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 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

```
R - CH - CH - R'
    |    |
    O    O
    |    |
R''- CH - CH - R'''
```

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

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 perhaps 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 autoclave 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 fanrenheit. 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.)

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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)

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 Distillate 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