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TECHNICAL REPORT No. 146-45

8C432

THE MANUFACTURE AND APPLICATION OF LUBRICATION IN GERMANY

July 1945

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22 Oct. 1945

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To: Commander, Naval Technical Mission in Europe

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

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

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

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

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

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

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By direction of
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New York, N.Y.

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

80434

Serial: 732

7 August 1945.

[redacted]

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

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

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

1. Enclosure (A) is forwarded herewith.

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

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

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TECHNICAL REPORT No. 146-45

THE MANUFACTURE AND APPLICATION OF LUBRICANTS IN GERMANY

July 1945

U. S. NAVAL TECHNICAL MISSION IN EUROPE

SUMMARY

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

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

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

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

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

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

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

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THE MANUFACTURE AND APPLICATION OF LUBRICANTS IN GERMANY

1. Introduction.

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

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

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

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

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

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

1. Introduction (Cont'd.)

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

2. Commercial Supply and Composition of German Lubricating Oils.

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

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

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

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

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TABLE I

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

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

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

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

or inhibitors were included.

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

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

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

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

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

3. Lubricating Oil from Petroleum.

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

TABLE II

PROPERTIES OF GERMAN AIRCRAFT OIL

	Air Ministry Specifications for Aircraft Oil	Typical Synthetic Oil from Olefin Polymerization	Typical Refined Mineral Oil Fraction	Typical Mixture of Equal Parts of Synthetic & Mineral Oils
Density at 68°F.	0.895 max	0.84	0.89	0.875
Viscosity, SSu at 212°F.	95 min	215	57	105
Viscosity, SSu at 122°F.	580-660	1450	250	590
Viscosity Index	96 min	120	98	110
Pour Point, °F	-4 max	-7	± 0	-13
Flash Point, °F	437 min	604	437	464
Fire Point, °F.	437 min	670	500	534
Conradson Carbon % wt.	0.25 max	0.38	0.16	0.22
Ash Content, % wt.	0.01 max	0.001	0.00	0.001
Neutralization Number, Mg.KOH/g.	0.06 max.	0.03	0.03	0.03
Saponification Number, Mg. KOH/g.	0.2 max.	0.11	0.11	0.08

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

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

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

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

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

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

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

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

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

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

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

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

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

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

TABLE III

MIXED POLYMERIZATION TREATMENT OF A LUBRICATING OIL DISTILLATE FROM PETROLEUM

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

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

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

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

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

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

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

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

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

5. The TTH Process for Lubricating Oil Manufacture

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

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

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

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

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

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

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

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

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

(a) Ethylene Polymers as Lubricating Oils.

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

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

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

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

To have a high VI, an oil must consist of molecules which can absorb energy without breaking away from each other. A long straight paraffin chain with no side chains, or with very short side chains, does not have a shape which allows it to interlock itself with other molecules. Aromatic and naphthenic nuclei agglomerations are easily forced apart. Paraffin molecules consisting of a few long chains, however, should be more difficult to pull apart. Paraffins consisting of long chains, which will repulse one another and tend to occupy a large space volume, should be high VI components. Long
side? paraffin chains on aromatic nuclei should also give molecules which tend to interlock themselves with one another, and hence be high in VI. In designing a molecule for high VI, therefore, a paraffin consisting of long side chains on a central structure, or an aromatic or naphthene nucleus with long paraffin chains, should be preferred forms.

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

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

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

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

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

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

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

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

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

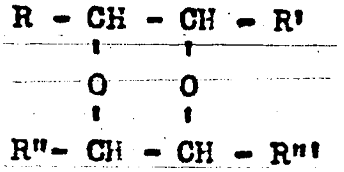
In setting out to synthesize paraffin molecules in the lubricating oil range the polymerization of many low boiling olefins was studied. Propylene alone could never be made to give a product of higher than 70 to 80 VI (I.G. found that by incorporating 1 to 2 percent of polystyrene in the polymerization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

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

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

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

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



$$\begin{array}{ccccccc} R & - & CH & - & CH & - & R' \\ & & | & & | & & \\ & & O & & O & & \\ & & | & & | & & \\ R'' & - & CH & - & CH & - & R''' \end{array}$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

(b) Manufacture of Ethylene Polymers.

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

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

TABLE IV

TYPICAL YIELDS AND PROPERTIES OF ETHYLENE POLYMERS

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

* Determined by boiling point elevation method

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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TABLE V

HYDROCARBON WEIGHT BALANCE FOR BATCH POLYMERIZATION OF ETHYLENE

(Volume of Autoclave = ca. 30 barrels)

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

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

(c) Polymerization of Higher Olefins:

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

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

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

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

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

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

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

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

In all cases, the polymerization was carried out in a stirred antoclane at temperatures of 140 to 175 degrees fahrenheit. AlCl$_3$ equal to approximately 6 percent weight of the feed was added and the reaction required 15 to 20 hours. Rhenania began the reaction at near room temperature, after 5 hours the temperature was raised to 175 degrees fahrenheit, and the reaction proceeded for 7 hours more.

In the polymerization, approximately 95 percent of the olefins were converted to material in the lubricating oil range. Of the total polymer, about 75 percent was recovered as primary product. A low viscosity spindle oil normally was separated. Some oil was recycled as AlCl$_3$ slurrying oil back to the polymerization step. This oil comprised approximately 15 percent of the total yield. Politz prepared in addition a cylinder oil by hydrolysis of the AlCl$_3$ sludge phase. The other two operators apparently did not.

Both Rhenania and Politz used fresh AlCl$_3$ for only one batch polymerization operation. Ruhrchemie, however, started with a 6 percent weight addition of AlCl$_3$, but in the second batch only one percent weight of fresh AlCl$_3$ was added and sludge from the first batch was used to make up the volume of slurry. This was repeated for each subsequent batch, withdrawing only enough sludge to keep the catalyst phase constant in volume. At the end of 60 batches, the total sludge was discarded and the process was then repeated for each 60 batches.

After completion of the polymerization step and removal of the AlCl$_3$ sludge phase, the oil phase was treated for removal of AlCl$_3$, neutralized, and fractionated over clay.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

8. Esters as Lubricating Oil Components:

(a) Development and Application

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

(b) Manufacture of Esters:

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

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

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

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

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

TABLE VI

PROPERTIES OF SOME SYNTHETIC LUBRICATING OIL ESTERS

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

* Half ester of each alcohol.

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

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

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

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

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

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

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

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

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

9. Other Synthetic Lubricating Oils

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

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

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9. Other synthetic Lubricating Oils.

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

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

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

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

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

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

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

10. Additives to Lubricating Oils:

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

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

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

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

(a) Oxidation Inhibitors:

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

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

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

See p. 41-42

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

(b) Corrosion Inhibitors:

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

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

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

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

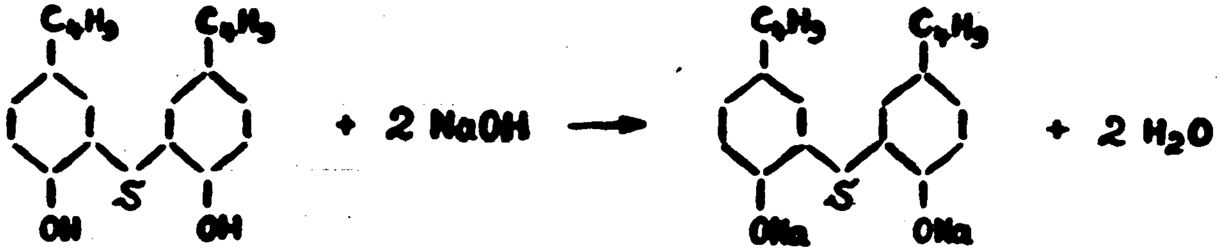
$$R - CH_2 - SO_2 - NH - CH_2COOH + R^1 - OH \longrightarrow$$
$$R - CH_2 - SO_2 - NH - CH_2 - COO - R^1$$

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

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

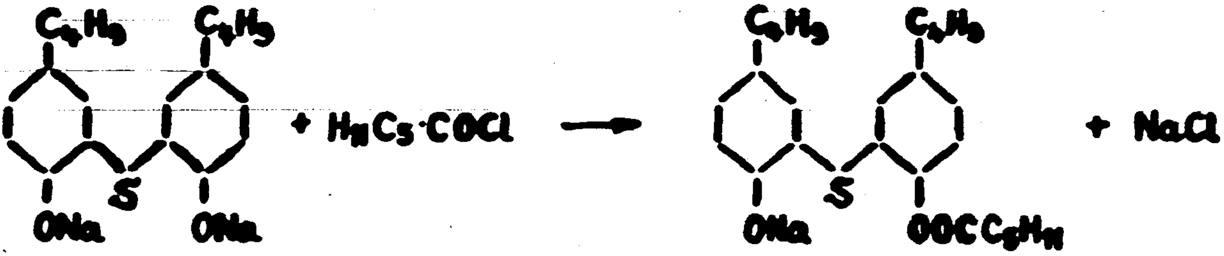
As an emulsifying soap in cutting oils, the soap usage is 4 to 6 percent weight. For the other applications, the ester is used in concentrations of about 3 percent weight.

Reaktionsschema für Inhibitor ([illegible])



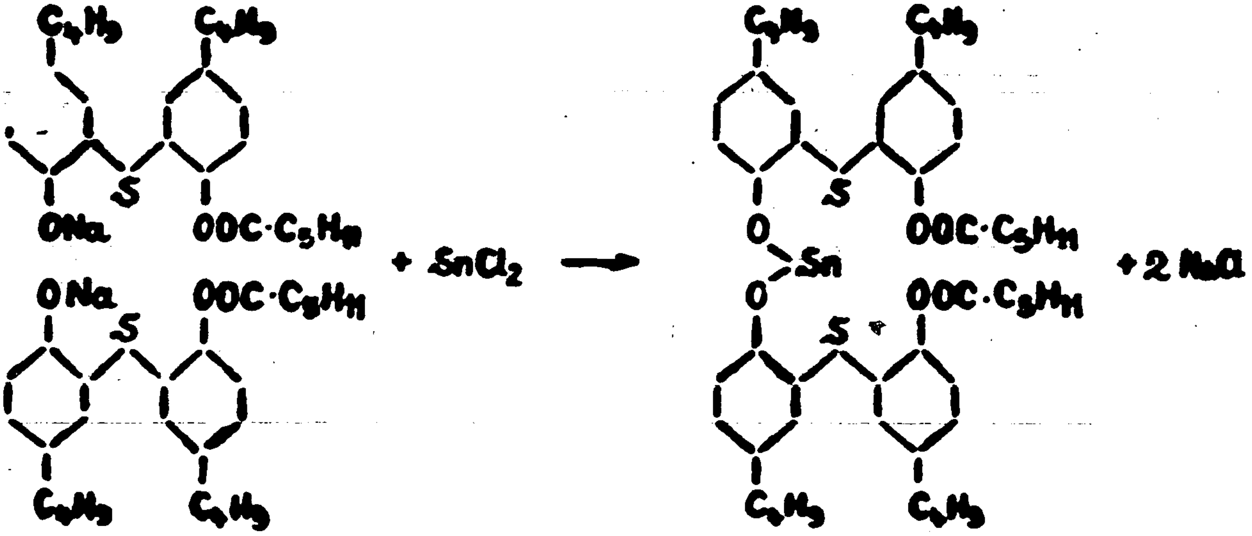
$C_{20}H_{26}O_2S + 2\,NaOH \longrightarrow C_{20}H_{24}O_2Na_2S + 2\,H_2O$

$330 + 80 \longrightarrow 374 + 36$



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

$374 + 134 \longrightarrow 450 + 58$



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

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

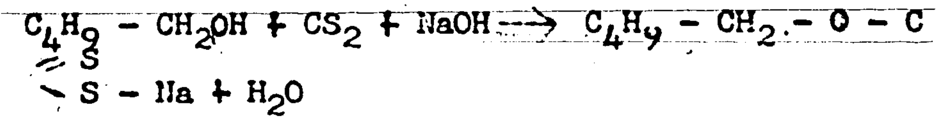
A sample of several gallons of KSE was obtained and forwarded to the Naval Research Laboratory in Anacostia, D. C.

(c) Extreme Pressure Additives:

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

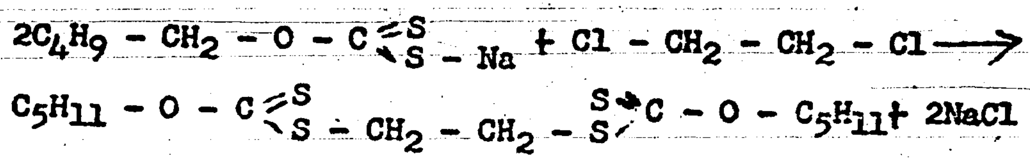
However, an extreme pressure agent should be "corrosive", forming metal compounds, only under the conditions of extreme load. Therefore, an agent should be chosen which is non-corrosive at low temperatures but which becomes suddenly corrosive at some elevated temperature. With such an agent, those spots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

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



$$C_4H_9 - CH_2OH + CS_2 + NaOH \longrightarrow C_4H_9 - CH_2 - O - C \begin{smallmatrix} \diagup\!\!\diagup S \\ \diagdown S - Na \end{smallmatrix} + H_2O$$

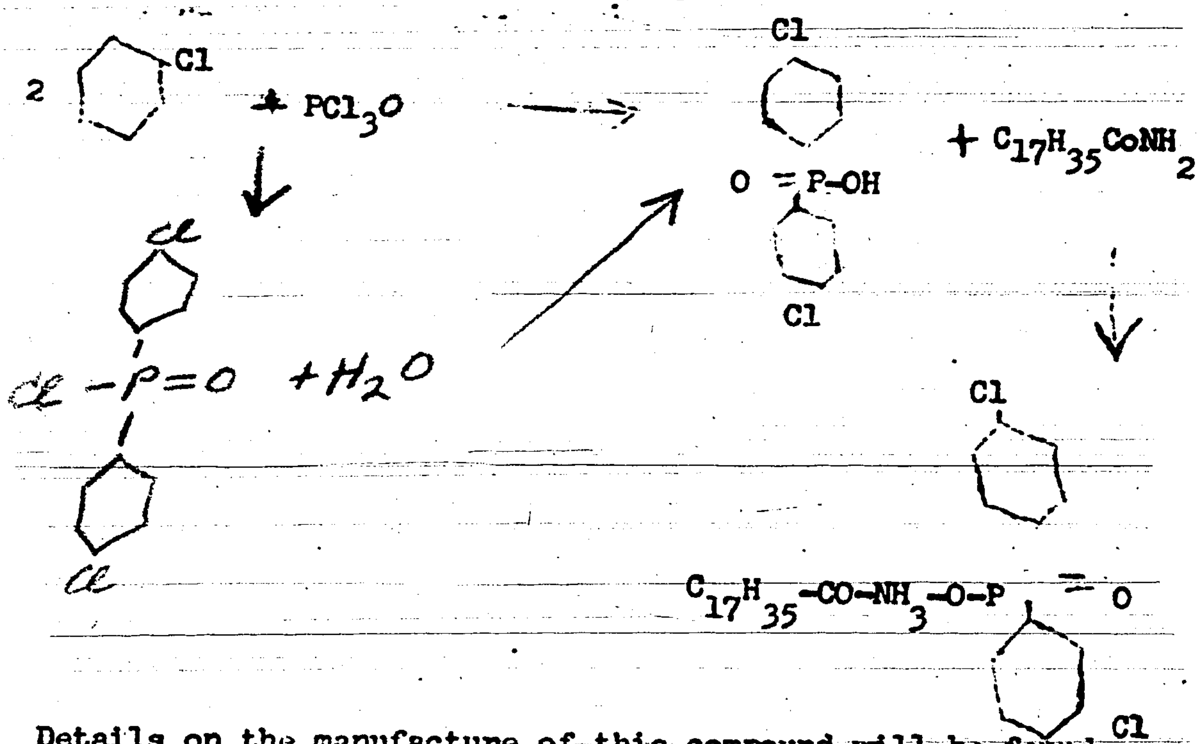
10. Additives to Lubricating Oils, (c) (Cont'd.)



$$2C_4H_9 - CH_2 - O - C\begin{smallmatrix}{=}S\\ \diagdown S - Na\end{smallmatrix} + Cl - CH_2 - CH_2 - Cl \longrightarrow$$

$$C_5H_{11} - O - C\begin{smallmatrix}{=}S\\ \diagdown S\end{smallmatrix} - CH_2 - CH_2 - \begin{smallmatrix}S{=}\\ S\diagup\end{smallmatrix}C - O - C_5H_{11} + 2NaCl$$

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



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

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

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

(d) Pour Point Depressors:

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

(e) Viscosity Index Enhancers:

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

(f) The Principle of Two-Phase Lubricants.

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

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11. Lubricating Greases:

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

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

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

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

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

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

12 Conclusions.

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

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

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

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

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

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

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

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12 Conclusions (Cont'd.)

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

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

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

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

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

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APPENDIX I.

THE MANUFACTURE OF ETHYLENE FROM ETHANE

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

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

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

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

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

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

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

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

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

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

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

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

Appendix I (Cont'd.)

regenerative and hence is costly for high CO concentrations.

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

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

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

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

XVIII Olefinabsorption mittels Cuprosalzlosungen II Mitteilung. (I. G. - Leuna - Dr. Hauber report of 22 July 1942)