te	

The plant was put into production about 1937 and ceased production in July–August, 1944, subsequent to a bombing attack.

(b) *Schkopau.*—The capacity of this plant was 10,000te/yr based on the partial hydrogenation of carbide acetylene. Starting operation at the beginning of 1944 the plant had produced, on average, 200–300te/month SS906 in the first quarter of 1945. It remained undamaged to the end of the war and is believed to be in operation under Russian control.

(c) *Heydebreck.*—Capacity was 22,000te/yr SS906 based on ethane from the nearby hydrogenation plant at Blechhammer. This ethane was to be thermally cracked without oxygen (Dr. Häuber's process, IG, Oppau) and the ethylene separated by means of a cuprous-diethanolamine salt solution. When the plant was ready to commence operation in the summer of 1944, bombing raids intervened.

(d) *Moosbierbaum.*—With a capacity of 3,000–4,000te/yr SS906, the plant was based on ethane from the hydro-forming plant. This was to be thermally cracked by the Häuber process and the ethylene separated by the Linde plant. Because of bombing, which commenced

in the summer of 1944, this plant also did not come into operation.

Modified Olefin Polymerisation Process

An interesting new process known as the mixed polymerisation process, which involves the polymerisation of mineral lubricating oil fractions concurrently with olefin fractions, was developed by IG and, although the process was never put into operation, due to the effect of air attacks, it was claimed that both the quality and quantity of product were improved over straight blends of synthetic and natural lubricating oil fractions.

In this process, the crude polymer (from the ethylene as well as the cracked wax olefin polymerisation) still containing all the $AlCl_3$ was transferred directly from the reaction vessel and at reaction temperature into contact with a mineral lubricating oil fraction previously heated to 120°C. This fraction, which was freed from wax and asphaltic compounds, had a viscosity of 45.2–53.0cs at 50°C. The mixture so obtained was agitated for about 3 hours at 120°C and then processed as usual for a synthetic oil.

It was claimed that during the agitation the following reactions took place. The $AlCl_3$ contained in the synthetic crude polymer has a polymerising action on those hydrocarbons in the mineral oil susceptible to such action; it has an isomerising action on the naphthenic hydrocarbons in the mineral oil whereby the thermally unstable six-ring systems are converted to stable five-ring hydrocarbons, and finally it brings about alkylation of the aromatic hydrocarbons in the mineral oil by the still reactive low-molecular olefinic synthetic polymer. The final mixed polymer was found to be a better lubricant with better engine performance than the mere physical blend occurring in the S3 oils. This mixed polymerisation process was to have been started in the Moosbierbaum works, the installation of a special mineral oil refinery intended to produce a suitable lubricating oil compound being commenced in 1943.

A refining process was developed specially for the purpose in the research laboratory at Leuna. In this, it was intended to carry out dewaxing and extraction with the same solvent, which consisted of a mixture of 65%wt ethylene dichloride, 25%wt tetrahydrofuran, and 10%wt methanol. After removal of the wax which separated at –20°C, 3–5% liquid ammonia was added to the oil/solvent mixture at –20°C. This caused immediate phase separation into an upper layer of raffinate with a little solvent and a lower layer of extract and a large proportion of solvent.

Owing to air-raids in the summer of 1944, the completion of the plant was prevented. However, the atmospheric and vacuum distillation sections, with a throughput of 1,500te/month crude oil, started up in January, 1945, and were running at full production until the entry of the Russians in April, 1945.

ii. RIENANIA-OSSAG PRODUCTION

The process used at the Harburg plant was the polymerisation of cracked wax olefins with $AlCl_3$.

Raw material.—The process was not very selective as regards the original wax, and the actual material used, which was the wax from Austrian crude, contained from 25 to 30% oil.

The wax was cracked in the vapour phase at a temperature of 560–590°C and gave 60% cracked distillate of 30–310°C boiling range, which had a bromine number of 80–110. Some of the wax was recycled and there was a continuous withdrawal of 10–15% calculated on the fresh feed.

Process.—The catalyst used for polymerisation was a commercial grade of sublimed AlCl_3 . This was pasted with lubricating oil and pumped into the reactors, which were of the batch type. It was not necessary to dry the olefin feed specially, a sufficiently dry material being obtained by ordinary settling; the process was, however, operated under slight pressure to prevent ingress of water vapour.

The basis of the plant was a reactor tank with a centrifugal pump circulating the material through a heat exchanger which would be used at first for removing the heat of reaction and later for heating the material towards the end of the process.

Various methods of operation had been tried, the original process being to operate a series of 7te batches and processing down to a bromine number of 2, the test being carried out by taking a sample of the reaction mixture and separating the catalyst by water washing. This process was carried out at about 10°C and the reaction took about 4–5hr; the reaction was, however, more rapid if the olefins were produced from oil-free wax.

It was later found that better yields were obtained in the following manner. Three 7te batches were started and run to a bromine number of 40. They were then transferred to a larger but similar reactor of about 25te capacity. Circulation was continued for another 6–7hr, the temperature being gradually raised to about 80°C . At a bromine number of 5, the sludge was allowed to settle and was drawn off to another vessel, where it was washed with water and the separated oil returned to the 25te tank and recirculated, while further polymerisation occurred, and the bromine number was finally reduced to about 2. This was an important stage in the process as it increased the yield of high viscosity oil.

The polymerised material was settled for 20hr and then drawn off to larger tanks for still further settling. The next stage in the treatment was to add 5% refining earth and 1% of lime, passing the mixture through a distillation unit to remove light ends, and filtering the residue. This would normally be of a pale yellow colour, but, if the original wax had been oil-free could, at best, have been almost white.

The various grades of oil required were separated by vacuum distillation, giving, essentially, spindle oil, machine oils and a heavy lubricating oil residue which was the required synthetic oil, and was known as SS1006. Part of the machine oil fraction was used for pasting the aluminium chloride catalyst as mentioned above, and the spindle oil cut was generally returned to the polymerisation process, as it was found that this helped considerably to increase the yield of high viscosity oils.

Products and properties.—It would appear that only one product was obtained in any quantity, namely, the SS1006, typical inspection data of which are given in Table LXX.

TABLE LXX

RHENANIA OSSAG SYNTHETIC OILS			
		SS1006	
		(aviation bright stock)	
Sp.gr at 20°C	0.870	
Viscosity at 38°C	700cs	
" " 100°C	45.5cs	
VI	111	
Pour point, $^\circ\text{C}$	-26	
Flash open, $^\circ\text{C}$	294	
Neutralisation no., mgKOH/gm	0.02	
Saponification no., mgKOH/gm	0.05	
Conradson carbon, %	0.25	
Ash	Trace	

Production.—The plant was commissioned in 1941 and reached its maximum production in 1943. It was designed for an output of about 400te/month, but actually reached 700te/month. About the middle of 1944 the plant was bombed and ceased production. It was dismantled and was to have been re-erected in the Hartz mountains, probably underground, but this was never completed.

iii. RUHRCHEMIE SYNTHETIC OIL PRODUCTION

Introduction.—In 1937 Ruhrchemie had developed a scheme of synthetic oil production in the laboratory and in the following year, a plant based on this commenced operation. Designed to produce 1,000te/month it eventually reached a capacity of 1,500te/month of oil of 6–8°E (45.2–60.8cs) at 50°C .

From the start of the project attempts had been made to produce an aviation quality oil, but little success attended the efforts until 1943, when a plant was to have been erected at Holten. Due to bombing attacks, this plant was eventually taken to Willingen, west of Kassel, to be erected underground, but the project was never really started as the plant was bombed at a railway siding near Willingen and partially destroyed. The oil produced was used entirely by the Army as automotive engine oil.

Raw materials.—Two types of raw material were used for the production of olefins, namely, Fischer-Tropsch gas oil and "sweater oil" from the manufacture of wax derived from the process. Gas oil from both atmospheric pressure units and those operating at 10–11ats was suitable, and Ruhrchemie supplemented their own production by purchasing from other plants, the gas oil having a boiling range of about $230\text{--}320^\circ\text{C}$.

The cracking was carried out in a Dubbs unit at $500\text{--}520^\circ\text{C}$, steam being added to the vapours leaving the furnace before entering the reaction chambers. The furnace outlet pressure was 4–5ats. The "sweater oil" was cracked separately at $480\text{--}500^\circ\text{C}$ and the olefins blended with those from the gas oil. It was considered essential that the melting point of the "sweater oil" should not be above 30°C . The following cracked products resulted from both procedures:—

Description	% wt	Properties
Liquid olefins in gasoline boiling range	68	Contained 70% olefins. Boiling range from gas oil, $30\text{--}200^\circ\text{C}$. Boiling range from "sweater oil," $30\text{--}220^\circ\text{C}$
Cracking gas	30	$\text{C}_2 + \text{C}_3$ 18% wt of charge C_2H_4 4% " $\text{C}_1 + \text{C}_2$ and inerts 8% wt of charge
Loss	2	—

Polymerisation.—After drying in a CaCl_2 tower to bring the water content down to 0.015% max, the olefin stock was charged into autoclaves equipped for heating and cooling. The autoclaves were charged at room temperature and 1.2–1.5% by weight of AlCl_3 added, the temperature being controlled according to the following schedule:—

Up to 40°C	2hr
40– 60°C	3,,
60– 80°C	3,,
80– 100°C	4–6hr

The first three steps were reached by control of the amount of cooling applied, whereas the last step required heating by steam.

A technical grade of AlCl_3 with an iron content of about 5% FeCl_3 was used and no advantages were found in using a catalyst of higher purity.

The crude product was transferred to settlers, a certain amount of the catalyst complex-oil mixture being left in the autoclave as solvent for the catalyst for the next charge. The oil, after settling and separating, was treated with 1.5% of Tonsil and 1.5% zinc oxide at 180°C for three hours, the two materials being added separately—apparently a certain amount of chlorinated products was formed. After cooling to 80°C and filtering, the product was distilled yielding, at atmospheric pressure, some gasoline, naphtha and diesel fuels and, under vacuum, diesel fuel and spindle oil as distillates, with the synthetic lubricating oil remaining as the residue. To finish the latter it was treated with 1% by weight of Tonsil at 130°C and filtered.

The yields obtained were:—

Diesel oil	33% wt of cracked feed
Lubricating oil	64% " " "
Loss (including low grade oil in sludge)	3% " " "
	100% " " "

For the month of August, 1940, when the production of lubricating oil was 557te, the cost of production from primary product was given as 20.69pf/kg, and in August, 1941, when the production was 970te, as 13.77pf/kg.

Products and inspection.—Inspection data of the spindle oil and automotive lubricating oil are given in Table LXXI, together with the inspection of a bright stock obtained by polymerising at 15°C with 4–6% of AlCl_3 followed by heating to 60°C.

TABLE LXXI

RUHRCHEMIE SYNTHETIC OILS

	Spindle oil	Motor oil	Bright stock
Sp.gr at 20°C	0.845	0.855	0.865
Viscosity at 50°C, cs	14.8	53.0	288.8
Pole height	1.75	1.75	1.82
Neutralisation no., mgKOH/gm	0.01	0.05	0.05
Saponification no., mgKOH/gm	0.04	0.10	0.10
Flash point, °C	195	220	320
Pour point, °C	—50	—45	—25
Conradson carbon, %	0.01	0.04	0.20
Iodine no.	About 50	About 50	About 30

Quality of products.—As would be expected from the unsaturated nature of the products, the oils were not very stable to oxidation. From the start, an effort was made to produce a bright stock of aviation quality and, although this was achieved by IG Farbenindustrie and Rhenania, Ruhrchemie did not succeed until the end of the war, and never put the process into production. According to Dr. Zorn of IG the difficulties experienced by Ruhrchemie were due entirely to the fact that the olefins produced did not have terminal double bonds. It seems remarkable that with the fund of knowledge available on this type of process no co-operation appears to have existed between the various concerns all working towards the same end.

In an arbitrary oxidation test the viscosity increase of the motor oil was as much as 150%. To improve this instability various methods were tried, four methods in particular being investigated. The first of these, earth treatment at 200°C gave no success; the second, treatment with 2% AlCl_3 for three hours at 180°C, did improve the stability considerably and gave fairly satisfactory results on the large scale, but was abandoned as the improvement was not permanent and the oil was satisfactory for its purpose without this treatment. The use of sulphur containing inhibitors was tried but it was

found that by far the best way of improving the stability was by the addition of these before the polymerising process. In the latest process phenthiazin, β thionaphthol or its anthracene analogue were added to the raw material but it was found that equally good or even superior results were obtained by the addition of ca. 0.3% of sulphur. During the polymerisation process this sulphur was eliminated, as the finished oil only contained a trace of sulphur; it required, however, two treatments with AlCl_3 , the second to eliminate the smell from the first-stage products. The finished oil was said to be "oxygen proof" and gave a viscosity change of only 10–20% in the above-mentioned oxidation test.

Planned Manufacture of Aviation Grade BS (Syntol Process)

Introduction.—Although in no way comparable with the work done by IG, Ruhrchemie had carried out some fundamental work on the best feedstock and the optimum conditions of polymerisation. For example, it was found that certain selected olefins, such as heptene C_7H_{14} , gave no catalyst sludge and produced an excellent lubricating oil of 60.8–76.0cs viscosity at 50°C, and a VI of 125–130, but the conditions could be modified to give a bright stock of 380cs at 50°C. In this polymerisation the catalyst remained granular and no loss by heavy polymers was experienced. This work was to have been continued at an evacuation location, but, due to the non-arrival of certain equipment, this could not be done.

Development work on the control of viscosity of the finished oil by changing conditions during the polymerisation step was also carried out. By using a small amount of AlCl_3 and a comparatively high temperature, an oil of low viscosity was obtained, whilst a reversal of these conditions led to the production of oils of high viscosity. For example, using 1.5%wt of AlCl_3 and keeping the polymerisation temperature at 100°C from the start of the reaction (by preheating the olefinic charge) an oil of 29.5cs at 50°C was produced. If 4–6% of AlCl_3 were used and the temperature kept down to 15°C for 12–20hr, followed by heating to 60°C for 2hr, an oil of 289cs at 50°C was obtained. These latter conditions were those chosen for the planned bright stock production except that, based on experience, the reaction time was limited to 12hr. Experimental work also showed that an improvement in the VI resulted when olefins with longer chains were polymerised as compared to those with short chains, or a mixed feedstock containing both long and short chains. Oils produced from long chains (above C_{12}) were also found to be more resistant to oxidation.

Preparation of feedstocks.—In order to obtain the optimum results in regard to quality it was proposed to polymerise olefins only in the range C_9 to C_{18} . To supplement the material obtained in the cracking process described earlier, it was proposed to add those obtained from the Fischer-Tropsch "recycle process." This process, which was designed to manufacture olefins, gives as product a mixture of olefins and about 20% alcohols, the latter being dehydrated by passing over activated alumina at 340–350°C. These conditions were chosen to avoid migration of the double bond from the terminal position. As the feed contained C_6 – C_{10} compounds it was necessary to separate the C_6 – C_8 fraction by distillation before adding it to the C_9 – C_{18} olefins from the cracking process.

Polymerisation.—The method of polymerisation only differed from that normally used in that phenthiazin (or sulphur) was added to the feedstock and the temperature and polymerisation time were controlled as

follows: 4-6% wt AlCl_3 were used and reacted for 10hr at 15°C , followed by 2hr at 60°C . The finishing of the crude product was analogous to that described for the automotive engine oil.

IV. PRODUCTION BY RHEINPREUSSEN AG, HOMBERG

General.—This process, which is the normal Friedel Crafts condensation of a chlorinated hydrocarbon on to naphthalene, was developed because it was considered that only by the introduction of aromatic rings into synthetic oils could the necessary oxidation and heat stability be obtained. The plant was commissioned in July, 1942, and ceased operating in October, 1944, due to cessation of supplies of Kogasin from the nearby Fischer-Tropsch plant.

Raw material.—The Kogasin cut used had a boiling range of $220\text{--}350^\circ\text{C}$. The process operated on the batch principle, the Kogasin and chlorine being preheated to the reaction temperature ($60\text{--}90^\circ\text{C}$) at which it was held by cooling, the reaction being exothermic. The chlorinated Kogasin contained about 25% of chlorine.

Polymerisation.—The charge to each of the condensation vessels consisted of:—

Chlorinated Kogasin	500-600kg
Naphthalene	200-300 ..
Aluminium	4.5 ..
Aluminium chloride	15-20 ..
Diluent (from overhead of fractionating column)	800-900 ..

The overhead from the fractionating column consisted of unchanged naphthalene, Kogasin, etc., and its composition was controlled by addition of a light Kogasin ($150\text{--}230^\circ\text{C}$). The time of reaction was about 3 hours, the HCl from the reaction being absorbed by water.

After settling to remove the sludge the crude product was neutralised with lime and treated with bleaching earth in one operation, filtered and run to storage. Initial fractionation was carried out at 200mm Hg, the unchanged naphthalene, Kogasin, etc., being removed overhead and the bottoms passed to the high vacuum distillation where it was split into gas oil, spindle, turbine oil and steam cylinder oil.

Products.—Typical inspections of products are given in Table LXXII. The motor oils were blends made from the steam cylinder oil. It is noteworthy that the spindle oil has a high pour point, due to the presence of low boiling-point waxes. Dewaxing plant to remove these was installed, using acetone as solvent, but it was never used, due to the fire hazard.

TABLE LXXII
RHEINPREUSSEN SYNTHETIC OILS

	Spindle oil	Turbine oil	Cylinder oil
Sp.gr at 25°C	0.901	0.928	0.965
Viscosity at 38°C , cs	16.11	43.9	1,939
VI " " 100°C , cs	3.21	5.5	52.4
Pour point, $^\circ\text{C}$	-4	-26	-4
Flash point (closed), $^\circ\text{C}$	171	202	274
Ramsbottom coke, %	0.17	0.24	0.11

N.B.—The motor oils were blended mainly from the turbine oil and the cylinder oil.

Production.—The capacity of the plant was stated to be 10te/day; the table below gives the production for the 3 years during which it operated:—

	Production in tonnes		
	1942	1943	1944
Spindle oil	14.4	236.6	104.8
Turbine oil	113.8	183.4	95.7
Motor oil 6	—	839.8	615.2
Motor oil 7	—	1,267.3	1,081.5
Steam cylinder oil	67.2	455.9	722.8
Hydrochloric acid	239.1	3,820.0	3,763.9

V. MISCELLANEOUS SYNTHETIC HYDROCARBON OILS

a. Cylinder Oils by Paraflow Synthesis

It would appear that a considerable shortage of superheated steam cylinder oils existed in Germany, especially of oils with low pour points for use on the Russian front. Besides the production at Stettin-Pöhlitz and at Rheinpreussen, Homberg, 50te/month was produced at Ludwigshafen by the Paraflow synthesis, using naphthalene and chlorinated wax (some doubt exists as to the exact nature of this material, as it has alternatively been stated to be produced by the action of AlCl_3 on chlorinated wax alone).

b. The TTH Process for Lubricating Oil Manufacture

The Tief-Temperatur Hydrierung process (TTH) is a mild high-pressure hydrogenation of brown coal tar. The only commercial installation in Germany was at the Brabag at Zeitz. The lubricating oil produced has a viscosity index of 50-60 and was sold for use as a motor lubricating oil. It is evident that this source of rather poor quality lubricant was only invoked because of the general shortage of lubricants in Germany during the war.

3. NON-HYDROCARBONS

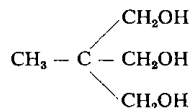
i. IG DEVELOPMENTS

Esters

Following the development of the ethylene polymer lubricating oils, IG had surveyed the field of lubricant application to determine what were the most serious shortcomings of available oils and what methods of improvement were practicable.

This followed discussions with the German Air Ministry, who had stated that castor oil had to be used for high output engines because of its outstanding "oiliness" qualities and in spite of its oxidation instability.

An investigation was carried out into the mechanism of oxidation of natural fats and it was found that their instability was due initially to the glycerol present. To eliminate this, synthetic fats were prepared using such natural fatty acids as oleic, stearic, etc., but using a tri-hydric alcohol which, unlike glycerol, contained only primary hydroxyl groups, the particular alcohol chosen being tri-methylol ethane.



Engine tests showed that such esters fulfilled expectations, combining good lubricating properties with high thermal stability.

Intensive research was then carried out on the connection between constitution and physical and practical lubricating properties. During the years 1938 to 1944, over 3,500 structurally different esters were made and examined. The aim was to develop an ester with high thermal stability combined with a good VI, the lowest possible pour point and the maximum flash point, good miscibility with natural and other synthetic lubricants,

TABLE LXXIII
PROPERTIES OF SOME SYNTHETIC LUBRICATING OIL ESTERS

Acid	Adipic	Beta methyl adipic	Sebacic	Mixed C ₇ monocarboxylic acids
Alcohol	Iso and normal octyl*	Normal octyl	Iso-octyl	Tri-methylol ethane
Sp. gr 20°C	0.922	0.920	0.912	0.958
Viscosity at 38°C cs	7.4	0.9	11.8	16.0
" " 100°C cs	5.9	6.7	8.5	10.8
VI	191	228	189	157
Pour point °C	-24	-36	Below -70	-70
Flash point °C	207	227	235	241

* Half ester of each alcohol.

together with greater lubricating ability or "oiliness" than hydrocarbon oils.

As an outcome of this research, it was found that of the materials available for full-scale production, adipic or methyl adipic acids were the most suitable. Various cuts of the higher alcohols from the isobutyl alcohol synthesis were used to esterify the acid.

Esterification

The actual production method, given below, does not require unusual purities of raw materials.

The required quantities of the alcohol and the acid are charged to a stainless steel reaction vessel fitted with agitators and about 1% of benzene or naphthalene sulphonic acid added as the catalyst. The mixture is heated to 150 to 180°C and the water of reaction distilled off as it is formed. 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 is then contacted with 0.5% wt bleaching earth at 70 to 80°C and filtered. The product thereafter is handled as a normal refined oil. No stabilisers are added and no special handling precautions are necessary.

While the preferred catalyst for the above reaction was a sulphonic acid, for more difficult esterification such as with tri-methylol ethane, when a temperature of above 200°C is used, the best catalyst is zinc dust.

Products.—Details of the range of esters produced are as follows:—

Number	Constitution
E455	Mixed adipic esters of the 140–180°C cuts from the higher, branched-chain alcohols from the isobutyl synthesis.
E504	Mixed adipic esters of the 160–200°C cut of above
E515	180–250°C " "
E1321	" " " " iso C ₈ alcohols. "
E1473	Adipic ester of the product obtained by condensing one molecule of ethylene oxide with i-nonyl alcohol.

Number	Constitution
E3022	Ester of cyclohexanol and 2-methyl adipic acid.
E3025	Adipic ester of p-methylcyclohexanol.

The properties of some of these esters are given in Table LXXIII.

ii. OTHER SYNTHETIC LUBRICANTS

Several other types of compounds were developed for special lubrication purposes, among which may be mentioned:—

- The IG Ludwigshafen product LK2200 made by the addition of about 20 molecules of ethylene oxide to one molecule of tri-methylol propane. These compounds are very viscous with a very good VI. They are soluble in water in all proportions but insoluble in hydrocarbons unless the terminal hydroxy group is esterified.
- Similar products had been made at Leverkusen by reacting tetra-hydrofuran, or mixtures with ethylene oxide, etc., with anhydrous metal chlorides, e.g. FeCl₃ when polymerisation took place.

Although work on these and related products was actively proceeding, they had been produced in small quantities only and had not reached a stage of useful application.

Bibliography

The most important CIOS reports which supplement the information given in this section are:—

XXIV-9	"Synthetic Lubricating Oil Plant—Rheinpreussen, Homburg."
XXVII-69	"The Fischer-Tropsch Plant of Ruhrchemie, Sterkrade-Holten."
XXXII-68	"The Manufacture and Application of Lubricants in Germany."
XXXII-94	"The German Petroleum Industry—Hamburg District."
XXXII-96	"Ruhrchemie, Sterkrade-Holten."
XXXII-107	"IG Farbenindustrie, Leuna."

H—Testing and Evaluation of Products

1. INTRODUCTION

The appraisal of the work done in the development of new fuels and lubricants was made the subject of a separate study, but since a valid appraisal is impossible until all the available documents have been examined, this report must be confined to a record of the major problems studied by the Germans which have so far come to light, without passing judgment on the work done.

2. FUELS

i. AVIATION PETROL

The German supply of aviation fuels was based on the hydrogenation of coal, and this fact caused them to follow a different path from that of the Allies to high engine performance. At the start of the war they had standardised on an 87ON grade (known as B4) of leaded hydropetrol from brown coal, and which contained 5–15% of aromatics. In 1940 an improved fuel (C2) of