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(54) Title: HIGH VISCOSITY POLYALPHAOLEFINS		
(57) Abstract A synthetic lubricant material is produced by forming a catalyst complex of a boron trifluoride catalyst and at least one alcohol promoter in the absence of olefinic monomer, then oligomerizing a C ₄₋₁₆ olefinic monomer by adding the olefinic monomer to a reaction vessel containing the catalyst complex, under boron trifluoride pressure, to produce an oligomer product. At least 50 weight % of the olefinic monomer is C ₈₋₁₆ olefinic monomer.		

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HIGH VISCOSITY POLYALPHAOLEFINS

5 The present invention relates to a process for producing polyalphaolefins that maximizes the degree of oligomerization, with good conversion and product quality.

BACKGROUND OF THE INVENTION

10 It is well known to make polyalphaolefins by admixing an olefinic feed (1-hexene to 1-hexadecene) with a promoter and a catalyst, such as boron trifluoride (BF_3), under mild pressure/temperature conditions. Polyalphaolefin product limitations, such as 100° C viscosity of less than 10 centistoke and oligomer distribution focused on the tetramer-hexamer fraction, arise from the
15 use of the aforementioned processes. In general, higher viscosity fluids (100° C viscosity of greater than 10 centistoke) can only be made with a severe production rate penalty, since longer residence times are required to achieve the target viscosity with current technology.

20 U.S. Patent No. 4,587,368 to Pratt et al. discloses the oligomerization of 1-alpha olefin in two stages to yield a mixture low in trimer and high in tetramer and higher oligomers. In the first stage, a C_{8-12} 1-alpha olefin is oligomerised in a conventional process until the monomer is totally reacted. During that first stage, a BF_3 :promoter complex is formed. In the second stage, an aliquot of
25 monomer is added and the reaction is allowed to go to completion. The final process yields a product viscosity of approximately 8 centistoke.

U.S. Patent No. 4,982,026 to Karn et al. discloses highly reactive polymers obtained from low carbon number monomers. The process involves the
30 preparation of a mixture of hexane solvent, phosphoric acid, and a catalyst substrate; cooling of mixture to -20° C, and saturating the mixture with BF_3 to form the catalyst complex. Propylene gas and BF_3 are then added to complex until the reaction is completed (Example 1). In Example 2, a silica gel is used as a catalyst substrate with hexane solvent and phosphoric acid: BF_3 complex
35 components. Notice that the catalyst complex is a BF_3 :acid complex, not a

BF₃:alcohol complex. The process yields polymers with mole weights of from 250 to 500, having a high degree of mono-unsaturation content.

U.S. Patent No. 4,650,917 to Dessau et al. discloses Viscosity Index improvers for synthetic lubricants produced by olefin oligomerization of olefin monomers by contact with BF₃ solid acidic catalyst. The catalyst complex is a BF₃:silica complex, not a BF₃:alcohol complex. The Example describes the oligomerization of propylene over a BF₃-containing acidic resin catalyst and the subsequent isomerization of lube fraction by contact with an unbound hydrogen exchange zeolite.

U.S. Patent No. 4,434,309 to Larkin et al. discloses the oligomerization of low molecular weight alpha olefins over a BF₃ protonic promoter complex. Specifically, Example 10 describes the introduction of an alpha-olefin mixture to complex of BF₃, 1-butanol, and cyclohexane, and the production low molecular weight synthetic lubricants. It appears that, in the examples using a BF₃ protonic promoter complex, the oligomerization does not occur under boron trifluoride pressure.

U.S. Patent No. 5,510,392 to Feuston et al. discloses the oligomerization of alpha olefins with a BF₃:promoter complex. The alpha olefins and the BF₃:promoter complex are added simultaneously to the reactor. The final product has a 100° C viscosity of 5.2 centistoke.

U.S. Patent Nos. 4,434,309, 4,587,368, 4,650,917, 4,982,026, and 5,510,392 are hereby incorporated by reference for all purposes.

SUMMARY OF THE INVENTION

The present invention provides a process for producing a high degree of olefin oligomerization not yet recognized by practitioners of the art. We have found that the oligomer distribution can be radically changed towards heavier (octamer) oligomers by introducing the olefinic feed into a pool of *in situ* formed alcohol:BF₃ complex. Moreover, we have found that the longer straight-chained alcohols produce a heavier product viscosity. The addition of an alpha-omega

diolefin as a co-monomer produces yet another significant product viscosity increase over and above that achieved in the present invention.

5 The synthetic lubricant material is produced by a two step process. In the first step, a catalyst complex of a boron trifluoride catalyst and at least one alcohol promoter is formed in the absence of olefinic monomer. In the second step, a C₄₋₁₆ olefinic monomer is oligomerized by adding the olefinic monomer to a reaction vessel containing the catalyst complex, under boron trifluoride pressure, to produce an oligomer product, wherein the olefinic monomer
10 comprises at least 50 weight % C₈₋₁₆ olefinic monomer.

The C₄₋₁₆ olefinic monomer can comprise an alpha-omega diolefin. Preferably, the alpha-omega diolefin constitutes from 2 to 50 weight % of the C₄₋₁₆ olefinic monomer.

15 Preferably, the alcohol promoter used in the catalyst complex comprises a straight-chain mono-alcohol having from four to twelve carbon atoms.

The raw oligomer product produced by this process has less than
20 10 weight % dimer and trimer, less than 75 weight % tetramer through heptamer, and at least 15 weight % octamer and higher oligomers.

BRIEF DESCRIPTION OF THE DRAWINGS

25 In order to assist the understanding of this invention, reference will now be made to the appended drawings. The drawings are exemplary only, and should not be construed as limiting the invention.

30 Figure 1 compares the oligomer distribution of examples in Table 1. Notice the relative percentages of C₂₀-C₃₀ and C₈₀₊. In Examples 1 and 2 the weight percent of C₂₀-C₃₀ oligomers declines dramatically, while C₈₀₊ oligomers increase significantly. This is the characteristic of the present invention, minor amount of C₂₀-C₃₀ and increasing octamer and higher oliomers.

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Figure 2 shows the effect of 1,9-decadiene on the oligomer distribution using the present invention (Examples 10-12). The 1,9-decadiene significantly increases the percentage of C₈₀₊ (octamer) oligomers in the product and thus dramatically increases the product viscosity (see Table 3).

5

DETAILED DESCRIPTION OF THE INVENTION

10 In its broadest aspect, the present invention involves a process for producing a synthetic lubricant material by forming a catalyst complex of a boron trifluoride catalyst and at least one alcohol promoter in the absence of olefinic monomer; then oligomerizing an olefinic monomer by contacting it with the catalyst complex, under boron trifluoride pressure, to produce an oligomer product.

OLEFINIC MONOMER

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By "olefinic monomer," we mean either an olefin or mixture of olefins having from four to sixteen carbon atoms. At least 50 weight % of the olefinic monomer comprises C₈₋₁₆ olefinic monomer.

20

Preferably, olefins used in making the oligomer are predominately (at least 50 mole %) straight-chain, mono-olefinically unsaturated hydrocarbons in which the olefinic unsaturation occurs at the 1- or α -position of the straight carbon chain. Straight-chain α -olefins are preferred because they are more reactive, commercially available, and make products having higher viscosity indexes.

25

Such α -olefins can be made by the thermal cracking of paraffinic hydrocarbons or by the well known Ziegler catalyzed ethylene chain growth and displacement on triethyl aluminum. Individual olefins may be used, as well as mixtures of such olefins. Examples of such olefins are 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tetradecene, and 1-hexadecene. The more preferred normal α -olefin monomers are those containing about 8 to 14 carbon atoms.

30

In one embodiment, the olefin monomers also contain from 2 to 50 weight % of an alpha-omega diolefin, such as 1,5-hexadiene, 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, and 1,9-decadiene. Most preferably, the olefin

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monomer contains 2 weight % 1,9-decadiene. The preparation of alpha-omega diolefins is disclosed in U.S. Patent No. 5,516,958 to Schaerfl, Jr. et al., which is hereby incorporated by reference for all purposes.

5 The olefin monomers can also contain minor amounts of up to about 50 mole %, and usually less than 25 mole %, of internal olefins and vinylidene olefins.

ALCOHOL PROMOTER

10 By "alcohol promoter," we mean an organic compound having at least one hydroxyl group (containing an -OH unit). Preferably, the alcohol promoter is an alkyl mono-alcohol, but alkyl diols could work. Most preferably, the alcohol promoter is a straight-chain mono-alcohol having from four to twelve carbon
15 atoms.

OLIGOMERIZATION REACTION

20 In the first step, a catalyst complex is formed of a boron trifluoride catalyst and at least one alcohol promoter in the absence of olefinic monomer. Preferably, this complex is formed *in situ* in the reactor where the oligomerization step will take place.

25 In the second step, a C₄₋₁₆ olefinic monomer is oligomerized by contacting the olefinic monomer with the catalyst complex, under boron trifluoride pressure, to produce an oligomer product.

30 The promoter can be used in minor, yet effective amounts. In general, boron trifluoride is used in molar excess to the amount of promoter. This can be accomplished by using a closed reactor and maintaining a positive boron trifluoride pressure over the reaction mixture. The olefinic monomer is contacted with the catalyst:promoter complex.

35 The reaction can be carried out in a batch or continuous process at temperatures of about -20° to 200° C and pressures ranging from atmospheric

up to, for example, 1,000 psig. The reaction temperature will change the oligomer distribution, with increasing temperatures favoring the production of tetramers through heptamers. Preferred reaction temperatures and pressures are about 0° to 90° C and 5 to 100 psig.

5

When a desired oligomer distribution is reached in the batch mode, the reaction is terminated by venting off excess boron trifluoride gas and purging with nitrogen gas to replace all boron trifluoride gaseous residue. The reaction product, unreacted monomer, and boron trifluoride-promoter complex residue are removed from the reactor for further processing. In the continuous mode the dissolved boron trifluoride may be degassed from the reactor effluent. The boron trifluoride-promoter complex may be separated by settling or coalescing from the reaction product.

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The crude reactor product is then washed with an aqueous caustic solution and followed by one or more water washes to ensure neutralization.

20

The oligomer mixture from the reaction contains minor amounts of monomer, dimer, and trimer, which can be removed by distillation. The monomer has been found to contain appreciable amounts of less reactive, isomerized material.

25

The product mixture can be further separated by distillation to provide one or more product fractions having the desired viscosities for use in various lubricant applications such as dielectric fluids, heat transfer fluids, gear oils and crankcase lubricants.

30

The oligomer product can be hydrogenated by conventional methods to increase the oxidation stability of the product. Supported nickel catalysts are useful. For example, nickel on a Kieselguhr support gives good results. Batch or continuous processes can be used. For example, the catalyst can be added to the liquid and stirred under hydrogen pressure or the liquid may be trickled through a fixed bed of the supported catalyst under hydrogen pressure. Hydrogen pressures of about 100 to 1,000 psig at temperatures of about 150° to 300° C are especially useful. Preferably, the hydrogen pressure is from 400 to 1,000 psig and the maximum temperature is 200° C to 300° C.

35

OLIGOMER PRODUCT

The oligomer product is that portion of the reaction product remaining after boron trifluoride, promoters, and unreacted monomer are removed. Preferably, the oligomer product has the following composition:

- (a) less than 10 weight % dimer and trimer,
- (b) less than 75 weight % tetramer through heptamer, and
- (c) at least 15 weight % octamer and higher oligomers.

EXAMPLES

The invention will be further illustrated by following examples, which set forth particularly advantageous method embodiments. While the Examples are provided to illustrate the present invention, they are not intended to limit it.

COMPARATIVE EXAMPLE A

The oligomerization reaction was carried out in an autoclave reactor equipped with a packless stirrer; and all wetted surfaces were made of 316 stainless steel. The reactor had an external electrical heater and an internal cooling coil for temperature control. The reactor was equipped with a dip tube, gas inlet, and vent valves, and a pressure relief rupture disc. Prior to the monomer charge, the reactor was cleaned, purged with nitrogen and pressure tested for leaks.

Eight hundred thirty grams of 1-decene was charge into the reactor. The promoter, 1-octanol, was added at 2 weight percentage feed charged or 2.1 mole %. The entire reactor content was under vacuum. Boron trifluoride gas was then sparged slowly and the contents agitated while temperature was controlled at 8° to 15° C via a cooling coil to avoid reaction exotherm. Additional boron trifluoride was added as necessary to maintain a reactor pressure of 100 psig. The reaction was terminated after two hours by venting excess boron trifluoride gas and purging with nitrogen. The reaction product was then washed with a 4 weight % aqueous sodium hydroxide solution followed by several water washes to ensure neutralization. The product was saved for further treatment

such as hydrogenation and fractionation. The final product had a calculated C_{20+} viscosity of 5.11 centistoke based on oligomer distribution.

COMPARATIVE EXAMPLES B AND C

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The purpose of Examples B and C is to demonstrate that, in a conventional batch process, increasing the concentration of promoter does not yield significantly heavier oligomer distribution or 100° C viscosity values. The procedure in Comparative Example A was followed except that the weight % of promoter to monomer was kept at 1.0% and 10.0%, respectively. After 15 minutes, 340 mls. of decene feed with the same respective promoter to feed weight % was introduced over a 45 minute period. Total run time was 75 minutes.

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EXAMPLES 1 AND 2

Examples 1 and 2 were run under the same pressure and temperature conditions as in Comparative Examples A, B, and C. In Example 1, the initial reactor charge was 0.5 moles 1-octanol with 35 grams of heptane and the feed consisted of 1-decene and 1 weight % 1-octanol. A vacuum was drawn on the reactor. Boron trifluoride was introduced to the reactor under agitation at 100 psi. Immediately, thereafter the 1-decene feed containing 1 weight % 1-octanol was introduced at approximately 440 mls per hour. The total feed introduced to the reactor was 4105 mls and the run time was 540 minutes.

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25

The same procedure as in Example 1 was followed in Example 2 except 0.75 moles 1-octanol and 41 grams heptane were charged to the reactor. The total run time was 230 minutes and 2010 mls of 1-decene with 1 weight % 1-octanol was introduced to the reactor. The results of Examples A, B, C, 1, and 2 are summarized in Table 1. The calculated product viscosity values at 100° C and the degree to which oligomerization (C_{80+}) is enhanced by the present invention is readily apparent.

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TABLE 1

Ex	Mole Promoter in Charge	Mole Monomer in Charge	Molar % Promoter in Feed	Mole % Total Promoter to Total Feed	% C ₂₀ -C ₃₀	% C ₄₀ -C ₇₀	%C ₈₀ +	C ₂₀ + Calculated viscosity
A	0.13	5.93	no feed	1.5	50.69	46.95	2.36	5.11
B	0.064	5.93	1.1	1.1	48.9	51.1	0	5.18
C	0.64	5.93	10.7	10.7	44.9	55.1	0	5.88
1	0.5	0	1.1	3.4	9.8	71.6	18.6	11.76
2	0.75	0	1.1	8.5	7.4	50.9	41.7	15.79

The product viscosity difference between Examples B and C is not significant. Further increasing the molar % promoter does not yield benefits of increased product viscosity and heavier oligomer distribution. However, these examples show, that using the present invention in the presence of a preformed catalyst complex, using the same promoter and under controlled feed rates, consistently yields 4 to 10 centistoke greater product viscosity.

EXAMPLES 3 THROUGH 8

Examples 3 through 8 were run following the present invention procedure under the same pressure, temperature, and feed rate conditions as Examples 1 and 2, but vary the alcohol promoter molecular weight. The results from Examples 3 through 8 are summarized in Table 2. The prior art teaches that the use of higher molecular weight alcohols favors an increase in the degree of oligomerization. This observation is confirmed and maintained in the present invention. Overall, the decanol runs yield 2 to 4 centistoke higher viscosities than hexanol.

The inclusion of these results demonstrates the product viscosity limitations of the traditional methodology of admixing the co-catalyst and feed streams simultaneously.

TABLE 2

TABLE 2									
	Ex	Type of Promoter	Mole Promoter to Charge	Molar % Promoter of Feed	Mole% Total Promoter to Total Feed	%C ₂₀ -C ₃₀	%C ₄₀ -C ₇₀	% C ₈₀ +	C ₂₀ + Calculated viscosity
5	3	Hexanol	0.25	5.5	9.70	6.32	71.7	22.4	13.59
	4	Hexanol	0.5	1.4	9.60	5.00	62.5	32.5	15.58
	5	Hexanol	1.0	1.5	21.50	7.53	54.4	37.8	16.61
	6	Decanol	0.25	0.72	8.80	7.00	52.6	40.4	15.15
	7	Decanol	0.5	0.72	18.20	7.80	45.2	47.0	19.48
10	8	Decanol	1.0	0.72	35.70	7.60	37.2	55.2	20.64

In summary, conventional methods for the oligomerization of an alpha olefin monomer feed, such as decene or dodecene, with a promoter complex yield product viscosities generally under 10 cSt. Higher viscosities are not achievable without utilizing significantly longer reaction times, slower feed rates, and or adding modifiers to alter the original reaction product. More active or aggressive Freidel-Crafts catalysts such as AlCl₃ or metal alkyls are generally used in order to produce a 1-decene product with viscosities greater than 10 centistoke. It has been demonstrated that significantly higher 100° C product viscosities can be attained by the present invention.

EXAMPLES 9 THROUGH 12

Contemporaneous with our novel process was the recognition that alpha-omega dienes (diolefins) when used as co-monomers, or second stage feeds, would change the resident oligomer distribution yielding a much heavier product weight and viscosity.

Examples 9 through 12 follow the present invention procedure. The pressure, temperature, and feed rates are the same as those in Examples 1 and 2. The feed contains 1-decene, the indicated molar % of a diolefin co-monomer, and a promoter. 1-Octanol promoter was used in all examples, except for Example 12, which used both 1-heptanol and 1-tetradecanol in two feeds of 1,9-decadiene co-monomer, where the first feed contained a 2:1 ratio of

olefin to diolefin and the second stage feed contained a 1:1 ratio of olefin to diolefin. The amount of promoter in the initial charge was 0.5 mole, except for Example 12, where it was 0.4 mole. The molar % of promoter in feed was 1.1, except for Example 12, where it was 1.2. The total mole % of promoter to feed was 8.1, except for Example 12, where it was 21.0. The results are summarized in Table 3.

TABLE 3

Ex.	Diene	Molar%	% C ₂₀₋₃₀	% C ₄₀₋₇₀	% C ₈₀₊	100° C viscosity	VI
		Diene				cSt C ₂₀₊	
9	C ₁₀	12.1	10.9	45.50	43.60	19.30	135
10	C ₁₀	27.4	13.6	34.10	52.30	27.60	140
11	C ₁₀	47.4	12.7	24.30	63.00	54.20	164
12	C ₁₀	50.2	7.9	25.70	66.40	162.5	298

While the present invention has been described with reference to specific embodiments, this application is intended to cover those various changes and substitutions that may be made by those skilled in the art without departing from the spirit and scope of the appended claims.

What is claimed is:

1. A process for producing a synthetic lubricant material comprising:
 - 5 (a) forming a catalyst complex of a boron trifluoride catalyst and at least one alcohol promoter in the absence of olefinic monomer; and
 - (b) oligomerizing a C₄₋₁₆ olefinic monomer by adding the olefinic monomer to a reaction vessel containing the catalyst complex, under boron trifluoride pressure, to produce an oligomer product, wherein said
10 olefinic monomer comprises at least 50 weight % C₈₋₁₆ olefinic monomer.
2. A process according to Claim 1 wherein said C₄₋₁₆ olefinic monomer comprises an alpha-omega diolefin.
15
3. A process according to Claim 2 wherein said alpha-omega diolefin constitutes from 2 to 50 weight % of the C₄₋₁₆ olefinic monomer.
4. A process according to Claim 1 wherein said alcohol promoter comprises a
20 straight-chain mono-alcohol having from four to twelve carbon atoms.
5. A process according to Claim 1 wherein said oligomer product has the following composition:
 - 25 (a) less than 10 weight % dimer and trimer,
 - (b) less than 75 weight % tetramer through heptamer, and
 - (c) at least 15 weight % octamer and higher oligomers.

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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
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According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 323 759 A (MOBIL OIL) 12 July 1989 see claims 1-12 -----	1-5

☐ Further documents are listed in the continuation of box C.

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