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SYNTHETIC LUBE COMPOSITION AND PROCESS.

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Description

This invention relates to novel compositions prepared from synthetic lubricants by reaction with olefins and to the process for their production. The invention particularly pertains to the modification of a high viscosity index synthetic lubricant oligomer fraction employing low molecular weight by-product oligomer fractions as reactant. The modified synthetic lubricants are themselves useful, inter alia, as lubricants with improved thermal stability.

Efforts to improve upon the performance of natural mineral oil based lubricants by the synthesis of oligomeric hydrocarbon fluids have been the subject of important research and development in the petroleum industry for at least fifty years and have led to the relatively recent market introduction of a number of superior polyalpha-olefin synthetic lubricants, primarily based on the oligomerization of alpha-olefins or 1-alkenes. In terms of lubricant property improvement, the thrust of the industrial research effort on synthetic lubricants has been toward fluids exhibiting useful viscosities over a wide range of temperature, i.e., improved viscosity index, while also showing lubricity, thermal and oxidative stability and pour point equal to or better than mineral oil. These new synthetic lubricants lower friction and hence increase mechanical efficiency across the full spectrum of mechanical loads from worm gears to traction drives and do so over a wider range of operating conditions than mineral oil lubricants.

One characteristic of the molecular structure of 1-alkene oligomers that has been found to correlate very well with improved lubricant properties in commercial synthetic lubricants is the ratio of methyl to methylene groups in the oligomer. The ratio is called the branch ratio and is calculated from infra red data as discussed in "Standard Hydrocarbons of High Molecular Weight", *Analytical Chemistry*, Vol.25, no.10, p.1466 (1953). Viscosity index has been found to increase with lower branch ratio. Until recently, as cited herein, oligomeric liquid lubricants exhibiting very low branch ratios have not been synthesized from 1-alkenes. For instance, oligomers prepared from 1-decene by either cationic polymerization or Ziegler catalyst polymerization have branch ratios of greater than 0.20. Shubkin, *Ind. Eng. Chem. Prod. Res. Dev.* 1980, 19, 15-19, provides an explanation for the apparently limiting value for branch ratio based on a cationic polymerization reaction mechanism involving rearrangement to produce branching. Other explanations suggest isomerization of the olefinic group in the one position to produce an internal olefin as the cause for branching. Whether by rearrangement, isomerization or a yet to be elucidated mechanism it is clear that in the art of 1-alkene oligomerization to produce synthetic lubricants as commercially practiced excessive branching occurs and constrains the limits of achievable lubricant properties, particularly with respect to viscosity index. Obviously, increased branching increases the number of isomers in the oligomer mixture, orienting the composition away from the structure which would be preferred from a consideration of the theoretical concepts discussed above.

U.S. Patent 4,282,392 to Cupples et al. discloses an alpha-olefin oligomer synthetic lubricant having an improved viscosity-volatility relationship and containing a high proportion of tetramer and pentamer via a hydrogenation process that effects skeletal rearrangement and isomeric composition. The composition claimed is a trimer to tetramer ratio no higher than one to one. The branch ratio is not disclosed.

A process using coordination catalysts to prepare high polymers from 1-alkenes, especially chromium catalyst on a silica support, is described by Weiss et al. in *Jour. Catalysis* 88, 424-430 (1984) and in Offen. DE 3,427,319. The process uses low temperatures to produce high polymer and does not disclose lubricants having unique structure.

Recently, novel lubricant compositions (referred to herein as HVI-PAO) comprising polyalpha-olefins and methods for their preparation employing as catalyst reduced chromium on a silica support have been disclosed in U.S. Patents 4,827,064 and 4,827,073. The HVI-PAO lubricants are made by a process which comprises contacting C₆-C₂₀ 1-alkene feedstock with reduced valence state chromium oxide catalyst on porous silica support under oligomerizing conditions in an oligomerization zone whereby high viscosity, high VI liquid hydrocarbon lubricant is produced having branch ratios less than 0.19 and pour point below -15°C. The process is distinctive in that little isomerization of the olefinic bond occurs compared to known oligomerization methods to produce polyalpha-olefins using Lewis acid catalyst. Lubricants produced by the process cover the full range of lubricant viscosities and exhibit a remarkably high viscosity index (VI) and low pour point even at high viscosity. The as-synthesized HVI-PAO oligomer has a preponderance of terminal olefinic unsaturation. Typically, the HVI-PAO oligomer is hydrogenated to improve stability for lubricant applications. Those modifications to HVI-PAO oligomers that result in improved thermal stability are particularly preferred.

In the preparation of the novel HVI-PAO lubricant, alpha-olefin dimer, containing olefinic unsaturation can be separated from the oligomerization reaction. The composition of the dimer mixture conforms to the unique specificity of the oligomerization reaction in that little double bond isomerization is found and shows a low branch ratio. Separation of the dimer, representing non-lube range molecular weight material, is necessitated to control product volatility and viscosity. However, as oligomerization conditions are changed to produce the

lower viscosity products of lower average molecular weight important to the marketplace, the non-lube range dimer fraction by-product yield increases in proportion to that lowering in average molecular weight of the oligomerization product. The increase in dimer by-product yield represents a substantial economic burden on the overall process to produce useful lower viscosity lubricant.

It would therefore be desirable to incorporate the non-lube range fractions into the product in order to avoid the economic penalty associated with the production of the lower viscosity lubricants.

It has been found that the non-lube range olefins produced in the oligomerization process can be effectively converted to lube range products by reaction with the lube range material. It has also been found that other olefins may also be used in a similar manner and that the reaction products possess unexpectedly better thermal stability than the original lube range material, regardless of the character of the olefin. The yield of lubricant material is also improved in this way.

According to the present invention, therefore, a method for improving the thermal stability of synthetic lube produced by the oligomerization of a 1-alkene (alpha-olefin) is provided which method comprises reacting the oligomer with an olefin. The reaction, which is believed to proceed mainly by alkylation with some side reactions such as cracking, isomerization and polymerization, is carried out in the presence of an alkylation catalyst under conditions appropriate for alkylation.

A preferred olefin for reaction with the lube oligomer is the lower molecular weight, non-lubricant olefin produced in the course of the oligomerization of the alpha-olefin starting material. Using these lower molecular weight materials in this way not only improves the thermal stability of the final lube products but also increases the product yield and olefin utilization, thus avoiding the economic penalty attached to the production of the lower viscosity range lubricants. In a preferred embodiment of the present invention, therefore, the lower molecular weight non-lubricant range olefinic hydrocarbons produced in the course of the oligomerization of 1-alkenes are used to upgrade the lube range oligomer.

The reaction is carried out using acidic catalyst. Effective acidic catalysts comprise alkylation catalysts, preferably the open-pore catalyst such as those derived from fluorided alumina.

The composition of the present invention is polymeric residue of linear C_6 - C_{20} 1-alkenes, which has at least one higher alkyl (C_{12} - C_{40}) branch per oligomer molecule. The hydrocarbon oligomer contains from 30 to 1300 carbon atoms per molecule. In a preferred embodiment the novel composition has a methyl to methylene branch ratio of less than 0.19 and pour point below -15°C .

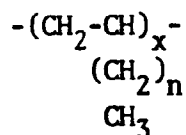
The process for the conversion of the alpha-olefins to the desired thermally stable, high viscosity index lubricant product comprises: contacting C_6 to C_{20} alpha-olefin feedstock, or mixtures thereof, under oligomerization conditions with a reduced valence state Group VIB metal catalyst on porous support whereby an oligomerization product mixture is produced containing oligomers comprising olefinic lubricant range hydrocarbons and olefinic non-lubricant range hydrocarbon by-product; separating the lubricant and non-lubricant hydrocarbons and hydrogenating the lubricant range hydrocarbons; contacting the hydrogenated hydrocarbons and the olefinic by-product hydrocarbons as alkylating agent in an alkylation zone under alkylating conditions with acidic catalyst whereby alkylated lubricant range hydrocarbons are produced.

In the drawings, Figure 1 shows the relationship between degree of alkylation and viscosity loss for modified HVI-PAO.

Figure 2 shows the relationship between viscosity and viscosity index for HVI-PAO oligomer and modified HVI-PAO oligomer.

In the preferred embodiments of the present invention synthetic hydrocarbon lubricants are modified by reaction with alkenes including the unique olefin dimers produced as by-product in the oligomerization reaction that produces the synthetic lubricant. The alkenes which can be used to react with HVI-PAO oligomers as described herein include C_2 - C_{40} linear or branched alkenes but, in particular, 1-alkenes and the olefinic dimer by-product of the HVI-PAO oligomerization reaction. Preferred 1-alkenes for reaction with HVI-PAO oligomers include those olefins containing from 6 to 14 carbon atoms such as 1-hexene, 1-octene, 1-decene, 1-dodecene and 1-tetradecene and branched chain isomers such as 4-methyl-1-pentene. Particularly preferred 1-alkenes are the C_8 to C_{10} alpha-olefins, e.g., 1-octene, 1-decene and the olefin dimers produced in the oligomerization process for producing the initial lube range materials.

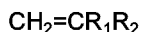
The oligomerization reaction is carried out by the oligomerization of 1-alkenes in contact with reduced metal catalysts, preferably reduced chromium oxide on a silica support. A characteristic of the novel oligomerization reaction from which the by-product dimers used as alkylating agent in the present invention are produced is the production of mixtures of dialkyl vinylidene and 1,2 dialkyl or trialkyl mono-olefin oligomers, or HVI-PAO oligomers, as determined by infra-red and NMR analysis. However, in general, the HVI-PAO oligomers have the following regular head-to-tail structure where n is preferably 0 to 17, terminating in olefinic unsaturation:



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with some head-to-head connections.

The HVI-PAO process produces a surprisingly simpler and useful dimer compared to the dimer produced by 1-alkene oligomerization with BF_3 or AlCl_3 as commercially practiced. Typically, in the present invention it has been found that a significant proportion of unhydrogenated dimerized 1-alkene, or alpha-olefin, has a vinylidenyl structure as follows:



where R_1 and R_2 are alkyl groups representing the residue from the head-to-tail addition of 1-alkene molecules. For example, the by-product dimer from 1-decene oligomerization according to the HVI-PAO process, which can be used as alkylating olefin in the present invention, has been found to contain three major components, as determined by gas chromatography (GC). Based on ^{13}C NMR analysis, the unhydrogenated components were found to be 8-eicosene, 9-eicosene, 2-octyldodecene and 9-methyl-8 or 9-methyl-9-nonadecene.

Olefins suitable for use as starting material in the preparation of olefinic HVI-PAO oligomers and the by-product dimer used as starting material in the present invention include those olefins containing from 6 to 14 carbon atoms such as 1-hexene, 1-octene, 1-decene, 1-dodecene and 1-tetradecene and branched chain isomers such as 4-methyl-1-pentene. A preferred 1-alkene is 1-decene. Also suitable for use are olefin-containing refinery feedstocks or effluents. However, the olefins used in this invention are preferably alpha olefinic as for example 1-octene to 1-dodecene and more preferably 1-decene, or mixtures of such olefins.

The lube range HVI-PAO oligomers of alpha-olefins used in this invention have a low branch ratio of less than 0.19 and superior lubricating properties compared to the alpha-olefin oligomers with a high branch ratio, as produced in all known commercial methods.

This class of unsaturated HVI-PAO alpha-olefin oligomers are prepared by oligomerization reactions in which a major proportion of the double bonds of the alpha-olefins are not isomerized. These reactions include alpha-olefin oligomerization by supported metal oxide catalysts, such as Cr compounds on silica or other supported IUPAC Periodic Table Group VIB compounds. The catalyst most preferred is a lower valence Group VIB metal oxide on an inert support. Preferred supports include silica, alumina, titania, silica alumina, magnesia and the like. The support material binds the metal oxide catalyst. Those porous substrates having a pore opening of at least 40 angstroms are preferred.

The support material usually has high surface area and large pore volumes with average pore size of $40 \times 10^{-7}\text{mm}$ to $350 \times 10^{-7}\text{mm}$. The high surface area is beneficial for supporting large amount of highly dispersive, active chromium metal centers and to give maximum efficiency of metal usage, resulting in very high activity catalyst. The support should have large average pore openings of at least $40 \times 10^{-7}\text{mm}$, with an average pore opening of $60 \times 10^{-7}\text{mm}$ to $300 \times 10^{-7}\text{mm}$ preferred. This large pore opening will not impose any diffusional restriction of the reactant and product to and away from the active catalytic metal centers, thus further optimizing the catalyst productivity. Also, for this catalyst to be used in fixed bed or slurry reactor and to be recycled and regenerated many times, a silica support with good physical strength is preferred to prevent catalyst particle attrition or disintegration during handling or reaction.

The supported metal oxide catalysts are preferably prepared by impregnating metal salts in water or organic solvents onto the support. Any suitable organic solvent known to the art may be used, for example, ethanol, methanol, or acetic acid. The solid catalyst precursor is then dried and calcined at 200 to 900°C by air or other oxygen-containing gas. Thereafter the catalyst is reduced by any of several various and well known reducing agents such as, for example, CO, H_2 , NH_3 , H_2S , CS_2 , CH_3SCH_3 , CH_3SSCH_3 , metal alkyl containing compounds such as R_3Al , R_3B , R_2Mg , RLi , R_2Zn , where R is alkyl, alkoxy, aryl and the like. Preferred are CO or H_2 or metal alkyl containing compounds.

Alternatively, the Group VIB metal may be applied to the substrate in reduced form, such as CrII compounds. The resultant catalyst is very active for oligomerizing olefins at a temperature range from below room temperature to 250°C at a pressure of 10.1 kPa (0.1 atmosphere) to 34580 kPa (5000 psi). However, oligomerization temperature is preferably between 90-250°C at a feedstock to catalyst weight ratio between 10:1 and 30:1. Contact time of both the olefin and the catalyst can vary from one second to 24 hours. The catalyst can be used in a batch type reactor or in a fixed bed, continuous-flow reactor.

In general the support material may be added to a solution of the metal compounds, e.g., acetates or nitrates, etc., and the mixture is then mixed and dried at room temperature. The dry solid gel is purged at successively higher temperatures to 600°C for a period of 16 to 20 hours. Thereafter the catalyst is cooled down

under an inert atmosphere to a temperature of 250 to 450°C and a stream of pure reducing agent is contacted therewith for a period when enough CO has passed through to reduce the catalyst as indicated by a distinct color change from bright orange to pale blue. Typically, the catalyst is treated with an amount of CO equivalent to a two-fold stoichiometric excess to reduce the catalyst to a lower valence CrII state. Finally the catalyst is cooled to room temperature and is ready for use.

The product oligomers have a very wide range of viscosities with high viscosity indices suitable for high performance lubrication use. The product oligomers also have atactic molecular structure of mostly uniform head-to-tail connections with some head-to-head type connections in the structure. These low branch ratio oligomers have high viscosity indices at least 15 to 20 units and typically 30-40 units higher than equivalent viscosity prior art oligomers, which regularly have higher branch ratios and correspondingly lower viscosity indices. These low branch oligomers maintain better or comparable pour points.

The branch ratios defined as the ratios of CH₃ groups to CH₂ groups in the reaction products and by-products are calculated from the weight fractions of methyl groups obtained by infrared methods, published in Analytical Chemistry, Vol. 25, No. 10, p. 1466 (1953).

$$\text{Branch ratio} = \frac{\text{wt fraction of methyl group}}{1 - (\text{wt fraction of methyl group})}$$

The unique olefinic dimers used as alkylating agent in the present invention are produced as by-product of the HVI-PAO oligomerization reaction. Typically, in the production of HVI-PAO oligomer lubricant base stock, the oligomerization reaction mixture is separated from the catalyst and separated by vacuum distillation to remove unreacted alpha-olefin and lower boiling by-products of the oligomerization reaction, such as alpha-olefin dimer. This provides a lubricant basestock of suitably high volatility and viscosity. While other methods known to those skilled in the art, such as solvent extraction, may be used to separate the alpha-olefin dimer by-product, distillation is preferred.

The following examples are presented to illustrate the oligomerization reaction and lubricant grade oligomers produced therefrom. The reaction provides as a by-product the olefinic dimer used as alkylating agent or reactant in the present invention. The dimer is separated by distillation from the oligomerization reaction mixture.

Example 1

Catalyst Preparation and Activation Procedure

1.9 grams of chromium (II) acetate (Cr₂(OCOCH₃)₄2H₂O) (5.58 mmole) (commercially obtained) is dissolved in 50 ml of hot acetic acid. Then 50 grams of a silica gel of 8-12 mesh size, a surface area of 300 m²/g, and a pore volume of 1 ml/g, also is added. Most of the solution is absorbed by the silica gel. The final mixture is mixed for half an hour on a rotavap at room temperature and dried in an open-dish at room temperature. First, the dry solid (20 g) is purged with N₂ at 250°C in a tube furnace. The furnace temperature is then raised to 400°C for 2 hours. The temperature is then set at 600°C with dry air purging for 16 hours. At this time the catalyst is cooled under N₂ to a temperature of 300°C. Then a stream of pure CO (99.99% from Matheson) is introduced for one hour. Finally, the catalyst is cooled to room temperature under N₂ and ready for use.

Example 2

The catalyst prepared in Example 1 (3.2 g) is packed in a 9.5 mm (3/8") stainless steel tubular reactor inside an N₂ blanketed dry box. The reactor under N₂ atmosphere is then heated to 150°C by a single-zone Lindberg furnace. Pre-purified 1-hexene is pumped into the reactor at 1069 kPa (140 psi) and 20 ml/hr. The liquid effluent is collected and stripped of the unreacted starting material and the low boiling material at 6.7 kPa (0.05 mm Hg). The residual clear, colorless liquid has viscosities and VI's suitable as a lubricant base stock.

<u>Sample</u>	<u>Prerun</u>	<u>1</u>	<u>2</u>	<u>3</u>
T.O.S.*, hr.	2	3.5	5.5	21.5
Lube Yield, wt%	10	41	74	31
Viscosity, mm ² /s (cS), at				
40°C	208.5	123.3	104.4	166.2
100°C	26.1	17.1	14.5	20.4
VI	159	151	142	143

***Time on stream**

Example 3

A commercial chrome/silica catalyst which contains 1% Cr on a large-pore volume synthetic silica gel is used. The catalyst is first calcined with air at 800°C for 16 hours and reduced with CO at 300°C for 1.5 hours. Then 3.5 g of the catalyst is packed into a tubular reactor and heated to 100°C under the N₂ atmosphere. 1-Hexene is pumped through at 28 ml per hour at 101 kPa (1 atmosphere). The products are collected and analyzed as follows:

<u>Sample</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>
T.O.S., hrs.	3.5	4.5	6.5	22.5
Lube Yield, %	73	64	59	21
Viscosity, mm ² /s(cS), at				
40°C	2548	2429	3315	9031
100°C	102	151	197	437
VI	108	164	174	199

Since the lubricants prepared by the methods described above contain olefinic unsaturation they are typically hydrogenated to stabilize them for lubricant use. However, very high molecular weight oligomers may not need to be hydrogenated since the number of olefin bonds in such oligomers is comparatively small. Lower molecular weight oligomers of particular interest in the present invention to provide low viscosity lubricants are hydrogenated by means well known to those skilled in the lubricant arts.

In the present invention, the thermal stability of the hydrogenated lubricant range oligomers is improved by reaction with an olefin, preferably the non-lube range olefins produced as a by-product in the oligomerization reaction. Without wishing to be held by theoretical consideration, the reaction employed herein to modify HVI-PAO oligomer is described as an alkylation reaction and the reactant alkene as an alkylating agent. Although alkylation is a significant reaction occurring in the instant invention carried out under alkylation conditions, other reactions are occurring as well, e.g., cracking, isomerization and polymerization. Accordingly, the term alkylation as used herein includes all those reactions occurring that result in the beneficial modification of HVI-PAO oligomers as herein described.

The catalyst used in the alkylation reaction of the present invention is preferably a porous, solid acidic catalyst containing large pore openings. A preferred catalyst is a fluorided alumina, prepared as described hereinafter. Other useful solid catalysts include acidic zeolites. Zeolites useful as catalysts in the present invention include all natural or synthetic acidic large pore size zeolites, typically with a pore size of 6.4 x 10⁻⁷mm to 7.5 x 10⁻⁷mm. In addition to fluorided alumina, particularly useful catalysts include the acidic form of ZSM-4, ZSM-12, ZSM-20, Faujasite X & Y with pore size of 7.4 x 10⁻⁷mm (7.4 Angstroms), Cancrinite, Gmelinite, Mazzite, Mordenite and Offretite. Other alkylation catalysts which are also useful in the process of the present invention include conventional alkylation catalysts known to those skilled in the art including HF, AlCl₃, BF₃ and BF₃ complexes, SbCl₅, SnCl₄, TiCl₄, P₂O₅, H₂SO₄, ZnCl₂ and acidic clays.

The alkylation reaction of the present invention produces alkylated synthetic lube containing large alkyl

branches. The alkyl branches contain between 12 and 40 carbon atoms, or mixtures thereof, depending on the olefin used in the alkylation reaction, e.g. the dimer of the C₆-C₂₀ alpha-olefin. Branches containing between 2 and 40 carbon atoms can be produced when monomeric olefins, e.g. ethylene, propylene, 1-decene, are used as alkylating agent. The degree of large branching, i.e. branching introduced by the olefin, can be controlled by the mole ratio of alkene such as dimer olefin to synthetic lube in the alkylation reaction. In general, the molar ratio of olefin to the lube range material will be between 40 to 1 and 1 to 1, preferably between 5 to 1 and 1 to 1 molar ratio. As a result the product characteristics can range from synthetic lube containing at least one large alkyl group per mole to a reaction product containing a mixture of alkylated synthetic lube and synthetic lube. Surprisingly, it has been found that when the synthetic lube is HVI-PAO oligomer, alkylation with alkene dimer according to the present invention produces an alkylated product that maintains the high VI and low pour point of the unalkylated HVI-PAO oligomer and shows an increase in thermal stability.

The following Examples illustrate the preparation of a preferred alkylation catalyst of the present invention and further illustrate the novel alkylation reaction.

Example 4

Alkylation Catalyst Preparation

25 grams of alumina (Harshaw Catapal-S, 0.8 mm (1/32 inch) extrudate) is contacted with 15.8 grams of aluminum nitrate nona hydrate in 30ml water for 1 hour. After the contact, excess water is removed under reduced pressure at 80°C. The aluminum nitrate impregnated alumina is then contacted with 8.17 grams ammonium fluoride in 50ml water to form aluminum fluoride in the alumina. The aluminum fluoride/alumina catalyst is dried under vacuum at 115°C for 18 hours and then calcined at 538°C for 12 hours.

Example 5

Synthetic Lube/Dimer Preparation

Synthetic lube is prepared according to the process for HVI-PAO reacting 1-decene over chromium supported silica as previously described herein. The unsaturated decene dimer is separated by distillation as a by-product to remove unreacted decene and lubricant product hydrogenated. The lube product viscosity was 9.2 mm²/s (9.2cS), measured at 100°C.

Example 6

Alkylation of HVI-PAO Lube

Alkylation reactions are performed in a fixed-bed reactor. The unit is maintained at 2861 kPa (400 psig) and the liquid hourly space velocity (LHSV) is 0.5. The feed is a mixture of 315 grams of 1-decene HVI-PAO lube and 140 grams of 1-decene dimer representing 30.8 weight percent. Alkylation reactions are carried out at reaction temperatures of 167, 204 and 250°C, Examples 7-1, 7-2 & 7-3. The results of these alkylation reactions are presented in Table 1

Table 1

Example	Feed	7-1	7-2	7-3
Reaction Temp. °C	-	167	204	250
LHSV	-	0.5	0.5	0.5
Pressure, kPa(PSIG)	-	2861(400)	2861(400)	2861(400)
HVI-PAO Charged,gms	-	40.3	50.3	46.2
HVI-PAO recovered,gms	-	46.7	57.3	50.1
% weight increase	-	15.9	13.9	8.4
KV, 40°C	50.0	74.0	79.5	70.5
KV, 100°C	9.2	11.7	12.1	11.3
Viscosity Index(VI)	167	153	148	154
Molecular Weight	710	786	795	825

Based upon the initial percent of HVI-PAO present in the feed, the amount of HVI-PAO fed can be calculated and is found in Table 1 for each example. After alkylation, a weight increase is expected and is noted in the table. Weight increases vary between 8.4 and 15.9 percent and appear to be a function of reaction temperature.

With this method the overall yield of final product is increased by the addition by alkylation of dimer by-product to the synthetic HVI-PAO lubricant. The alkylated product has an increased viscosity compared to the starting HVI-PAO lubricant and maintains the high VI characteristic of these oligomers.

The following examples further illustrate the process of the present invention. Surprisingly, as illustrated hereinafter, it has been discovered that the process of alkylation imparts a substantial increase in the thermal stability of the resulting lubricants. Unalkylated HVI-PAO loses 35% of its viscosity, measured at 100°C, when subjected to a temperature of 300°C for 24 hours in an inert environment. When the same HVI-PAO is alkylated with by-product dimer, to the extent of 30% alkylation, the viscosity loss is reduced to 10%.

Example 7

Catalyst Preparation

25 grams of alumina is contacted with a solution comprised of 5.3 grams of alumina nitrate (nona-hydrate) in 30ml of water for one hour. Excess water is removed by vacuum. The dried alumina nitrate impregnated alumina is then contacted with another solution containing 2.7 grams of ammonium fluoride in 50ml of water. After five minutes the excess water is decanted and the resulting fluorided alumina is dried in vacuum at 95°C for three days. This catalyst contains 5% aluminum fluoride.

Example 8

Alkylation Reaction

7.0 grams of the above fluorided alumina catalyst is placed into a fixed-bed reactor and calcined at 538°C for 18 hours. A feed comprised of 300grams (61.2% by weight) of a 18.9mm²/s(cS) (@100°C) HVI-PAO and 190 grams (38.8% by weight) of by-product decene dimers is passed over the fluorided alumina catalyst under condition found in Table 2 for Examples 9-1, 9-2 and 9-3. The degree of alkylation is measured by the percent weight increase of the examples. The degree of alkylation varies from 7.5 to 30.6%.

In Table 3 the results of the thermal stability studies on the above alkylation products is presented. The unalkylated HVI-PAO, when subjected to a temperature of 300°C for 24 hours in an inert atmosphere losses 35.4% of its viscosity, measure at 100°C. As the degree of alkylation is increased the stability of the alkylated HVI-PAO increases. At 30.6% alkylation the viscosity loss is reduced to 10.1% (@ 100°C).

In the figure the relationship between degree of alkylation and viscosity loss is presented. This demonstrates the increased thermal stability of alkylated HVI-PAO, according to the present invention.

Table 2

Example	Feed	9-1	9-2	9-3
Reaction Temp. °C	-	138	139	139
LHSV	-	0.5	0.5	0.5
Pressure, kPa(PSIG)	-	2861(400)	2413(350)	2413(350)
HVI-PAO Charged,gms	-	22.2	23.8	53.0
HVI-PAO recovered,gms	-	29.0	26.7	57.0
% weight increase	-	30.6	12.2	7.5
KV, 40°C	18.9	15.4	17.0	16.5
KV, 100°C	130.9	103.6	115.2	108.5
Viscosity Index(VI)	164.1	157.5	161.3	165.3
Molecular Weight	1054	871	997	978

Table 3

Thermal Stability (300°C for 24 hours)

Example	Before thermal treatment			After thermal treatment			
	KV,40 ⁰ C	KV,100 ⁰ C	VI	KV,40 ⁰ C	KV,100 ⁰ C	VI	% loss
HVI-PAO	130.9	18.9	164	75.9	12.3	159	35.4*
9-1	103.6	15.4	158	91.3	13.9	155	10.1*
9-2	115.2	17.0	161	84.7	13.5	163	20.4*
9-3	108.5	16.5	165	74.8	12.3	163	25.7*

*based on 100°C viscosity loss

In the following Example, HVI-PAO is alkylated as described above using the same fluorided alumina catalyst, except 1-decene alone was mixed with the HVI-PAO for reaction instead of HVI-PAO dimer.

Example 918.9mm²/s (cS) HVI-PAO Oligomer alkylated with 1-decene**Conditions:**

Reaction temp, °C	169
Pressure, kPa (psig)	2861(400)
LHSV	0.4
HVI-PAO charged, gms	30.7

Results:

HVI-PAO recovered, gms	36.6
% weight increase	19.2
KV, 40°C	13.1
KV, 100°C	84.7
VI	155.6

Table 4 presents the thermal stability test results on the product of Example 9.

<u>Table 4</u>				
	KV, 40°C	KV, 100°C	VI	% Loss
Before Thermal Treatment	84.7	13.1	156	---
After Thermal Treatment	75.7	12.0	154	8.4

Figure 2 shows a comparison of viscosity and VI for unreacted vs reacted HVI-PAO illustrating that VI remains unchanged for the reacted product of the invention.

While the invention has been described with preferred embodiments, the inventive concept is not limited except as set forth in the following claims.

Claims

1. A process for the conversion of alpha-olefins to high viscosity index lubricant range oligomers in increased yield, which process comprises:
 - i. contacting C₆ to C₂₀ alpha-olefin feedstock, or mixtures thereof, under oligomerization conditions with a reduced valence state Group VIB metal catalyst on porous support to produce a product mixture comprising oligomers having high viscosity indices, lower boiling olefinic by-product hydrocarbons and unreacted alpha-olefin feedstock;
 - ii. separating the oligomers, olefinic by-product hydrocarbons and unreacted feedstock and hydrogenating the oligomers; and
 - iii. contacting the hydrogenated oligomers with an alkylating agent comprising the olefinic by-product hydrocarbons of step ii. in an alkylating zone under alkylating conditions with a solid acidic catalyst to produce high viscosity index lubricant range alkylated oligomers.
2. The process of claim 1 wherein the alkylating agent comprises the olefinic C₁₂-C₄₀ dimer fraction of the oligomerization product.
3. The process of claim 1 wherein the solid acidic catalyst is taken from the group comprising large pore size zeolite and fluoridized alumina.
4. The process of claim 1 wherein the alkylated lubricant range hydrocarbons have viscosity index greater than 130, pour point below -15°C and viscosity between 3 and 750mm²/S.
5. The process of claim 1 wherein the Group VIB metal catalyst comprises chromium oxide on silica reduced with carbon monoxide.
6. The process of claim 1 wherein the alkylating agent comprises C₂-C₄₀ alkene.
7. The process of claim 1 wherein the acidic catalyst is taken HF, AlCl₃, BF₃ and BF₃ complexes, SbCl₅, SnCl₄, TiCl₄, P₂O₅, H₂SO₄, ZnCl₂ and acidic clays.
8. The process of claim 1 wherein the acidic catalyst comprises large pore size zeolites.
9. The process of claim 1 wherein the acidic catalyst comprises fluoridized alumina.
10. The process of claim 1 wherein the reduced valence state Group VIB metal catalyst on porous support comprises reduced chromium oxide on silica.
11. The process of claim 10 wherein the metal catalyst is reduced with carbon monoxide.
12. The process of claim 2 wherein the alkylating agent comprises olefinic C₁₂-C₄₀ non-lubricant range hydrocarbon fraction of the oligomerization product.
13. A liquid lubricant oligomer composition made by the process of any of claims 1 to 12 and comprising C₃₀-C₁₃₀₀ hydrocarbons containing at least one higher alkyl branch per oligomer molecule, the alkyl branch

containing between 12 and 40 carbon atoms.

14. The composition of claim 13 wherein the composition has a methyl to methylene branch ratio of less than 0.19 and pour point below -15°C.
- 5 15. The composition of claim 13 having a viscosity index greater than 130 and viscosity at 100°C between 3 and 750mm²/s.
16. The composition of claim 13 wherein the alkyl branch contains 20 carbon atoms.
- 10 17. The composition of claim 13 wherein the liquid lubricant oligomer comprises an essentially linear liquid lubricant oligomer.
18. The composition of claim 13 wherein the oligomer composition comprises the hydrogenated polymeric residue of 1-alkenes taken from linear C₆-C₂₀ 1-alkenes.
- 15 19. The composition of claim 18 wherein the 1-alkenes comprise 1-decene and the higher alkyl branch contains 20 carbon atoms.
- 20 20. The composition of claim 18 having a viscosity index greater than 130 and viscosity at 100°C between 3mm²/s and 750mm²/s.

Patentansprüche

- 25 1. Verfahren zur Umwandlung von α -Olefinen in Oligomere im Schmiermittelbereich mit hohem Viskositätsindex und mit erhöhter Ausbeute, wobei dieses Verfahren umfaßt:
 - i. Kontakt des α -Olefin-Ausgangsmaterials mit C₆ bis C₂₀ oder Mischungen davon bei Oligomerisierungsbedingungen mit einem Metallkatalysator der Gruppe VIB mit reduziertem Wertigkeitszustand auf einem porösen Träger, um eine Produktmischung zu erzeugen, die Oligomere mit hohem Viskositätsindex, geringersiedende olefinische Kohlenwasserstoff-Nebenprodukte und ein unreaktiertes α -Olefin-Ausgangsmaterial umfaßt;
 - 30 ii. Trennung der Oligomere, der olefinischen Kohlenwasserstoff-Nebenprodukte und des unreaktierten Ausgangsmaterials und Hydrierung der Oligomere; und
 - 35 iii. Kontakt der hydrierten Oligomere mit einem Alkylierungsmittel, das die olefinischen Kohlenwasserstoff-Nebenprodukte vom Schritt ii. umfaßt, in einer Alkylierungszone bei Alkylierungsbedingungen mit einem festen sauren Katalysator, um alkylierte Oligomere im Schmiermittelbereich mit hohem Viskositätsindex zu erzeugen.
2. Verfahren nach Anspruch 1, worin das Alkylierungsmittel die olefinische C₁₂-C₄₀-Dimerfraktion des Oligomerisierungsprozesses umfaßt.
- 40 3. Verfahren nach Anspruch 1, worin der feste saure Katalysator aus der Gruppe genommen wird, die einen großporigen Zeolith und fluoridiertes Aluminiumoxid umfaßt.
- 45 4. Verfahren nach Anspruch 1, worin die alkylierten Kohlenwasserstoffe im Schmiermittelbereich einen Viskositätsindex von mehr als 130, einen Pourpoint von weniger als -15°C und eine Viskosität zwischen 3 und 750 mm²/s aufweisen.
5. Verfahren nach Anspruch 1, worin der Metallkatalysator der Gruppe VIB mit Kohlenmonoxid reduziertes Chromoxid auf Siliciumdioxid umfaßt.
- 50 6. Verfahren nach Anspruch 1, worin das Alkylierungsmittel C₂-C₄₀ -Alken umfaßt.
7. Verfahren nach Anspruch 1, worin der saure Katalysator aus HF, AlCl₃, BF₃ und BF₃-Komplexen, SbCl₅, SnCl₄, TiCl₄, P₂O₅, H₂SO₄, ZnCl₄ und sauren Tonen ausgewählt wird.
- 55 8. Verfahren nach Anspruch 1, worin der saure Katalysator großporige Zeolithe umfaßt.
9. Verfahren nach Anspruch 1, worin der saure Katalysator fluoridiertes Aluminiumoxid umfaßt.

10. Verfahren nach Anspruch 1, worin der Metallkatalysator der Gruppe VIB mit reduziertem Wertigkeitszustand auf dem porösen Träger reduziertes Chromoxid auf Siliciumdioxid umfaßt.
11. Verfahren nach Anspruch 10, worin der Metallkatalysator mit Kohlenmonoxid reduziert wird.
12. Verfahren nach Anspruch 2, worin das Alkylierungsmittel eine olefinische C_{12} - C_{40} -Kohlenwasserstofffraktion außerhalb des Schmiermittelbereichs des Oligomerisierungsproduktes umfaßt.
13. Flüssige Oligomer-Schmiermittelzusammensetzung, die nach dem Verfahren nach einem der Ansprüche 1 bis 12 hergestellt wurde und C_{30} - C_{1300} -Kohlenwasserstoffe umfaßt, die mindestens eine höhere Alkylverzweigung pro Oligomermolekül umfassen, wobei diese Alkylverzweigung 12 bis 40 Kohlenstoffatome umfaßt.
14. Zusammensetzung nach Anspruch 13, worin diese ein Methyl/Methylen-Verzweigungsverhältnis von weniger als 0,19 und einen Pourpoint unterhalb -15°C aufweist.
15. Zusammensetzung nach Anspruch 13, die einen Viskositätsindex von mehr als 130 und eine Viskosität bei 100°C von 3 bis $750\text{ mm}^2/\text{s}$ aufweist.
16. Zusammensetzung nach Anspruch 13, worin die Alkylverzweigung 20 Kohlenstoffatome enthält.
17. Zusammensetzung nach Anspruch 13, worin das flüssige Oligomer-Schmiermittel ein im wesentlichen lineares flüssiges Oligomer-Schmiermittel umfaßt.
18. Zusammensetzung nach Anspruch 13, worin die Oligomerzusammensetzung den hydrierten polymeren Rückstand von 1-Alkenen umfaßt, der von linearen 1-Alkenen mit C_6 - C_{20} entnommen wurde.
19. Zusammensetzung nach Anspruch 18, worin die 1-Alkene 1-Decen umfassen und die höhere Alkylverzweigung 20 Kohlenstoffatome enthält.
20. Zusammensetzung nach Anspruch 18 mit einem Viskositätsindex von mehr als 130 und einer Viskosität bei 100°C zwischen $3\text{ mm}^2/\text{s}$ und $750\text{ mm}^2/\text{s}$.

Revendications

1. Un procédé de conversion d'alpha-oléfinés en oligomères de la classe des lubrifiants à indice de viscosité élevé, avec un rendement élevé, ledit procédé comprenant:
 - i. le contact d'une charge d'alpha-oléfinés en C_6 à C_{20} , ou de leur mélange, dans des conditions d'oligomérisation, avec un catalyseur à base d'un métal du groupe IVB ayant un état de valence réduit fixé et sur un support poreux pour produire un mélange comprenant des oligomères ayant des indices de viscosité élevés, des sous-produits consistant en hydrocarbures oléfiniques à faible point d'ébullition et une charge d'alpha-oléfine n'ayant pas réagi;
 - ii. la séparation des oligomères, des sous-produits consistant en hydrocarbures oléfiniques et de la charge n'ayant pas réagi et l'hydrogénation des oligomères; et
 - iii. la mise en contact des oligomères hydrogénés avec un agent d'alkylation comprenant les hydrocarbures oléfiniques sous-produits de l'étape ii. dans une zone d'alkylation, dans les conditions d'alkylation, avec un catalyseur acide solide pour produire des oligomères alkylés de la classe des lubrifiants présentant un indice de viscosité élevé.
2. Le procédé selon la revendication 1, dans lequel l'agent d'alkylation comprend la fraction dimère oléfinique en C_{12} à C_{40} du produit d'oligomérisation.
3. Le procédé selon la revendication 1, dans lequel le catalyseur solide acide est choisi dans le groupe comprenant les zéolites et les aluminés fluorés à dimensions de pores importantes.
4. Le procédé selon la revendication 1, dans lequel les hydrocarbures alkylés de la classe des lubrifiants ont un indice de viscosité supérieur à 130, un point de coulée inférieur à -15°C et une viscosité comprise entre 3 et $750\text{ mm}^2/\text{s}$.

5. Le procédé selon la revendication 1, dans lequel le catalyseur métallique du groupe VIB comprend un oxyde de chrome, sur un support à base de silice, réduit par le monoxyde de carbone.
6. Le procédé selon la revendication 1, dans lequel l'agent d'alkylation comprend un alcène en C₂ à C₄₀.
- 5 7. Le procédé selon la revendication 1, dans lequel le catalyseur acide est choisi parmi: HF, AlCl₃, BF₃ et complexes de BF₃, SbCl₅, SnCl₄, TiCl₄, P₂O₅, H₂SO₄, ZnCl₂ et des argiles acides.
8. Le procédé selon la revendication 1, dans lequel le catalyseur acide comprend les zéolites à dimension de pores importante.
- 10 9. Le procédé selon la revendication 1, dans lequel le catalyseur acide comprend de l'alumine fluorée.
10. Le procédé selon la revendication 1, dans lequel le catalyseur à base d'un métal du groupe VIB à état de valence réduit est fixé sur un support poreux et comprend de l'oxyde de chrome sur silice.
- 15 11. Le procédé selon la revendication 10, dans lequel le catalyseur métallique est réduit avec du monoxyde de carbone.
12. Le procédé selon la revendication 2, dans lequel l'agent d'alkylation comprend une fraction d'hydrocarbures oléfiniques en C₁₂ à C₄₀ de la classe des non-lubrifiants du produit d'oligomérisation.
- 20 13. Une composition oligomère lubrifiante liquide obtenue par le procédé selon l'une quelconque des revendications 1 à 12 et comprenant des hydrocarbures en C₃₀ à C₁₃₀₀ contenant au moins une branche alkyle supérieure par molécule d'oligomère, la branche alkyle contenant de 12 à 40 atomes de carbone.
- 25 14. La composition selon la revendication 13, dans laquelle la composition a un rapport de ramification méthyle/méthylène inférieur à 0,19 et un point de coulée inférieur à -15°C.
15. La composition selon la revendication 13, ayant un indice de viscosité supérieur à 130 et une viscosité à 100°C comprise entre 3 et 750 mm²/s.
- 30 16. La composition selon la revendication 13, dans laquelle la ramification alkylique contient 20 atomes de carbone.
17. La composition selon la revendication 13, dans laquelle l'oligomère de lubrifiant liquide comprend essentiellement un oligomère lubrifiant liquide linéaire.
- 35 18. La composition selon la revendication 13, dans laquelle la composition oligomère comprend le résidu polymère hydrogéné des 1-alcènes choisis parmi les 1-alcènes linéaires en C₆ à C₂₀.
- 40 19. La composition selon la revendication 18, dans laquelle les 1-alcènes comprennent le 1-décène et la ramification alkyle supérieure contient 20 atomes de carbone.
20. La composition selon la revendication 18, ayant un indice de viscosité supérieur à 130 et une viscosité à 100°C comprise entre 3 mm²/s et 750 mm²/s.

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