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

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.

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

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 bri'-ging 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. Rheingsreussen 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 degredation 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

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 Components, (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 stoichiometric 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.

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