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## HIGH VISCOSITY SYNTHETIC LUBRICANTS FROM ALPHA-OLEFINS

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This invention relates to a method of preparing high viscosity synthetic lubricants from alpha-olefins having the structural formula  $R-CH=CH_2$ , wherein R is an alkyl radical containing from 4 to 14 carbon atoms, and more particularly, the invention relates to a method of preparing high viscosity synthetic lubricating oils by polymerizing these alpha-olefins utilizing a catalyst containing titanium and aluminum.

For many years lubricating oils have been prepared from petroleum distillate fractions by various solvent refining techniques. These oils have been improved further by the incorporation of additives to increase their stability towards oxidation, to reduce their pour point and to increase their viscosity index.

Petroleum base lubricants, however, even with the addition of the best additives have not been improved sufficiently to meet the requirements for the lubrication of certain engines operating under extremely severe conditions or for unusually severe specialty uses. For example, these lubricants could not provide the performance characteristics required of a lubricating oil to be used in a jet engine for aircraft. Thus synthetic lubricants were investigated.

The polymers produced from alpha-olefins, after hydrogenation, gave considerable promise of having the required properties of a high performance lubricant. They had excellent thermal stability and exceedingly good oxidation inhibitor susceptibility, i.e., the addition of oxidation inhibitors rendered the oils extremely resistant to oxidation. They also had relatively low pour points and very good viscosity indexes.

These synthetic oils made from alpha-olefins, however, had one important disadvantage for certain applications since they had a rather low viscosity. Although compounds are available which when added to a hydrocarbon oil will increase its viscosity, they are generally rather troublesome to incorporate into the oil, with the result it is difficult to attain a predetermined desired viscosity or to produce batches of oil having a uniform viscosity from batch to batch.

There now has been found a method whereby alpha-olefins containing from 6 to 16 carbon atoms in the molecule having the structural formula  $R-CH=CH_2$ , wherein R is an alkyl radical containing from 4 to 14 carbon atoms may be polymerized to high viscosity synthetic lubricating oils by contacting the alpha-olefin with a catalyst comprising a titanium halide and an organo aluminum compound.

It is an object of this invention, therefore, to provide a method of preparing high viscosity synthetic lubricants from alpha-olefins having the structural formula  $R-CH=CH_2$ , wherein R is an alkyl radical containing from 4 to 14 carbon atoms.

It is another object of this invention to provide a method of preparing high viscosity synthetic lubricating oils from alpha-olefins having the structural formula  $R-CH=CH_2$ , wherein R is an alkyl radical containing from 4 to 14 carbon atoms by contacting the alpha-olefins with a catalyst containing titanium and aluminum.

It is another object of this invention to provide a method of preparing synthetic lubricating oils having a high viscosity, a high viscosity index and a low pour

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point by contacting alpha-olefins having the structural formula  $R-CH=CH_2$ , wherein R is an alkyl radical containing from 4 to 14 carbon atoms with a catalyst containing titanium and aluminum in which the atomic ratio of titanium to aluminum is adjusted to be within successive specific ranges.

Other objects of the invention will be apparent from the description and claims that follow.

In accordance with the invention an alpha-olefin having the structural formula  $R-CH=CH_2$ , wherein R is an alkyl radical containing from 4 to 14 carbon atoms, is polymerized in the presence of a catalyst consisting essentially of a titanium halide combined with an organo aluminum compound having the formula  $AlR'_nX_{3-n}$ , wherein Al represents aluminum, R' represents a hydrocarbyl group, X is hydrogen or halogen and n is an integer from 1 to 3, and wherein the titanium to aluminum atomic ratio of the catalyst ranges from 1:1 to 1:20. This initial polymerization is carried out for a time ranging from 1 minute to 2 hours, preferably from 1 minute to 45 minutes, to produce high molecular weight polymers which remain dissolved in the unpolymerized monomer and solvent. These polymers are sufficiently high in molecular weight that, if recovered, they would be solids at normal room temperatures, i.e., they are normally solid polymers.

After the desired quantity of high molecular weight polymer has been produced, additional titanium halide is added to the reaction mixture in an amount sufficient to adjust the titanium to aluminum atomic ratio of the catalyst to within the range of from 2:1 to 20:1 and preferably from 2.0:1 to 7:1. This ratio of titanium to aluminum produces lower molecular weight normally liquid polymers, i.e., polymers which are liquid at normal room temperatures of 70° F. to 80° F. This polymerization with the catalyst having the titanium to aluminum atomic ratio ranging from 2:1 to 20:1 is carried out for a time ranging from 1 hour to 16 hours which time is in addition to the time employed for the initial polymerization to produce the high molecular weight solid polymers.

The product prepared, as described, is a synthetic oil in which the high molecular weight solid polymers are contained in the lower molecular weight normally liquid polymers. Thus, the oil not only has all of the desirable properties associated with liquid alpha-olefin polymers, but it also has a high viscosity. Moreover, it has been found that as the quantity of high molecular weight polymers initially produced is increased, the viscosity of the final product oil is also increased. The quantity of high molecular weight solid polymers initially formed depends upon the length of time the initial polymerization reaction is carried on. Consequently, the viscosity of the final synthetic oil may be controlled by the time the initial polymerization is carried on.

The alpha-olefins useful in the preparation of the synthetic oils of this invention are those containing from 6 to 16 carbon atoms in the molecule and include alpha-olefins such as hexene-1, heptene-1, octene-1, nonene-1, decene-1, undecene-1, dodecene-1, tridecene-1, tetradecene-1, pentadecene-1, and hexadecene-1. The pure compounds or mixtures thereof, including mixtures of these alpha-olefins produced by the controlled cracking of petroleum paraffin waxes, may be employed. All of these compounds are characterized by having the general formula  $R-CH=CH_2$ , wherein R is an alkyl radical containing from 4 to 14 carbon atoms. While it is preferred that the alkyl radical be a straight-chain radical, the synthetic oils may be obtained with the branched-chain alkyl radicals. In order to obtain polymers having exceptionally high viscosity indexes and low pour points, however, which polymers are particularly suitable for the produc-

tion of the synthetic lubricants of this invention, it is necessary to employ alpha-olefins wherein the R, or alkyl group, of the  $R-CH=CH_2$  olefin ranges from 6 to 10 carbon atoms and averages 8 carbon atoms. Moreover, it is also necessary in order to produce the high quality synthetic lubricants that the alkyl radicals be straight-chain radicals since, if they are branched-chain, although they may be within the desired  $C_6$  to  $C_{10}$  range when polymerized, the polymers will have materially lower viscosity indexes and higher pour points than those obtained using the straight-chain alpha-olefins.

It has been found particularly important that the average molecular weight of these straight-chain olefins should correspond to about a  $C_{10}$  alpha-olefin since if there is present excessive amounts either of higher or lower molecular weight alpha-olefins such that the average is somewhat above or below the  $C_{10}$  average, the viscosity index and pour point of the polymers produced from such mixtures will be inferior to the corresponding properties of polymers produced from alpha-olefin mixtures averaging 10 carbon atoms per molecule.

The preferred titanium halide to be combined with the organo aluminum compounds to produce the catalysts useful in this invention is titanium tetrachloride although other titanium halides may be used such as titanium tetrabromide, titanium trichloride, and titanium dichloride.

The organo aluminum compounds which constitute the second essential component of the catalysts useful in this invention have the general formula  $AlR'_nX_{3-n}$ . In this formula Al represents aluminum,  $R'$  represents a hydrocarbyl radical, X represents hydrogen or halogen, preferably Cl, Br, or F, and  $n$  is an integer from 1 to 3. The preferred organo aluminum compounds are the aluminum trihydrocarbyls,  $AlR'_3$  ( $n$  being 3, there is no X substituent), and the aluminum dihydrocarbyl hydrides,  $AlR'_2H$ . The aluminum trihydrocarbyls are preferably aluminum trialkyls having from 1 to 18 carbon atoms in the alkyl radical, although other hydrocarbon substituents may be utilized, such as aryl radicals, alkaryl radicals, or the aralkyl radicals. It is preferred that these hydrocarbyl radicals have from 6 to 8 carbon atoms each, and in the aluminum trialkyls it is particularly preferred that each alkyl radical has from 2 to 4 carbon atoms.

In the second group of preferred organo aluminum compounds, the aluminum dihydrocarbyl hydrides, the hydrocarbon substituent may be any of the hydrocarbon radicals enumerated under the aluminum trihydrocarbyls with the aluminum dialkyls being the most preferred. Included in the preferred classes of compounds are the following specific compounds which may be employed as the organo aluminum component of the catalyst: aluminum trimethyl, aluminum triethyl, aluminum tripropyl, aluminum tributyl, aluminum triisobutyl, aluminum diethyl methyl, aluminum diethyl propyl, aluminum diethyl isobutyl, aluminum triphenyl, aluminum tribenzyl, aluminum trixylyl, aluminum diethyl phenyl, aluminum tricyclohexyl, aluminum diethyl hydride, aluminum dipropyl hydride, aluminum diisobutyl hydride, and the like.

Other organo aluminum compounds which may be utilized are the aluminum hydrocarbyl dihydrides such as aluminum ethyl dihydride, the aluminum dihydrocarbyl halides and the aluminum hydrocarbyl dihalides, for example, respectively, aluminum diethyl chloride and aluminum ethyl dichloride.

The titanium halides may be prepared by conventional methods and the organo aluminum compounds also may be prepared by well-known procedures. As is well known, the catalyst should be prepared and handled in the absence of moisture and other harmful materials such as oxygen. This may be accomplished in accordance with established techniques employing a blanket of an inert gas such as nitrogen when preparing, handling, or transferring the catalyst.

The ratio of the titanium halide to the organo alumi-

num compound should be adjusted initially such that the atomic ratio of the titanium to aluminum ranges from 1:1 to 1:20 in order that high molecular weight normally solid polymers will be produced initially by the polymerization of the described alpha-olefins. As has been described, this step of the polymerization is continued until the quantity of high molecular weight polymer is produced which is necessary to give the desired viscosity to the final oil. In general, times ranging from 1 minute to 2 hours are satisfactory, however, for the longer times it is frequently found that so much high molecular weight polymer is produced that the final lubricant may have more the consistency of a grease rather than an oil, i.e., it will be extremely viscous. It is preferable, therefore, to utilize times ranging from 1 minute to 45 minutes since the amount of high molecular weight polymer produced in this length of time is sufficient to produce only viscous oils.

The ratio of titanium to aluminum should not be greater than about 1:1, for example 2:1 or higher, in order that only the desired high molecular weight polymers will be produced. If the ratio of titanium to aluminum is less than about 1:20, the yield of polymer is too low to produce useful amounts of polymer.

After the desired amount of high molecular weight normally solid polymer has been produced, which polymer remains dissolved or dispersed in the unpolymerized monomer and diluent to be described, an additional quantity of titanium halide is added to the reaction mixture. The quantity added should be sufficient to adjust the ratio of titanium to aluminum to within the range of from 2:1 to 20:1 and preferably within the range of from 2:1 to 7:1. It is necessary to use a catalyst having a titanium to aluminum ratio within this range in order to produce normally liquid polymers. As has been stated, if the atomic ratio of titanium to aluminum of the catalyst is less than about 2:1, for example 1:1 or lower, only high molecular weight normally solid polymers are produced. If the ratio of titanium to aluminum is greater than about 20:1, the conversion is exceedingly low with the result no practical amounts of normally liquid polymer are formed. Preferably the atomic ratio of titanium to aluminum should be adjusted to be within the range from 2:1 to 7:1 since the polymers produced by such catalysts are in the highest yield range and have the highest viscosity indexes with the lowest pour points.

The reaction time for the polymerization reaction to produce the liquid polymers ranges from about 1 hour to 16 hours although, in general, little increase in polymers yield has been observed with times in excess of about 2 hours. Some yield of polymer is obtained with times less than 1 hour, of course, particularly with reaction temperatures at the higher end of the range to be described; but, in general, times of at least about 1 hour are preferred in order to produce satisfactory yields of liquid polymers.

The polymerization reactions are preferably performed with the solid catalyst phase as a dispersion in an inert, liquid reaction medium, e.g., a hydrocarbon which does not polymerize in the presence of the polymerization catalyst and which also serves as a diluent for the alpha-olefin. If no diluent is employed, it becomes exceedingly difficult to obtain uniform polymerization because of mixing difficulties so that there may be a considerable variation in the properties of the finished oil from batch to batch. Consequently, it is preferable to employ an inert liquid reaction medium or diluent. The hydrocarbons which may be utilized as a liquid reaction medium and diluent are the saturated hydrocarbons and aromatic hydrocarbons boiling below about 400° F. Preferable hydrocarbons include the pentanes, hexanes, heptanes, octanes, nonanes, decanes, the cycloparaffins, such as cyclohexane, methylcyclohexane, the dimethylcyclohexanes, and the aromatic hydrocarbons, such as benzene, toluene,

and the xylenes. Mixtures of these hydrocarbons also may be employed. It is necessary that the hydrocarbon liquid reaction medium or diluent boil below about 400° F. since after the polymerization reaction it must be separated from the polymer by distillation. If the diluent boils above about 400° F., it cannot be separated from the polymer by distillation since the boiling range of the polymer and the diluent will then overlap.

The quantity of liquid reaction medium or diluent may range between 20 volume percent and 80 volume percent based upon the total volume of the diluent and the alpha-olefin. A convenient range is from 35 volume percent to 65 volume percent based on the volume of the diluent and alpha-olefin.

The quantity of titanium halide-organo aluminum compound catalyst may range, after the addition of all of the titanium halide, from 1 percent to 10 percent by weight based on the weight of the alpha-olefin monomer. Preferably, however, the final quantity of catalyst, after addition of all of the titanium halide, should range from 4 percent to 8 percent based on the weight of the alpha-olefin charged to the reaction.

Both the initial and final polymerization reactions may be carried out at temperatures ranging from about 40° F. to 200° F. and preferably from 60° F. to 120° F. Reaction temperatures slightly above normal room temperatures, i.e., from 80° F. to 90° F., have been found to be particularly useful and convenient.

When the final polymerization reaction has been performed for the desired length of time, the catalyst is destroyed, for example, by adding the polymerization reaction mixture to water, to an aqueous solution of an alcohol, such as aqueous methyl alcohol, or to a dilute aqueous acid solution. The aqueous phase is separated by conventional decantation methods from the hydrocarbon phase and the liquid reaction medium or diluent is removed from the polymer by distillation of the separated hydrocarbon phase.

The initial high molecular weight polymers produced from the alpha-olefins having from 6 to 16 carbon atoms according to the method of this invention have an average molecular weight ranging from about 10,000 to 100,000 or higher. The average molecular weight obtained is determined to some extent by the reaction conditions, but more particularly by the atomic ratio of titanium to aluminum in the catalyst within the range described. The liquid polymers produced from these alpha-olefins according to the method of this invention have an average molecular weight in the range from about 300 to about 2000. When straight-chain alpha-olefins containing from 8 to 12 carbon atoms per molecule and averaging 10 carbon atoms per molecule are polymerized to produce the liquid polymers, such polymers have an average molecular weight from about 400 to about 700.

The polymers produced by the method of this invention are oils having a high viscosity index although they may or may not have a low pour point dependent upon the particular alpha-olefin or mixture of alpha-olefins being polymerized. If the alpha-olefin contains from 8 to 12 carbon atoms and average 10 carbon atoms per molecule, the polymer will have a viscosity index of at least about 140 and a pour point not higher than about -45° F. Accordingly, these polymers without further treatment are useful as lubricants. However, since the polymers as produced are partially unsaturated, i.e., in general about 50 percent of the molecules are unsaturated, it is preferable that the polymer be hydrogenated to remove the unsaturation and consequently increase the oxidation inhibitor susceptibility of the oil although this treatment may raise the pour point somewhat. The amount that the pour point is raised is dependent upon the degree of removal of the low molecular weight olefins from the polymer product. Thus, if dimers, for example, are not removed from the polymer product,

when the product is hydrogenated, the pour point of the hydrogenated product may be as much as 100° F. above the pour point of the product before hydrogenation. If most of the dimers are removed, the pour point may be increased by only 20° F. to 40° F.

The hydrogenation of the polymers may be carried out according to conventional procedures and with conventional hydrogenation catalysts. It has been found that polymers may be hydrogenated at pressures ranging from 2000 to 3000 p.s.i. at temperatures ranging between 350° F. and 450° F. employing either a nickel-on-kieselguhr commercial hydrogenation catalyst or a platinum dioxide commercial hydrogenation catalyst. In general, reaction times of about 8 hours have been used to insure complete hydrogenation of the polymer. Both lower and higher hydrogenation pressures, e.g., at about 1000 p.s.i. to about 10,000 p.s.i., and lower and higher reaction temperatures may also be employed. In addition, any of the conventional hydrogenation catalysts may be utilized although those which are available commercially are preferred.

The following examples are illustrative of specific embodiments of the invention and will serve to demonstrate many of the critical features of the invention. These examples, however, are not to be construed as limiting the invention to the specific embodiments set forth therein. In the examples, the viscosity index is determined by ASTM Method D 567-53 and pour point by ASTM Method D 97-57.

#### EXAMPLE I

A number of experiments were carried out on the polymerization of decene-1 employing a series of titanium tetrachloride-aluminum triisobutyl catalysts wherein the atomic ratio of the titanium to aluminum was varied from catalyst to catalyst in order to demonstrate the criticality of the titanium to aluminum ratio with respect to the molecular weight of the polymers produced.

The reaction temperature ranged from about 80° F. to 95° F., reaction times were from 8 hours to 16 hours, and 100 milliliters of isooctane per 100 grams of decene-1 was utilized as the reaction medium or diluent. The amount of catalyst in each experiment was 5 weight percent based on the decene-1. The results obtained are shown in Table I.

Table I

| Experiment Number | Atomic Ratio of Ti:Al in Catalyst | Total Yield of Polymer <sup>1</sup> | Polymer Pour Point, ° F. |
|-------------------|-----------------------------------|-------------------------------------|--------------------------|
| 1.-----           | 1:10                              | 17.5                                | ( <sup>2</sup> )         |
| 2.-----           | 1:1                               | 65.3                                | ( <sup>2</sup> )         |
| 3.-----           | 2:1                               | 70.8                                | -60                      |
| 4.-----           | 3:1                               | 82.8                                | -65                      |
| 5.-----           | 5:1                               | 81.7                                | -70                      |
| 6.-----           | 7:1                               | 75.3                                | -55                      |
| 7.-----           | 20:1                              | 32.8                                | -50                      |

<sup>1</sup> Weight percent, based on weight of decene-1, after monomer has been removed from polymer by distillation.

<sup>2</sup> Solid at room temp.

The data obtained by these experiments demonstrate that, if high molecular weight solid polymers are to be produced, the atomic ratio of the titanium to aluminum in the catalyst must not be greater than about 1:1 and as the atomic ratio of titanium to aluminum decreases to 1:10, the yield of polymer also decreases markedly; hence, at ratios of about 1:20 the yield is too low to be useful.

The data also demonstrate that, if normally liquid polymers are to be produced, the atomic ratio of titanium to aluminum must be maintained within the range of 2:1 to 20:1 since at ratios below about 2:1 solid polymers are obtained, while at 20:1 the yield obtained is markedly below that of 7:1. Thus, ratios of titanium to aluminum of more than 20:1 should be avoided, but ratios from 2:1 to 7:1 are preferred.

## 7 EXAMPLE II

A second series of experiments was carried out on the polymerization of pentene-1 utilizing the catalysts of Example I, the isooctane diluent of Example I and the same catalyst concentrations as well as reaction temperatures and times utilized in Example I. In every experiment solid polymers were produced even within the range of 2:1 to 20:1 of titanium to aluminum, thus demonstrating that alpha-olefins of less than 6 carbon atoms in the molecule cannot be utilized to produce the synthetic oils of this invention.

## EXAMPLE III

In another series of experiments, hexadecene-1 was employed as the alpha-olefin monomer. The same catalyst and reaction conditions employed in Example I were utilized in these experiments. The results obtained are set forth in Table II.

Table II

| Experiment Number | Atomic Ratio of Ti:Al in Catalyst | Total Yield of Polymer <sup>1</sup> | Polymer Pour Point, ° F. |
|-------------------|-----------------------------------|-------------------------------------|--------------------------|
| 8                 | 1:2                               | 74.5                                | ( <sup>2</sup> )         |
| 9                 | 3:1                               | 91.2                                | 70                       |
| 10                | 5:1                               | 93.2                                | 70                       |
| 11                | 7:1                               | 91.0                                | 70                       |
| 12                | 10:1                              | 82.8                                | 70                       |

<sup>1</sup> Weight percent, based on weight of hexa-decene-1, after monomer has been removed by distillation.

<sup>2</sup> Solid at room temp.

These data demonstrate that the same ranges of titanium to aluminum are applicable to a C<sub>16</sub> alpha-olefin monomer; but it is also apparent from these results that, if a higher molecular weight monomer were used, it would be impossible to obtain polymers liquid at room temperatures.

The experiments in each of Examples I, II, and III were carried out with a single catalyst wherein the titanium to aluminum atomic ratio was held constant during that experiment in order to demonstrate the criticality of the atomic ratio ranges with respect to the molecular weight of the alpha-olefin polymer produced, and to demonstrate the critical range of molecular weight of the alpha-olefin monomer which may be used in the invention. The following example demonstrates the desirable effects obtained when the atomic ratio of the titanium to aluminum is adjusted to provide initially normally solid polymers and thereafter normally liquid polymers in accordance with the method of the invention.

## EXAMPLE IV

In each experiment decene-1 was employed as the monomer and isooctane was the diluent in an amount corresponding to 1 milliliter of diluent per gram of monomer. The catalyst components were titanium tetrachloride and aluminum triisobutyl. Reaction temperatures of 80° F. to 85° F. were maintained throughout.

In the first experiment the calculated amount of aluminum triisobutyl was added to the monomer and diluent, followed immediately by addition of titanium tetrachloride to give a titanium to aluminum atomic ratio of 5:1 and a total catalyst concentration of 5 weight percent based on monomer. The polymerization was carried on for 16 hours, following which the oil was recovered by stripping off the isooctane at atmospheric pressure and distilling off the unreacted monomer at 10 mm. of mercury pressure. This oil was produced for comparison purposes.

In the second experiment the same amount of aluminum triisobutyl as in the first experiment of this example was added to the monomer and diluent, followed immediately by addition of titanium tetrachloride to give a titanium to aluminum ratio of 1:10. After the polymerization had been carried on for one minute, additional titanium tetrachloride was added to adjust the titanium

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to aluminum ratio to 5:1 and give a final catalyst concentration of 5 weight percent based on the decene-1 monomer. The polymerization was carried on for 16 hours with the 5:1 ratio catalyst and the oil was recovered in the same manner as described for the first experiment of this example.

In the third experiment the same procedure as in the second experiment was followed except that a time of 20 minutes was employed for the initial polymerization before the additional titanium tetrachloride was added to increase the ratio from 1:10 to 5:1. The concentration of the final catalyst was 5 weight percent based on the monomer and after polymerizing for 16 hours using the catalyst having the 5:1 ratio, the oil was recovered in the same manner as employed in the first two experiments. The results are shown in Table III. Viscosities are in Saybolt Seconds Universal.

Table III

| Experiment Number                                            | 1     | 2                  | 3                   |
|--------------------------------------------------------------|-------|--------------------|---------------------|
| Yield of Polymer                                             | 81    | 84                 | 80                  |
| Al( <i>i</i> Bu) <sub>3</sub> , g. per 100 g. of decene      | 0.833 | 0.833              | 0.833               |
| TiCl <sub>4</sub> , g. per 100 g. decene, first added        | 4.155 | 0.083              | 0.083               |
| TiCl <sub>4</sub> , g. per 100 g. decene, subsequently added | 0.0   | 4.083 after 1 min. | 4.083 after 20 min. |
| Viscosity Index                                              | 157   | 155                | 149                 |
| Pour Point (° F.)                                            | -50   | -45                | -45                 |
| Viscosity at 100° F. SSU                                     | 161.4 | 188.6              | 40.80               |
| Viscosity at 210° F. SSU                                     | 50.2  | 53.8               | 85.2                |

These data demonstrate how the viscosity of the synthetic oil is increased by polymerizing a portion of the monomer initially to high molecular weight normally solid polymers and thereafter polymerizing the remaining monomer to normally liquid polymers. It is not known whether the high molecular weight polymers are dissolved in the liquid polymers or whether there is obtained an extremely intimate dispersion of these high molecular weight polymers in the liquid polymers. The result, however, is the production of synthetic lubricants of high and controllable viscosity.

When these polymers are hydrogenated, after dimers have been removed by distillation at about 2 mm. mercury pressure, using a nickel-on-kieselguhr hydrogenation catalyst, for example, at temperatures ranging from 400° F. to 450° F. under pressure of from 1000 to 2000 p.s.i.g. for 8 hours, hydrogenated high viscosity fractions are obtained having viscosity indexes of at least about 135 and pour points not higher than about -25° F. Moreover, the saturated oils exhibit high oxidation inhibitor susceptibility and thus are useful for the lubrication of jet engines, as hydraulic fluids and similar uses which require such high quality performance characteristics.

I claim:

1. The method of preparing high viscosity synthetic lubricating oils from alpha-olefins having the structural formula R-CH=CH<sub>2</sub>, wherein R is an alkyl radical containing from 4 to 14 carbon atoms which comprises contacting the alpha-olefin for a time ranging from 1 minute to 2 hours with a catalyst comprising a titanium halide combined with an organo aluminum compound having the formula AlR'<sub>n</sub>X<sub>3-n</sub>, wherein Al is aluminum, R' is a hydrocarbyl group, X is selected from the group consisting of hydrogen and halogen, and *n* is an integer from 1 to 3, wherein the titanium to aluminum atomic ratio of the catalyst ranges from 1:1 to 1:20 to produce normally solid polymers, thereafter adding a sufficient quantity of said titanium halide to adjust said titanium to aluminum atomic ratio of the catalyst to within the range from 2:1 to 20:1 and continuing the contacting for an additional time ranging from 1 hour to 16 hours to produce normally liquid polymers.

2. The method according to claim 1 wherein the time of contacting with the catalyst having the titanium to

aluminum atomic ratio of 1:1 to 1:20 ranges from 1 minute to 45 minutes.

3. The method of preparing a high viscosity synthetic lubricating oil from alpha-olefins having the structural formula  $R-CH=CH_2$ , wherein R is an alkyl radical containing from 4 to 14 carbon atoms which comprises contacting the alpha-olefin for a time ranging from 1 minute to 2 hours with a catalyst comprising titanium tetrachloride and an aluminum trialkyl wherein the titanium to aluminum atomic ratio ranges from 1:1 to 1:20 to produce normally solid polymers, thereafter adding a sufficient quantity of said titanium tetrachloride to adjust said titanium to aluminum atomic ratio of the catalyst to within the range of from 2:1 to 20:1 and continuing the contacting for an additional time ranging from 1 hour to 16 hours to produce normally liquid polymers.

4. The method according to claim 3 wherein the time of contacting with the catalyst having the titanium to aluminum atomic ratio of 1:1 to 1:20 ranges from 1 minute to 45 minutes.

5. The method of preparing a high viscosity synthetic lubricating oil from alpha-olefins having the structural formula  $R-CH=CH_2$ , wherein R is an alkyl radical containing from 4 to 14 carbon atoms which comprises contacting the alpha-olefin for a time ranging from 1 minute to 2 hours with a catalyst comprising titanium tetrachloride and aluminum triethyl wherein the titanium to aluminum atomic ratio ranges from 1:1 to 1:20 to produce normally solid polymers, thereafter adding a sufficient quantity of said titanium tetrachloride to adjust said titanium to aluminum atomic ratio of the catalyst to within the range of from 2:1 to 20:1 and continuing the contacting for an additional time ranging from 1 hour to 16 hours to produce normally liquid polymers.

6. The method according to claim 5 wherein the time of contacting with the catalyst having the titanium to aluminum atomic ratio of 1:1 to 1:20 ranges from 1 minute to 45 minutes.

7. The method of preparing a high viscosity synthetic lubricating oil from alpha-olefins having the structural formula  $R-CH=CH_2$ , wherein R is an alkyl radical containing from 4 to 14 carbon atoms which comprises contacting the alpha-olefin for a time ranging from 1 minute to 2 hours with a catalyst comprising titanium tetrachloride and aluminum tripropyl wherein the titanium to aluminum atomic ratio ranges from 1:1 to 1:20 to produce normally solid polymers, thereafter adding a sufficient quantity of said titanium tetrachloride to adjust said titanium to aluminum atomic ratio of the catalyst to within the range of from 2:1 to 20:1 and continuing the contacting for an additional time ranging from 1 hour to 16 hours to produce normally liquid polymers.

8. The method according to claim 7 wherein the time of contacting with the catalyst having the titanium to aluminum atomic ratio of 1:1 to 1:20 ranges from 1 minute to 45 minutes.

9. The method of preparing a high viscosity synthetic lubricating oil from alpha-olefins having the structural formula  $R-CH=CH_2$ , wherein R is an alkyl radical containing from 4 to 14 carbon atoms which comprises contacting the alpha-olefin for a time ranging from 1 minute to 2 hours with a catalyst comprising titanium tetrachloride and aluminum triisobutyl wherein the titanium to aluminum atomic ratio range from 1:1 to 1:20 to produce normally solid polymers, thereafter adding a sufficient quantity of said titanium tetrachloride to adjust said titanium to aluminum atomic ratio of the catalyst to within the range of from 2:1 to 20:1 and continuing the contacting for an additional time ranging from 1 hour to 16 hours to produce normally liquid polymers.

10. The method according to claim 9 wherein the time of contacting with the catalyst having the titanium to

aluminum atomic ratio of 1:1 to 1:20 ranges from 1 minute to 45 minutes.

11. The method of preparing a high viscosity synthetic lubricating oil from alpha-olefins having the structural formula  $R-CH=CH_2$ , wherein R is an alkyl radical containing from 4 to 14 carbon atoms which comprises contacting the alpha-olefins for a time ranging from 1 minute to 2 hours with a catalyst comprising titanium tetrachloride and aluminum dialkyl hydride wherein the titanium to aluminum atomic ratio ranges from 1:1 to 1:20 to produce normally solid polymers, thereafter adding a sufficient quantity of said titanium tetrachloride to adjust said titanium to aluminum atomic ratio of the catalyst to within the range of from 2:1 to 20:1 and continuing the contacting for an additional time ranging from 1 hour to 16 hours to produce normally liquid polymers.

12. The method according to claim 11 wherein the time of contacting with the catalyst having the titanium to aluminum atomic ratio of 1:1 to 1:20 ranges from 1 minute to 45 minutes.

13. The method of preparing a high viscosity synthetic lubricating oil from alpha-olefins having the structural formula  $R-CH=CH_2$ , wherein R is an alkyl radical containing from 4 to 14 carbon atoms which comprises contacting the alpha-olefin for a time ranging from 1 minute to 2 hours with a catalyst comprising titanium tetrachloride and aluminum diisobutyl hydride wherein the titanium to aluminum atomic ratio ranges from 1:1 to 1:20 to produce normally solid polymers thereafter adding a sufficient quantity of said titanium tetrachloride to adjust said titanium to aluminum atomic ratio of the catalyst to within the range of from 2:1 to 20:1 and continuing the contacting for an additional time ranging from 1 hour to 16 hours to produce normally liquid polymers.

14. The method according to claim 13 wherein the time of contacting with the catalyst having the titanium to aluminum atomic ratio of 1:1 to 1:20 ranges from 1 minute to 45 minutes.

15. The method of preparing a high viscosity synthetic lubricating oil from alpha-olefins having the structural formula  $R-CH=CH_2$ , wherein R is an alkyl radical containing from 4 to 14 carbon atoms which comprises contacting the alpha-olefin for a time ranging from 1 minute to 45 minutes with a catalyst comprising a titanium halide combined with an organo aluminum compound having the formula  $AlR'_nX_{3-n}$ , wherein Al is aluminum, R' is a hydrocarbon group, X is selected from the group consisting of hydrogen and halogen, and n is an integer from 1 to 3, wherein the titanium to aluminum atomic ratio of the catalyst ranges from 1:1 to 1:20 to produce normally solid polymers, thereafter adding a sufficient quantity of said titanium halide to adjust said titanium to aluminum atomic ratio of the catalyst to within the range of from 2:1 to 7:1 and continuing the contacting for an additional time ranging from 1 hour to 16 hours to produce normally liquid polymers.

16. The method of preparing a high viscosity synthetic lubricating oil from alpha-olefins having the structural formula  $R-CH=CH_2$ , wherein R is an alkyl radical containing from 4 to 14 carbon atoms which comprises contacting the alpha-olefin for a time ranging from 1 minute to 45 minutes with a catalyst comprising titanium tetrachloride and aluminum triisobutyl wherein the titanium to aluminum atomic ratio ranges from 1:1 to 1:20 to produce normally solid polymers, thereafter adding a sufficient quantity of said titanium tetrachloride to adjust said titanium to aluminum atomic ratio of the catalyst to within the range of from 2:1 to 7:1 and continuing the contacting for an additional time ranging from 1 hour to 16 hours to produce normally liquid polymers.

17. The method of preparing a high viscosity synthetic lubricating oil from alpha-olefins having the structural formula  $R-CH=CH_2$ , wherein R is an alkyl radical containing from 4 to 14 carbon atoms which comprises contacting the alpha-olefin for a time ranging from 1 minute

to 45 minutes with a catalyst comprising titanium tetrachloride and aluminum diisobutyl hydride wherein the titanium to aluminum atomic ratio ranges from 1:1 to 1:20 to produce normally solid polymers, thereafter adding a sufficient quantity of said titanium tetrachloride to adjust said titanium to aluminum atomic ratio of the catalyst to within the range of from 2:1 to 7:1 and continuing the contacting for an additional time ranging from 1 hour to 16 hours to produce normally liquid polymers.

18. The method of preparing a high viscosity synthetic lubricating oil having a viscosity index of at least 140 and a pour point not higher than  $-45^{\circ}$  F. which comprises contacting an alpha-olefin having the structural formula  $R-CH=CH_2$ , wherein R is a straight-chain alkyl radical containing from 6 to 10 carbon atoms and having an average of 8 carbon atoms for a time ranging from 1 minute to 45 minutes with a catalyst comprising a titanium halide combined with an organo aluminum compound having the formula  $AlR'_nX_{3-n}$ , wherein Al is aluminum, R' is a hydrocarbyl group. X is selected from the group consisting of hydrogen and halogen, and n is an integer from 1 to 3, wherein the titanium to aluminum atomic ratio of the catalyst ranges from 1:1 to 1:20 to produce normally solid polymers, thereafter adding a sufficient quantity of said titanium halide to adjust said titanium to aluminum atomic ratio of the catalyst to within the range of from 2:1 to 20:1 and continuing the contacting for an additional time ranging from 1 hour to 16 hours to produce normally liquid polymers.

19. The method according to claim 18 wherein the

quantity of titanium halide added is sufficient to adjust the titanium to aluminum atomic ratio of the catalyst to within the range of from 2:1 to 7:1.

20. The method of preparing a high viscosity synthetic lubricating oil having a high oxidation inhibitor susceptibility, a viscosity index of at least 135 and a pour point not higher than about  $-25^{\circ}$  F. which comprises contacting an alpha-olefin having the structural formula  $R-CH=CH_2$ , wherein R is a straight-chain alkyl radical containing from 6 to 10 carbon atoms and having an average of 8 carbon atoms for a time ranging from 1 minute to 45 minutes with a catalyst comprising a titanium halide combined with an organo aluminum compound having the formula  $AlR'_nX_{3-n}$ , where Al is aluminum, R' is a hydrocarbyl group, X is selected from the group consisting of hydrogen and halogen, and n is an integer from 1 to 3, wherein the titanium to aluminum atomic ratio of the catalyst ranges from 1:1 to 1:20 to produce normally solid polymers, thereafter adding a sufficient quantity of said titanium halide to adjust said titanium to aluminum atomic ratio of the catalyst to within the range of from 2:1 to 20:1, continuing the contacting for an additional time ranging from 1 hour to 16 hours to produce normally liquid polymers, and hydrogenating the polymer product to produce the saturated oil.

#### References Cited in the file of this patent

##### FOREIGN PATENTS

873,067 Great Britain ----- July 19, 1961

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,113,167

December 3, 1963

Richard W. Sauer

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 44, for "has" read -- have --; column 7, line 29, footnote 1, for "hexa-decene" read -- hexadecene --; column 8, Table III, fourth column, line 9 thereof, for "40.80" read -- 408.0 --; same column 8, line 71, after "range" insert -- of --; column 10, line 47, for "hydrocarbon" read -- hydrocarbyl --; column 11, line 20, strike out the period and insert a comma; column 12, line 14, for "where" read -- wherein --.

Signed and sealed this 12th day of May 1964.

(SEAL)

Attest:

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