

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
28 June 2001 (28.06.2001)

PCT

(10) International Publication Number
WO 01/46339 A2(51) International Patent Classification⁷: **C10G 2/00**,
C07C 6/00, C10M 175/00

(21) International Application Number: PCT/US00/33950

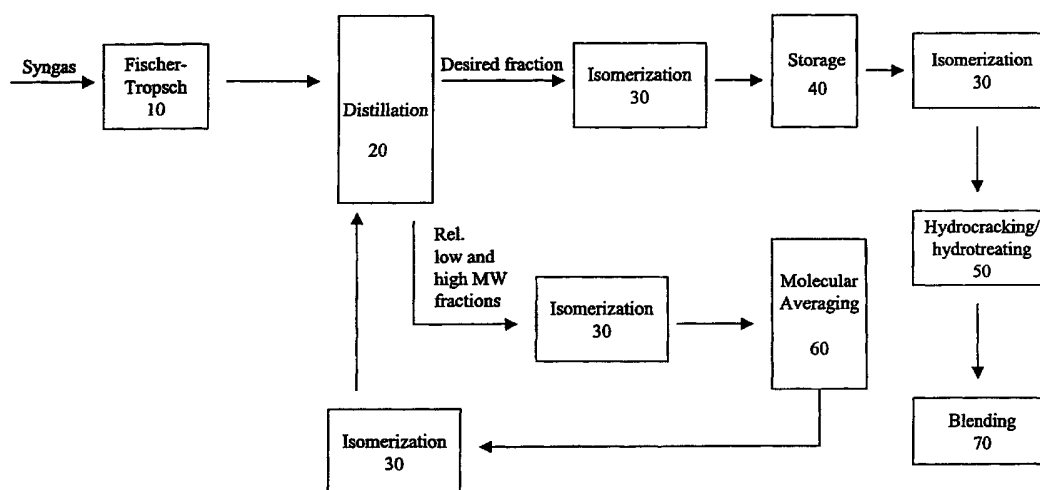
(22) International Filing Date:
15 December 2000 (15.12.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/469,574 22 December 1999 (22.12.1999) US(71) Applicant: **CHEVRON U.S.A. INC.** [US/US]; 3rd Floor,
2613 Camino Ramon, San Ramon, CA 94583-4289 (US).(72) Inventors: **O'REAR, Dennis, J.**; 40 Upland Drive,
Petaluma, CA 94952 (US). **KRUG, Russell**; 44 Olympia
Way, Novato, CA 94949 (US).(74) Agents: **AMBROSIUS, James, W. et al.**; Chevron Corpo-
ration, Law Dept., P.O. Box 6006, San Ramon, CA 94583-
0806 (US).(81) Designated States (*national*): AE, AL, AM, AT, AU, AZ,
BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE,
DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID,
IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT,
LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL,
PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ,
UA, UG, VN, YU, ZA, ZW.(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,
CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).**Published:**— Without international search report and to be republished
upon receipt of that report.*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*

(54) Title: SYNTHESIS OF NARROW LUBE CUTS FROM FISCHER-TROPSCH PRODUCTS



(57) Abstract: A process for preparing hydrocarbons in the lube base oil range, lube base oils and lube oil compositions from a fraction with an average molecular weight above a target molecular weight and a fraction with an average molecular weight below a target molecular weight via molecular averaging is described. The fractions can be obtained, for example, from Fischer-Tropsch reactions, and/or obtained from the distillation of crude oil. Molecular averaging converts the fractions to a product with a desired molecular weight, for use in preparing a lube oil composition. The product can optionally be isomerized to lower the pour point, and also can be blended with suitable additives for use as a lube oil composition.

1 **SYNTHESIS OF NARROW LUBE CUTS**
2 **FROM FISCHER-TROPSCH PRODUCTS**

3
4 RELATED APPLICATION

5
6 This application is related to "Process for Conversion of Natural Gas and
7 Associated Light Hydrocarbons to Salable Products" by Dennis J. O'Rear,
8 Charles L. Kibby and Russell R. Krug, filed concurrently with this application.
9

10 FIELD OF THE INVENTION

11
12 This invention relates to the molecular averaging of various feedstocks to form
13 lube oils.
14

15 BACKGROUND OF THE INVENTION

16
17 There is a need for lubricating oils in the C₃₀+ range which have a high
18 viscosity index (VI) and good oxidation stability. The majority of lubricating
19 oils used in the world today are derived from crude oil, and include a
20 petroleum base oil and an additive package. The base oils are refined from
21 crude oil through a plurality of processes such as distillation, hydrocracking,
22 hydroprocessing, catalytic dewaxing, and the like. Hydrocarbons in the lube
23 oil boiling range from these processes needs to be further processed to create
24 the finished base oil. In creating the base oil, the refiner desires to obtain the
25 highest possible yield while preserving the VI of the oil.
26

27 Crude oil fractions in the C₃₀+ range often tend to include waxes. Since the
28 presence of wax in lube oil adversely affects various physical properties, such
29 as the pour point and cloud point, the waxy components are typically
30 removed. The waxy components of the oil can be removed using various
31 processes, including solvent dewaxing and/or catalytic dewaxing, both of

1 which tend to provide lower yields at a given VI. It would be highly desirable
2 to have a process that optimizes the yield of lube oil at a given VI.

3

4 The use of crude oil as a feedstock for preparing lube oils is limited by the
5 product loss associated with the steps required to remove the waxy
6 components. Further, crude oil is in limited supply, it includes aromatic
7 compounds believed to cause cancer, and contains sulfur and nitrogen-
8 containing compounds that can adversely affect the environment.

9

10 Lube oils can also be prepared from natural gas. This involves converting
11 natural gas, which is mostly methane, to synthesis gas (syngas), which is a
12 mixture of carbon monoxide and hydrogen, and subjecting the syngas to
13 Fischer-Tropsch reaction conditions. An advantage of using fuels prepared
14 from syngas is that they do not contain significant amounts of nitrogen or
15 sulfur and generally do not contain aromatic compounds. Accordingly, they
16 have minimal health and environmental impact.

17

18 A limitation associated with Fischer-Tropsch chemistry is that it tends to
19 produce a broad spectrum of products, ranging from methane to wax. While
20 the product stream includes a fraction useful as lube oils, it is not the major
21 product. Product slates for syngas conversion over Fischer-Tropsch catalysts
22 (for example, Fe, Co and Ru) are controlled by polymerization kinetics with
23 fairly constant chain growth probabilities that fix the possible product
24 distributions. Heavy products with a relatively high selectivity for wax are
25 produced when chain growth probabilities are high. Methane is produced with
26 high selectivity when chain growth probabilities are low.

27

28 It is generally possible to isolate various fractions from a Fischer-Tropsch
29 reaction, for example, by distillation. The fractions include, among others, a
30 gasoline fraction (B.P. about 68-450°F/20-232°C), a middle distillate fraction
31 (B.P. about 250-750°F/121-399°C), a wax fraction (B.P. about

1 650-1200°F/343-649°C) primarily containing C₂₀ to C₅₀ normal paraffins with a
2 small amount of branched paraffins and a heavy fraction (B.P. above about
3 1200°F/649°C) and tail gases. A suitable fraction for use in preparing a lube
4 oil can be isolated from the product stream by distillation. However,
5 depending on market considerations, it might be advantageous to provide a
6 process that would convert the other fractions into fractions suitable for use in
7 preparing lube oils. The present invention provides such a process.

8

9

SUMMARY OF THE INVENTION

10

11 In its broadest aspect, the present invention is directed to an integrated
12 process for producing hydrocarbons in the lube base oil range, lube base oils
13 and lube oils. As used herein, lube base oils are generally combined with an
14 additive package to provide finished lube oils. Hydrocarbons in the lube base
15 oil range are prepared via molecular averaging of a relatively low molecular
16 weight fraction and a relatively high molecular weight fraction.

17

18 The resulting hydrocarbons tend to be waxy unless they are isomerized prior
19 to the molecular averaging step. Isomerization of the hydrocarbons provides
20 a lube base oil, which, when combined with the additive package, provides a
21 lube oil composition. Catalytic isomerization improves the pour point and
22 viscosity index. Hydrotreatment can optionally be performed on the
23 hydrocarbons or lube base oil to hydrotreatment to remove olefins,
24 oxygenates and other impurities.

25

26 Depending on the desired physical and chemical properties of the lube oil
27 composition, the product of the molecular averaging reaction can include
28 virtually any combination of hydrocarbons between C₂₀ and C₅₀. Preferably,
29 the lube oil composition includes mostly hydrocarbons in the range of around
30 C₃₀. When preparing a lube base oil composition in the C₂₀ to C₅₀ range, one
31 can combine hydrocarbon materials below C₂₀ and above C₅₀ and subject

1 them to molecular averaging to arrive at a composition in the desired range.
2 When preparing a lube base oil composition in the C₃₀ range, for example, C₂₀
3 and C₄₀ fractions can be combined and subjected to molecular averaging.

4
5 In one embodiment, the process involves performing Fischer-Tropsch
6 synthesis on syngas to provide a range of products, isolating various fractions
7 via fractional distillation, and performing molecular averaging on a relatively
8 low molecular weight fraction and a relatively high molecular weight fraction to
9 provide a product with a molecular weight between the low and high
10 molecular weights, which is suitable for use in preparing a lube base oil
11 composition. In another embodiment, relatively low molecular weight and/or
12 relatively high molecular weight fractions are obtained from another source,
13 for example, via distillation of crude oil, provided that the fractions do not
14 include appreciable amounts (i.e., amounts which would adversely affect the
15 catalyst used for molecular averaging) of thiols, amines, or cycloparaffins.

16
17 It may be advantageous to take representative samples of each fraction and
18 subject them to molecular averaging reactions, adjusting the relative
19 proportions of the fractions until a product with desired properties is obtained.
20 Then, the reaction can be scaled up using the relative ratios of each of the
21 fractions that resulted in the desired product. Using this method, one can "dial
22 in" a molecular weight distribution which can be roughly standardized between
23 batches and result in a reasonably consistent product.

24 BRIEF DESCRIPTION OF THE DRAWING

25
26
27 The Figure is a schematic flow diagram representing one embodiment of the
28 invention.

29

DETAILED DESCRIPTION OF THE INVENTION

In its broadest aspect, the present invention is directed to an integrated process for producing hydrocarbons in the lube base oil range, lube base oils and lube oils via molecular averaging of relatively low molecular weight and relatively high molecular weight fractions, for example, C₂₀ and C₄₀ fractions. The lube base oil composition includes hydrocarbons in the range of between about C₂₀ and C₅₀, but is preferably around C₃₀.

As used herein, "hydrocarbons in the lube base oil range" are hydrocarbons having a boiling point in the lube oil range (i.e., between 650°F and 1200°F). As used herein, a "relatively low molecular weight fraction" is a fraction with an average molecular weight lower than the average molecular weight of the desired lube oil composition. A "relatively high molecular weight fraction" is a fraction with an average molecular weight higher than the average molecular weight of the desired lube oil composition. "Average molecular weight" is molar average molecular weight. Preferably, the relatively high and relatively low molecular weight fractions are each within about 10 carbons from that of the desired product. However, the process described herein can tolerate broader differences in molecular weight.

An important consideration for determining an appropriate ratio of high molecular weight and low molecular weight fractions is that the average molecular weight of the two fractions, taking into consideration the relative proportions of each fraction, is close to the desired average molecular weight. Because of reactivity differences, it is possible to have an excess of one component, in particular, the lower molecular weight fraction.

In one embodiment, the process involves performing Fischer-Tropsch synthesis on syngas to provide a range of products, isolating various fractions via fractional distillation (including relatively high and relatively low molecular

1 weight fractions), and performing molecular averaging on the relatively low
2 molecular weight and relatively high molecular weight fractions. Alternatively,
3 the relatively low molecular weight and/or relatively high molecular weight
4 fractions are obtained from another source, for example, via distillation of
5 crude oil, provided that the fractions do not include an appreciable amount of
6 olefins, heteroatoms or saturated cyclic compounds.

7
8 The product from the molecular averaging reaction typically includes
9 hydrocarbons with molecular weights between the low and high molecular
10 weights. A suitable fraction can be isolated, for example, by distillation, which
11 fraction contains hydrocarbons in the lube base oil range. These
12 hydrocarbons generally are waxy solids, but can be readily isomerized to form
13 a lube base oil composition. The lube base oil composition can be blended
14 with suitable additives to form the lube base oil composition.

15
16 The process described herein is an integrated process. As used herein, the
17 term "integrated process" refers to a process which involves a sequence of
18 steps, some of which may be parallel to other steps in the process, but which
19 are interrelated or somehow dependent upon either earlier or later steps in the
20 total process.

21
22 An advantage of the present process is the effectiveness with which the
23 present process may be used to prepare high quality base oils useful for
24 manufacturing lubricating oils, and particularly with feedstocks which are not
25 conventionally recognized as suitable sources for such base oils.

26 27 Lube Base Oil Composition

28
29 The lube base oil prepared according to the process described herein can
30 have virtually any desired molecular weight, depending on the desired
31 physical and chemical properties of the lube oil composition, for example,
32 pour point, viscosity index and the like. The molecular weight can be

1 controlled by adjusting the molecular weight and proportions of the high
2 molecular weight and low molecular weight fractions. Lube oil compositions
3 with boiling points in the range of between about 650°F and 1200°F are
4 preferred, with boiling points in the range of between about 700°F and 1100°F
5 being more preferred. The currently most preferred average molecular weight
6 is around C₃₀, which has a boiling point in the range of roughly 840°F,
7 depending on the degree of branching. However, the process is adaptable to
8 generate higher molecular weight lube oils, for example, those in the C₃₅-C₄₀
9 range, or lower molecular weight lube oils, for example, those in the C₂₀-C₂₅
10 range. Preferably, the majority of the composition includes compounds within
11 about 8 carbons of the average, more preferably, within around 5 carbons of
12 the average.

13

14 In a preferred embodiment, the composition includes branched hydrocarbons.
15 The products of the Fischer-Tropsch synthesis tend to be linear, which can
16 result in a relatively high pour point. However, the linear products can be
17 isomerized readily using known isomerization chemistry, or, alternatively, the
18 reactants subjected to molecular averaging can be isomerized before the
19 molecular averaging step. Accordingly, the preferred lube base oil
20 composition can generally be described as including hydrocarbons in the
21 C₂₀-C₅₀, preferably around C₃₀ range which include branching typical of that
22 observed in compositions subjected to catalytic dewaxing and/or
23 isomerization dewaxing processes.

24

25 The lube base oil and/or lube oil preferably have a pour point in the range of
26 10°C or lower, more preferably 0°C or lower, still more preferably, -15°C or
27 lower, and most preferably, between -15°C and -40°C. The degree of
28 branching in the composition is preferably kept to the minimum amount
29 needed to arrive at the desired pour point. Pour point depressants can be
30 added to adjust the pour point to a desired value.

31

1 The lube base oil and/or lube oil composition preferably have a kinematic
2 viscosity of at least 3 centistokes, more preferably at least 4 centistokes, still
3 more preferably at least 5 centistokes, and most preferably at least
4 6 centistokes, where the viscosity is measured at 40°C. They also have a
5 viscosity index (a measure of the resistance of viscosity change to changes in
6 temperature) of at least 100, preferably 140 or more, more preferably over
7 150, and most preferably over 160.

8
9 Another important property for the lube base oil and lube oil composition is
10 that it has a relatively high flash point for safety reasons. Preferably, the flash
11 point is above 90°C, more preferably above 110°C, still more preferably
12 greater than 175°C, and most preferably between 175°C and 300°C. The
13 following table (Table 1) shows a correlation between viscosity and flash point
14 of preferred lubricants for use in automobiles.

15

16

Table 1

Viscosity at 40°C (cSt)	Flash Point (D93), °C	Flash Point (D92), °C
3.0	175	175
4.08	205	208
4.18	201	214
6.93	230	237
11.03	251	269

17

18 *D92 and D93 listed in the above table refer to ASTM tests for measuring
19 flash point:

20

21 Flash Point, COC, °C D 92

22 Flash Point, PMCC, °C D 93

23

24 The lube oil can be used, for example, in automobiles. The high paraffinic
25 nature of the lube oil gives it high oxidation and thermal stability, and the lube
26 oil has a high boiling range for its viscosity, i.e., volatility is low, resulting in
27 low evaporative losses.

1 The lube oil can also be used as a blending component with other oils. For
2 example, the lube oil can be used as a blending component with
3 polyalphaolefins, or with mineral oils to improve the viscosity and viscosity
4 index properties of those oils, or can be combined with isomerized petroleum
5 wax. The lube oils can also be used as workover fluids, packer fluids, coring
6 fluids, completion fluids, and in other oil field and well-servicing applications.
7 For example, they can be used as spotting fluids to unstick a drill pipe that
8 has become stuck, or they can be used to replace part or all of the expensive
9 polyalphaolefin lubricating additives in downhole applications. Additionally,
10 they can also be used in drilling fluid formulations where shale-swelling
11 inhibition is important, such as those described in U.S. Pat. No. 4,941,981 to
12 Perricone et al.

13

14 Preferably, the lube oil is obtained via molecular averaging of Fischer-Tropsch
15 products and, therefore, contains virtually no heteroatoms or saturated cyclic
16 compounds. Alternatively, the lube oil can be obtained by molecular
17 averaging of other feedstocks, preferably in which at least the heteroatoms,
18 and more preferably the saturated cyclic compounds, have been removed.

19

20 Additives

21

22 The lube oil composition includes various additives, such as lubricants,
23 emulsifiers, wetting agents, densifiers, fluid-loss additives, viscosity modifiers,
24 corrosion inhibitors, oxidation inhibitors, friction modifiers, demulsifiers,
25 anti-wear agents, dispersants, anti-foaming agents, pour point depressants,
26 detergents, rust inhibitors and the like. Other hydrocarbons, such as those
27 described in U.S. Patent No. 5,096,883 and/or U.S. Patent No. 5,189,012,
28 may be blended with the lube oil provided that the final blend has the
29 necessary pour point, kinematic viscosity, flash point, and toxicity properties.
30 The total amount of additives is preferably between 1-30 percent. All
31 percentages listed herein are weight percentages unless otherwise stated.

32

1 Examples of suitable lubricants include polyol esters of C₁₂-C₂₈ acids.

2

3 Examples of viscosity modifying agents include polymers such as ethylene
4 alpha-olefin copolymers which generally have weight average molecular
5 weights of from about 10,000 to 1,000,000 as determined by gel permeation
6 chromatography.

7

8 Examples of suitable corrosion inhibitors include phosphosulfurized
9 hydrocarbons and the products obtained by reacting a phosphosulfurized
10 hydrocarbon with an alkaline earth metal oxide or hydroxide.

11

12 Examples of oxidation inhibitors include antioxidants such as alkaline earth
13 metal salts of alkylphenol thioesters having preferably C₅-C₁₂ alkyl side chain
14 such as calcium nonylphenol sulfide, barium t-octylphenol sulfide,
15 dioctylphenylamine, as well as sulfurized or phosphosulfurized hydrocarbons.
16 Additional examples include oil soluble antioxidant copper compounds such
17 as copper salts of C₁₀ to C₁₈ oil soluble fatty acids.

18

19 Examples of friction modifiers include fatty acid esters and amides, glycerol
20 esters of dimerized fatty acids and succinate esters or metal salts thereof.

21

22 Dispersants are well known in the lubricating oil field and include high
23 molecular weight alkyl succinimides being the reaction products of oil soluble
24 polyisobutylene succinic anhydride with ethylene amines such as
25 tetraethylene pentamine and borated salts thereof.

26

27 Pour point depressants such as C₈-C₁₈ dialkyl fumarate vinyl acetate
28 copolymers, polymethacrylates and wax naphthalene are well known to those
29 of skill in the art.

30

31 Examples of anti-foaming agents include polysiloxanes such as silicone oil
32 and polydimethyl siloxane; acrylate polymers are also suitable.

1

2 Examples of anti-wear agents include zinc dialkyldithiophosphate, zinc diaryl
3 diphosphate, and sulfurized isobutylene.

4

5 Examples of detergents and metal rust inhibitors include the metal salts of
6 sulfonic acids, alkylphenols, sulfurized alkylphenols, alkyl salicylates,
7 naphthenates and other oil soluble mono and dicarboxylic acids such as
8 tetrapropyl succinic anhydride. Neutral or highly basic metal salts such as
9 highly basic alkaline earth metal sulfonates (especially calcium and
10 magnesium salts) are frequently used as such detergents. Also useful is
11 nonylphenol sulfide. Similar materials made by reacting an alkylphenol with
12 commercial sulfur dichlorides. Suitable alkylphenol sulfides can also be
13 prepared by reacting alkylphenols with elemental sulfur. Also suitable as
14 detergents are neutral and basic salts of phenols, generally known as
15 phenates, wherein the phenol is generally an alkyl substituted phenolic group,
16 where the substituent is an aliphatic hydrocarbon group having about 4 to 400
17 carbon atoms.

18

19 Antioxidants can be added to the lube oil to neutralize or minimize oil
20 degradation chemistry. Examples of antioxidants include those described in
21 U.S. Pat. No. 5,200,101, which discloses certain amine/hindered phenol, acid
22 anhydride and thiol ester-derived products.

23

24 The combination of a metallic dithiophosphate hydroperoxide decomposer
25 and aminic antioxidant is reported to have a synergistic effect on lubricant
26 antioxidant performance. See Maleville et al., *Lubrication Science*, V9, No. 1,
27 pg. 3-60 (1996). Sulfur-substituted derivatives of mercapto carboxylic esters
28 also are reported to possess antioxidant properties. See M. A. Mirozopeva
29 et al., *Naftekhimiya*, V28, No. 6, pg. 831-837 (1988).

30

31 Additional lube oils additives are described in U.S. Patent No. 5,898,023 to
32 Francisco et al., the contents of which are hereby incorporated by reference.

Feedstocks for the Molecular Averaging Reaction

Examples of feedstocks that can be molecularly averaged in accordance with the present invention include oils that generally have relatively high pour points which it is desired to reduce to relatively low pour points. Numerous petroleum feedstocks, for example, those derived from crude oil, are suitable for use. Examples include petroleum distillates having a normal boiling point above about 100°C, gas oils and vacuum gas oils, residuum fractions from an atmospheric pressure distillation process, solvent-deasphalted petroleum residues, shale oils, cycle oils, petroleum and slack wax, waxy petroleum feedstocks, NAO wax, and waxes produced in chemical plant processes. Straight chain n-paraffins either alone or with only slightly branched chain paraffins having 16 or more carbon atoms are sometimes referred to herein as waxes.

The feedstocks should not include appreciable amounts of olefins, heteroatoms, or saturated cyclic compounds. Preferred feedstocks are products from Fischer-Tropsch synthesis or waxes from petroleum products. If any heteroatoms, olefins or saturated cyclic compounds are present in the feedstock, they should be removed before the molecular averaging reaction. Olefins and heteroatoms can be removed by hydrotreating. Saturated cyclic hydrocarbons can be separated from the desired feedstock paraffins by use of adsorption with molecular sieves or by deoiling or by complexing with urea.

Preferred petroleum distillates for use in the relatively low molecular weight fraction boil in the normal boiling point range of 200°C to 700°C, more preferably in the range of 260°C to 650°C. Suitable feedstocks also include those heavy distillates normally defined as heavy straight-run gas oils and heavy cracked cycle oils, as well as conventional FCC feed and portions thereof. Cracked stocks may be obtained from thermal or catalytic cracking of various stocks. The feedstock may have been subjected to a hydrotreating

1 and/or hydrocracking process before being supplied to the present process.
2 Alternatively, or in addition, the feedstock may be treated in a solvent
3 extraction process to remove aromatics and sulfur- and nitrogen-containing
4 molecules before being dewaxed.

5
6 As used herein, the term "waxy petroleum feedstocks" includes petroleum
7 waxes. The feedstock employed in the process of the invention can be a
8 waxy feed which contains greater than about 50% wax, and in some
9 embodiments, even greater than about 90% wax. Highly paraffinic feeds
10 having high pour points, generally above about 0°C, more usually above
11 about 10°C are also suitable for use in the process of the invention. Such
12 feeds can contain greater than about 70% paraffinic carbon, and in some
13 embodiments, even greater than about 90% paraffinic carbon.

14
15 Examples of additional suitable feeds include waxy distillate stocks such as
16 gas oils, lubricating oil stocks, synthetic oils and waxes such as those
17 produced by Fischer-Tropsch synthesis, high pour point polyalphaolefins,
18 foots oils, synthetic waxes such as normal alpha-olefin waxes, slack waxes,
19 deoiled waxes and microcrystalline waxes. Foots oil is prepared by
20 separating oil from the wax, where the isolated oil is referred to as foots oil.

21

22 Fischer-Tropsch Chemistry

23

24 In one embodiment, the relatively low molecular weight fraction (for example,
25 a C₂₀ fraction) and the relatively high molecular weight fraction (for example, a
26 C₄₀ fraction) are obtained via Fischer-Tropsch chemistry. Fischer-Tropsch
27 chemistry tends to provide a wide range of products from methane and other
28 light hydrocarbons to heavy wax. Syngas is converted to liquid hydrocarbons
29 by contact with a Fischer-Tropsch catalyst under reactive conditions.
30 Depending on the quality of the syngas, it may be desirable to purify the
31 syngas prior to the Fischer-Tropsch reactor to remove carbon dioxide

1 produced during the syngas reaction and any sulfur compounds, if they have
2 not already been removed. This can be accomplished by contacting the
3 syngas with a mildly alkaline solution (e.g., aqueous potassium carbonate) in
4 a packed column.

5
6 In general, Fischer-Tropsch catalysts contain a Group VIII transition metal on
7 a metal oxide support. The catalyst may also contain a noble metal
8 promoter(s) and/or crystalline molecular sieves. Pragmatically, the two
9 transition metals that are most commonly used in commercial
10 Fischer-Tropsch processes are cobalt or iron. Ruthenium is also an effective
11 Fischer-Tropsch catalyst but is more expensive than cobalt or iron. Where a
12 noble metal is used, platinum and palladium are generally preferred. Suitable
13 metal oxide supports or matrices which can be used include alumina, titania,
14 silica, magnesium oxide, silica-alumina, and the like, and mixtures thereof.

15
16 Although Fischer-Tropsch processes produce a hydrocarbon product having a
17 wide range of molecular sizes, the selectivity of the process toward a given
18 molecular size range as the primary product can be controlled to some extent
19 by the particular catalyst used. In the present process, it is preferred to
20 produce C₂₀-C₅₀ paraffins as the primary product, and therefore, it is preferred
21 to use a cobalt catalyst although iron catalysts may also be used. One
22 suitable catalyst that can be used is described in U.S. Patent No. 4,579,986
23 as satisfying the relationship:

$$(3 + 4R) > L/S > (0.3 + 0.4R),$$

24
25
26
27 wherein:

28 L = the total quantity of cobalt present on the catalyst, expressed as mg
29 Co/ml catalyst,
30 S = the surface area of the catalyst, expressed as m²/ml catalyst, and
31 R = the weight ratio of the quantity of cobalt deposited on the catalyst by
32 kneading to the total quantity of cobalt present on the catalyst.

1 Preferably, the catalyst contains about 3-60 ppw cobalt, 0.1-100 ppw of at
2 least one of zirconium, titanium or chromium per 100 ppw of silica, alumina, or
3 silica-alumina and mixtures thereof. Typically, the synthesis gas will contain
4 hydrogen, carbon monoxide and carbon dioxide in a relative mole ratio of
5 about from 0.25 to 2 moles of carbon monoxide and 0.01 to 0.05 moles of
6 carbon dioxide per mole of hydrogen. It is preferred to use a mole ratio of
7 carbon monoxide to hydrogen of about 0.4 to 1, more preferably 0.5 to
8 0.7 moles of carbon monoxide per mole of hydrogen with only minimal
9 amounts of carbon dioxide; preferably less than 0.5 mole percent carbon
10 dioxide.

11

12 The Fischer-Tropsch reaction is typically conducted at temperatures between
13 about 300°F and 700°F (149°C to 371°C), preferably, between about 400°F
14 and 550°F (204°C to 228°C). The pressures are typically between about 10
15 and 500 psia (0.7 to 34 bars), preferably between about 30 and 300 psia (2 to
16 21 bars). The catalyst space velocities are typically between about from 100
17 and 10,000 cc/g/hr., preferably between about 300 and 3,000 cc/g/hr.

18

19 The reaction can be conducted in a variety of reactors for example, fixed bed
20 reactors containing one or more catalyst beds, slurry reactors, fluidized bed
21 reactors, or a combination of different type reactors.

22

23 In a preferred embodiment, the Fischer-Tropsch reaction is conducted in a
24 bubble column slurry reactor. In this type of reactor synthesis gas is bubbled
25 through a slurry that includes catalyst particles in a suspending liquid.

26 Typically, the catalyst has a particle size of between 10 and 110 microns,
27 preferably between 20 and 80 microns, more preferably between 25 and
28 65 microns, and a density of between 0.25 and 0.9 g/cc, preferably between
29 0.3 and 0.75 g/cc. The catalyst typically includes one of the aforementioned
30 catalytic metals, preferably cobalt on one of the aforementioned catalyst
31 supports. Preferably, the catalyst comprises about 10 to 14 percent cobalt on

1 a low density fluid support, for example alumina, silica and the like having a
2 density within the ranges set forth above for the catalyst. Since the catalyst
3 metal may be present in the catalyst as oxides, the catalyst is typically
4 reduced with hydrogen prior to contact with the slurry liquid. The starting
5 slurry liquid is typically a heavy hydrocarbon which is viscous enough to keep
6 the catalyst particles suspended (typically a viscosity between
7 4-100 centistokes at 100°C) and a low enough volatility to avoid vaporization
8 during operation (typically an initial boiling point range of between about
9 350°C and 550°C). The slurry liquid is preferably essentially free of
10 contaminants such as sulfur, phosphorous or chlorine compounds. Initially, it
11 may be desirable to use a synthetic hydrocarbon fluid such as a synthetic
12 olefin oligomer as the slurry fluid.

13
14 Often, a paraffin fraction of the product having the desired viscosity and
15 volatility is recycled as the slurry liquid. The slurry typically has a catalyst
16 concentration of between about 2 and 40 percent catalyst, preferably between
17 about 5 and 20 percent, and more preferably between about 7 and 15 percent
18 catalyst based on the total weight of the catalyst, i.e., metal plus support. The
19 syngas feed typically has a hydrogen to carbon monoxide mole ratio of
20 between about 0.5 and 4 moles of hydrogen per mole of carbon monoxide,
21 preferably between about 1 and 2.5 moles, and more preferably between
22 about 1.5 and 2 moles.

23
24 The bubble slurry reactor is typically operated at temperatures within the
25 range of between about 150°C and 300°C, preferably between about 185°C
26 and 265°C, and more preferably between about 210°C and 230°C, at
27 pressures within the range of between about 1 and 70 bar, preferably
28 between about 6 and 35 bar, and most preferably between about 10 and
29 30 bar (1 bar = 14.5 psia). Typical synthesis gas linear velocity ranges in the
30 reactor are from about 2 to 40 cm per sec., preferably from about 6 to 10 cm
31 per sec. Additional details regarding bubble column slurry reactors can be

1 found, for example, in Y. T. Shah et al., "Design Parameters Estimations for
2 Bubble Column Reactors", *AIChE Journal*, 28 No. 3, pp. 353-379 (May 1982);
3 Ramachandran et al., "Bubble Column Slurry Reactor, Three-Phase Catalytic
4 Reactors", Chapter 10, pp. 308-332, Gordon and Broch Science Publishers
5 (1983); Deckwer et al., "Modeling the Fischer-Tropsch Synthesis in the Slurry
6 Phase", *Ind. Eng. Chem. Process Des. Dev.*, v 21, No. 2, pp. 231-241 (1982);
7 Kölbel et al., "The Fischer-Tropsch Synthesis in the Liquid Phase", *Catal.*
8 *Rev.-Sci. Eng.*, v. 21(n), pp. 225-274 (1980); and U.S. Patent No. 5,348,982,
9 the contents of each of which are hereby incorporated by reference in their
10 entirety.

11

12 Although the relatively high and relatively low molecular weight fractions used
13 in the process described herein are described herein in terms of a
14 Fischer-Tropsch reaction product, these fractions can also be obtained
15 through various modifications of the literal Fischer-Tropsch process by which
16 hydrogen (or water) and carbon monoxide (or carbon dioxide) are converted
17 to hydrocarbons (e.g., paraffins, ethers, etc.) and to the products of such
18 processes. Thus, the term Fischer-Tropsch type product or process is
19 intended to apply to Fischer-Tropsch processes and products and the various
20 modifications thereof and the products thereof. For example, the term is
21 intended to apply to the Kolbel-Engelhardt process typically described by the
22 reactions

23



26

27 The Separation of Product From the Fischer-Tropsch Reaction

28

29 The products from Fischer-Tropsch reactions generally include a gaseous
30 reaction product and a liquid reaction product. The gaseous reaction product
31 includes hydrocarbons boiling below about 650°F (e.g., tail gases through

1 middle distillates). The liquid reaction product (the condensate fraction)
2 includes hydrocarbons boiling above about 650°F (e.g., vacuum gas oil
3 through heavy paraffins).

4
5 The minus 650°F product can be separated into a tail gas fraction and a
6 condensate fraction, i.e., about C₅ to C₂₀ normal paraffins and higher boiling
7 hydrocarbons, using, for example, a high pressure and/or lower temperature
8 vapor-liquid separator or low pressure separators or a combination of
9 separators. While the preferred fractions for preparing the lube oil
10 composition generally include C₂₀ and C₄₀ paraffins, paraffins with a lower
11 molecular weight, such as those in the above fractions, can also be used.

12
13 The fraction boiling above about 650°F (the condensate fraction), after
14 removal of the particulate catalyst, is typically separated into a wax fraction
15 boiling in the range of about 650°F-1200°F primarily about containing C₂₀ to
16 C₅₀ linear paraffins with relatively small amounts of higher boiling branched
17 paraffins and one or more fractions boiling above about 1200°F. Typically,
18 the separation is effected by fractional distillation.

19
20 Products in the desired range (for example, C₂₀-C₅₀, preferably around C₃₀)
21 are preferably isolated and used directly to prepare lube base oil
22 compositions. Products in the relatively low molecular weight fraction (for
23 example, C₂₀, distillate fuels) and the relatively high molecular weight fraction
24 (for example, C₄₀, 1000°F+ wax) can be isolated and combined for molecular
25 redistribution/averaging to arrive at a desired fraction. The product of the
26 molecular averaging reaction can be distilled to provide a desired fraction, and
27 also relatively low and high molecular weight fractions, which can be
28 reprocessed in the molecular averaging stage.

29
30 To prepare a product in the C₂₀-C₅₀ range, one can combine the fractions
31 below C₂₀ with those above C₅₀ (1000°F+ wax, or the "heavy" fraction). To

1 prepare a product in the C₃₀ range, it may be preferable to combine a C₂₀
2 fraction with a C₄₀ fraction, as the molecular averaging tends to provide a
3 roughly statistical mixture of products intermediate in molecular weight to the
4 starting materials. More product in the desired range is produced when the
5 reactants have molecular weights closer to the target molecular weight. Of
6 course, following fractional distillation and isolation of the product of the
7 molecular averaging reaction, the other fractions can be isolated and
8 re-subjected to molecular averaging conditions.

9
10 In one embodiment, since the fractions will be averaged, the fraction with the
11 desired molecular weight is not removed prior to molecular averaging.
12 However, the molecular averaging tends to somewhat reduce the VI and other
13 beneficial properties of the resulting lube oil compositions, so it is preferred
14 that the desired fraction be obtained directly from the Fischer-Tropsch
15 chemistry, and a second desired fraction obtained via molecular averaging.

16 17 Hydrotreating and/or Hydrocracking Chemistry

18
19 Fractions used in the molecular averaging chemistry may include heteroatoms
20 such as sulfur or nitrogen that may adversely affect the catalysts used in the
21 molecular averaging reaction. If sulfur impurities are present in the starting
22 materials, they can be removed using means well known to those of skill in
23 the art, for example, extractive Merox, hydrotreating, adsorption, etc.
24 Nitrogen-containing impurities can also be removed using means well known
25 to those of skill in the art. Hydrotreating and hydrocracking are preferred
26 means for removing these and other impurities.

27
28 Accordingly, it is preferred that these fractions be hydrotreated and/or
29 hydrocracked to remove the heteroatoms before performing the molecular
30 averaging process described herein. Hydrogenation catalysts can be used to
31 hydrotreat the products resulting from the Fischer-Tropsch, molecular
32 averaging and/or isomerization reactions.

1 As used herein, the terms "hydrotreating" and "hydrocracking" are given their
2 conventional meaning and describe processes that are well known to those
3 skilled in the art. Hydrotreating refers to a catalytic process, usually carried
4 out in the presence of free hydrogen, in which the primary purpose is the
5 desulfurization and/or denitrification of the feedstock. Generally, in
6 hydrotreating operations, cracking of the hydrocarbon molecules, i.e.,
7 breaking the larger hydrocarbon molecules into smaller hydrocarbon
8 molecules, is minimized and the unsaturated hydrocarbons are either fully or
9 partially hydrogenated.

10

11 Hydrocracking refers to a catalytic process, usually carried out in the
12 presence of free hydrogen, in which the cracking of the larger hydrocarbon
13 molecules is a primary purpose of the operation. Desulfurization and/or
14 denitrification of the feed stock usually will also occur.

15

16 Catalysts used in carrying out hydrotreating and hydrocracking operations are
17 well known in the art. See, for example, U.S. Patent Nos. 4,347,121 and
18 4,810,357 for general descriptions of hydrotreating, hydrocracking, and typical
19 catalysts used in each process.

20

21 Suitable catalysts include noble metals from Group VIIIA (according to the
22 1975 rules of the International Union of Pure and Applied Chemistry), such as
23 platinum or palladium on an alumina or siliceous matrix, and unsulfided Group
24 VIIIA and Group VIB, such as nickel-molybdenum or nickel-tin on an alumina
25 or siliceous matrix. U.S. Pat. No. 3,852,207 describes a suitable noble metal
26 catalyst and mild conditions. Other suitable catalysts are described, for
27 example, in U.S. Pat. No. 4,157,294 and U.S. Pat. No. 3,904,513. The
28 non-noble metal (such as nickel-molybdenum) hydrogenation metal are
29 usually present in the final catalyst composition as oxides, or more preferably
30 or possibly, as sulfides when such compounds are readily formed from the
31 particular metal involved. Preferred non-noble metal catalyst compositions
32 contain in excess of about 5 weight percent, preferably about 5 to about

1 40 weight percent molybdenum and/or tungsten, and at least about 0.5, and
2 generally about 1 to about 15 weight percent of nickel and/or cobalt
3 determined as the corresponding oxides. The noble metal (such as platinum)
4 catalyst contains in excess of 0.01 percent metal, preferably between 0.1 and
5 1.0 percent metal. Combinations of noble metals may also be used, such as
6 mixtures of platinum and palladium.

7
8 The hydrogenation components can be incorporated into the overall catalyst
9 composition by any one of numerous procedures. The hydrogenation
10 components can be added to matrix component by co-mulling, impregnation,
11 or ion exchange and the Group VI components, i.e., molybdenum and
12 tungsten can be combined with the refractory oxide by impregnation,
13 co-mulling or co-precipitation. Although these components can be combined
14 with the catalyst matrix as the sulfides, that is generally not preferred, as the
15 sulfur compounds can interfere with the molecular averaging or
16 Fischer-Tropsch catalysts.

17
18 The matrix component can be of many types including some that have acidic
19 catalytic activity. Ones that have activity include amorphous silica-alumina or
20 may be a zeolitic or non-zeolitic crystalline molecular sieve. Examples of
21 suitable matrix molecular sieves include zeolite Y, zeolite X and the so-called
22 ultra stable zeolite Y and high structural silica:alumina ratio zeolite Y such as
23 that described in U.S. Patent Nos. 4,401,556, 4,820,402 and 5,059,567.
24 Small crystal size zeolite Y, such as that described in U.S. Patent
25 No. 5,073,530, can also be used. Non-zeolitic molecular sieves which can be
26 used include, for example, silicoaluminophosphates (SAPO),
27 ferroaluminophosphate, titanium aluminophosphate, and the various ELAPO
28 molecular sieves described in U.S. Patent No. 4,913,799 and the references
29 cited therein. Details regarding the preparation of various non-zeolite
30 molecular sieves can be found in U.S. Patent Nos. 5,114,563 (SAPO);
31 4,913,799 and the various references cited in U.S. Patent No. 4,913,799.
32 Mesoporous molecular sieves can also be used, for example, the M41S family

1 of materials (*J. Am. Chem. Soc.* 1992, 114, 10834-10843), MCM-41 (U.S.
2 Patent Nos. 5,246, 689, 5,198,203 and 5,334,368), and MCM-48 (Kresge
3 et al., *Nature* 359 (1992) 710).

4

5 Suitable matrix materials may also include synthetic or natural substances as
6 well as inorganic materials such as clay, silica and/or metal oxides such as
7 silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia,
8 silica-titania as well as ternary compositions, such as silica-alumina-thoria,
9 silica-alumina-zirconia, silica-alumina-magnesia, and silica-magnesia zirconia.

10 The latter may be either naturally occurring or in the form of gelatinous
11 precipitates or gels including mixtures of silica and metal oxides. Naturally
12 occurring clays which can be composited with the catalyst include those of the
13 montmorillonite and kaolin families. These clays can be used in the raw state
14 as originally mined or initially subjected to calumination, acid treatment or
15 chemical modification.

16

17 Furthermore, more than one catalyst type may be used in the reactor. The
18 different catalyst types can be separated into layers or mixed. Typical
19 hydrotreating conditions vary over a wide range. In general, the overall LHSV
20 is about 0.25 to 2.0, preferably about 0.5 to 1.0. The hydrogen partial
21 pressure is greater than 200 psia, preferably ranging from about 500 psia to
22 about 2000 psia. Hydrogen recirculation rates are typically greater than
23 50 SCF/Bbl, and are preferably between 1000 and 5000 SCF/Bbl.

24 Temperatures range from about 300°F to about 750°F, preferably ranging
25 from 450°F to 600°F.

26

27 The contents of each of the patents and publications referred to above are
28 hereby incorporated by reference in its entirety.

29

Molecular Redistribution/Averaging

1

2

3 As used herein, "molecular redistribution" is a process in which a single
4 paraffin is converted into a mixture of lighter and heavier paraffins, or in which
5 a mixture of paraffins is converted into a paraffin with a narrow size
6 distribution. The latter technique is also known as "molecular averaging".
7 The term "disproportionation" is also used herein to describe molecular
8 averaging.

9

10 Molecular averaging uses conventional catalysts, such as Pt/Al₂O₃ and
11 WO₃/SiO₂ (or inexpensive variations). The chemistry does not require using
12 hydrogen gas, and therefore does not require relatively expensive recycle gas
13 compressors. The chemistry is typically performed at mild pressures
14 (100-5000 psig). The chemistry is typically thermoneutral and, therefore,
15 there is no need for additional equipment to control the temperature.

16

17 Molecular averaging is very sensitive to sulfur impurities in the feedstock, and
18 these must be removed prior to the reaction. Typically, if the paraffins being
19 averaged result from a Fischer-Tropsch reaction, they do not contain sulfur.
20 However, if the paraffins resulted from another process, for example,
21 distillation of crude oil, they may contain sufficient sulfur impurities to
22 adversely effect the molecular averaging chemistry.

23

24 The presence of excess olefins and hydrogen in the disproportionation zone
25 are also known to effect the equilibrium of the disproportionation reaction and
26 to deactivate the catalyst. Since the composition of the fractions may vary,
27 some routine experimentation will be necessary to identify the contaminants
28 that are present and identify the optimal processing scheme and catalyst to
29 use in carrying out the invention.

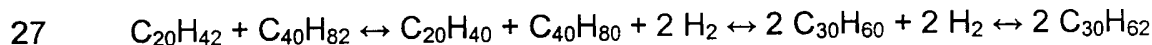
30

31 Molecular averaging generally involves two distinct chemical reactions. First,
32 the paraffins are converted into olefins on the platinum catalyst in a process

1 known as dehydrogenation or unsaturation. The olefins are disproportionated
2 into lighter and heavier olefins by a process known as olefin metathesis. The
3 metathesized olefins are then converted into paraffins on the platinum catalyst
4 in a process known as hydrogenation or saturation.

5
6 The relatively low molecular weight fractions (i.e., at or below C₂₀) and
7 relatively high molecular weight fraction (i.e., at or above C₄₀) are molecularly
8 averaged to a desired fraction (i.e., at or around C₃₀) fraction using an
9 appropriate molecular averaging catalyst under conditions selected to convert
10 a significant portion of the relatively high molecular weight and relatively low
11 molecular weight fractions to a desired fraction.

12
13 Various catalysts are known to catalyze the molecular averaging reaction.
14 The catalyst mass used to carry out the present invention must have both
15 dehydrogenation/hydrogenation activity and molecular averaging activity. The
16 dehydrogenation activity is believed to be necessary to convert the alkanes in
17 the feed to olefins, which are believed to be the actual species that undergo
18 olefin metathesis. Following olefin metathesis, the olefin is converted back
19 into an alkane. It is theorized that the dehydrogenation/hydrogenation activity
20 of the catalyst also contributes to rehydrogenation of the olefin to an alkane.
21 While it is not intended that the present invention be limited to any particular
22 mechanism, it may be helpful in explaining the choice of catalysts to further
23 discuss the sequence of chemical reactions which are believed to be
24 responsible for molecular averaging of the alkanes. As an example, the
25 general sequence of reactions for C₂₀ and C₄₀ fractions is believed to be:



28
29 The catalyst mass for use in the molecular averaging reaction will be dual
30 function and may have the two functions on the same catalyst particle or may
31 consist of different catalysts having separate dehydrogenation/hydrogenation
32 and molecular averaging components within the catalyst mass. The

1 dehydrogenation/hydrogenation function within the catalyst mass usually will
2 include a Group VIII metal from the Periodic Table of the Elements which
3 includes iron, cobalt, nickel, palladium, platinum, rhodium, ruthenium,
4 osmium, and iridium.

5
6 Platinum and palladium or the compounds thereof are preferred for inclusion
7 in the dehydrogenation/hydrogenation component, with platinum or a
8 compound thereof being especially preferred. As noted previously, when
9 referring to a particular metal in this disclosure as being useful in the present
10 invention, the metal may be present as elemental metal or as a compound of
11 the metal. As discussed above, reference to a particular metal in this
12 disclosure is not intended to limit the invention to any particular form of the
13 metal unless the specific name of the compound is given, as in the examples
14 in which specific compounds are named as being used in the preparations.

15
16 In the event the catalyst deactivates with the time-on-stream, specific
17 processes that are well known to those skilled in art are available for the
18 regeneration of the catalysts.

19
20 Usually, the molecular averaging component of the catalyst mass will include
21 one or more of a metal or the compound of a metal from Group VIB or Group
22 VIIB of the Periodic Table of the Elements, which include chromium,
23 manganese, molybdenum, rhenium and tungsten. Preferred for inclusion in
24 the molecular averaging component are molybdenum, rhenium, tungsten, and
25 the compounds thereof. Particularly preferred for use in the molecular
26 averaging component is tungsten or a compound thereof. As discussed, the
27 metals described above may be present as elemental metals or as
28 compounds of the metals, such as, for example, as an oxide of the metal. It is
29 also understood that the metals may be present on the catalyst component
30 either alone or in combination with other metals.

31

1 In most cases, the metals in the catalyst mass will be supported on a
2 refractory material. Refractory materials suitable for use as a support for the
3 metals include conventional refractory materials used in the manufacture of
4 catalysts for use in the refining industry. Such materials include, but are not
5 necessarily limited to, alumina, zirconia, silica, boria, magnesia, titania and
6 other refractory oxide material or mixtures of two or more of any of the
7 materials. The support may be a naturally occurring material, such as clay, or
8 synthetic materials, such as silica-alumina and borosilicates. Molecular
9 sieves, such as zeolites, also have been used as supports for the metals used
10 in carrying out the dual functions of the catalyst mass. See, for example, U.S.
11 Patent 3,668,268. Mesoporous materials such as MCM-41 and MCM-48,
12 such as described in Kresge, C.T., et al., *Nature* (Vol. 359) pp. 710-712, 1992,
13 may also be used as a refractory support. Other known refractory supports,
14 such as carbon, may also serve as a support for the active form of the metals
15 in certain embodiments of the present invention. The support is preferably
16 non-acidic, i.e., having few or no free acid sites on the molecule. Free acid
17 sites on the support may be neutralized by means of alkali metal salts, such
18 as those of lithium. Alumina, particularly alumina on which the acid sites have
19 been neutralized by an alkali salt, such as lithium nitrate, is usually preferred
20 as a support for the dehydrogenation/hydrogenation component, and silica is
21 usually preferred as the support for the disproportionation component.

22

23 The amount of active metal present on the support may vary, but it must be at
24 least a catalytically active amount, i.e., a sufficient amount to catalyze the
25 desired reaction. In the case of the dehydrogenation/hydrogenation
26 component, the active metal content will usually fall within the range from
27 about 0.01 weight percent to about 50 weight percent on an elemental basis,
28 with the range of from about 0.1 weight percent to about 20 weight percent
29 being preferred. For the molecular averaging component, the active metals
30 content will usually fall within the range of from about 0.01 weight percent to
31 about 50 weight percent on an elemental basis, with the range of from about
32 0.1 weight percent to about 15 weight percent being preferred.

1 A typical molecular averaging catalyst for use in the present invention
2 includes a platinum component and a tungsten component is described in
3 U.S. Patent 3,856,876, the entire disclosure of which is herein incorporated by
4 reference. In one embodiment of the present invention, a catalyst is
5 employed which comprises a mixture of platinum-on-alumina and tungsten-
6 on-silica, wherein the volumetric ratio of the platinum component to the
7 tungsten component is greater than 1:50 and less than 50:1. Preferably, the
8 volumetric ratio of the platinum component to the tungsten component in this
9 particular embodiment is between 1:10 and 10:1. The percent of surface of
10 the metals should be maximized with at least 10% of the surface metal atoms
11 exposed to the reactant.

12

13 Both the dehydrogenation/hydrogenation component and the molecular
14 averaging component may be present within the catalyst mass on the same
15 support particle as, for example, a catalyst in which the
16 dehydrogenation/hydrogenation component is dispersed on an unsupported
17 molecular averaging component such as tungsten oxide. In another
18 embodiment of the invention, the catalyst components may be separated on
19 different particles. When the dehydrogenation/hydrogenation component and
20 the molecular averaging component are on separate particles, it is preferred
21 that the two components be in close proximity to one another, as for example,
22 in a physical mixture of the particles containing the two components.
23 However, in other embodiments of the invention, the components may be
24 physically separated from one another, as for example, in a process in which
25 separate dehydrogenation/hydrogenation and molecular averaging zones are
26 present in the reactor.

27

28 In a reactor having a layered fixed catalyst bed, the two components may, in
29 such an embodiment, be separated in different layers within the bed. In some
30 applications, it may even be advantageous to have separate reactors for
31 carrying out the dehydrogenation and molecular averaging steps. However,
32 in processing schemes where the dehydrogenation of the alkanes to olefins

1 occurs separately from the molecular averaging reaction of the olefins, it may
2 be necessary to include an additional hydrogenation step in the process,
3 since the rehydrogenation of the olefins must take place after the molecular
4 averaging step.

5
6 The process conditions selected for carrying out the present invention will
7 depend upon the molecular averaging catalyst used. In general, the
8 temperature in the reaction zone will be within the range of from about 400°F
9 (200°C) to about 1000°F (540°C) with temperatures in the range of from about
10 500°F (260°C) to about 850°F (455°C) usually being preferred. In general,
11 the conversion of the alkanes by molecular averaging increases with an
12 increase in pressure. Therefore, the selection of the optimal pressure for
13 carrying out the process will usually be at the highest practical pressure under
14 the circumstances. Accordingly, the pressure in the reaction zone should be
15 maintained above 100 psig, and preferably the pressure should be maintained
16 above 500 psig. The maximum practical pressure for the practice of the
17 invention is about 5000 psig. More typically, the practical operating pressure
18 will be below about 3000 psig. The feedstock to the molecular averaging reactor
19 should contain a minimum of olefins, and preferably should contain no added
20 hydrogen.

21
22 Saturated and partially saturated cyclic hydrocarbons (cycloalkanes, aromatic-
23 cycloalkanes, and alkyl derivatives of these species) can form hydrogen
24 during the molecular averaging reaction. This hydrogen can inhibit the
25 reaction, thus these species should be substantially excluded from the feed.
26 The desired paraffins can be separated from the saturated and partially
27 saturated cyclic hydrocarbons by deoiling or by use of molecular sieve
28 adsorbents, or by deoiling or by extraction with urea. These techniques are
29 well known in the industry. Separation with urea is described by Hepp, Box
30 and Ray in Ind. Eng. Chem., 45: 112 (1953). Fully aromatic cyclic
31 hydrocarbons do not form hydrogen and can be tolerated. Polycyclic

1 aromatics can form carbon deposits, and these species should also be
2 substantially excluded from the feed. This can be done by use of
3 hydrotreating and hydrocracking.

4

5 Platinum/tungsten catalysts are particularly preferred for carrying out the
6 present invention because the molecular averaging reaction will proceed
7 under relatively mild conditions. When using the platinum/tungsten catalysts,
8 the temperature should be maintained within the range of from about 400°F
9 (200°C) to about 1000°F (540°C), with temperatures above about 500°F
10 (260°C) and below about 800°F being particularly desirable.

11

12 The molecular averaging reaction described above is reversible, which means
13 that the reaction proceeds to an equilibrium limit. Therefore, if the feed to the
14 molecular averaging zone has two streams of alkanes at different molecular
15 weights, then equilibrium will drive the reaction to produce product having a
16 molecular weight between that of the two streams. The zone in which the
17 molecular averaging occurs is referred to herein as a molecular averaging
18 zone. It is desirable to reduce the concentration of the desired products in the
19 molecular averaging zone to as low a concentration as possible to favor the
20 reactions in the desired direction. As such, some routine experimentation
21 may be necessary to find the optimal conditions for conducting the process.

22

23 Any number of reactors can be used, such as fixed bed, fluidized bed,
24 ebulated bed, and the like. An example of a suitable reactor is a catalytic
25 distillation reactor.

26

27 When the relatively high molecular weight and relatively low molecular weight
28 fractions are combined, it may be advantageous to take representative
29 samples of each fraction and subject them to molecular averaging, while
30 adjusting the relative amounts of the fractions until a product with desired
31 properties is obtained. Then, the reaction can be scaled up using the relative

1 ratios of each of the fractions that resulted in the desired product. Using this
2 method, one can "dial in" a molecular weight distribution which can be roughly
3 standardized between batches and result in a reasonably consistent product.
4

5 Isomerization Chemistry

6

7 The relatively low molecular weight fraction can be isomerized prior to
8 molecular averaging to incorporate branching into the product of the
9 molecular averaging reaction. In addition, the product of the molecular
10 averaging and/or any other hydrocarbon fractions in the lube base oil range
11 which need their pour point adjusted can be isomerized. The processes for
12 isomerizing relatively low molecular weight fractions tend to be different than
13 those for isomerizing hydrocarbons in the lube base oil range.
14

15 Isomerization processes for light fractions boiling lighter than C₁₀ are generally
16 carried out at a temperature between 200°F. and 700°F, preferably 300°F to
17 550°F. The liquid hourly space velocity (LHSV) is typically between 0.1 and 5,
18 more preferably between 0.25 and 2.0, employing hydrogen such that the
19 hydrogen to hydrocarbon mole ratio is between 1:1 and 5:1. Catalysts useful
20 for isomerization are generally bifunctional catalysts comprising a
21 hydrogenation component (preferably selected from the Group VIII metals of
22 the Periodic Table of the Elements, and more preferably selected from the
23 group consisting of nickel, platinum, palladium and mixtures thereof) and an
24 acid component. Examples of an acid component useful in the preferred
25 isomerization catalyst include a crystalline molecular sieve, a halogenated
26 alumina component, or a silica-alumina component. Such paraffin
27 isomerization catalysts are well known in the art.
28

29 The heavier molecular weight products and reactants can be isomerized using
30 slightly different conditions and catalysts. Suitable catalysts for isomerizing
31 these products and reactants are described, for example, in U.S. Patent

1 Nos. 5,282,958, 5,246,566, 5,135,638 and 5,082,986, the contents of which
2 are hereby incorporated by reference. Although the crystal size limits
3 described in U.S. Patent No. 5,282,958 may be preferred, they are not
4 essential, and larger and/or smaller crystal sizes can be used. A molecular
5 sieve is used as one component. The sieve has pore sizes of less than about
6 7.1 angstroms, preferably less than about 6.5 angstroms, has at least one
7 pore diameter greater than about 4.8 angstroms. The catalyst is further
8 characterized in that it has sufficient acidity to convert at least 50% of
9 hexadecane at 370°C, and exhibits a 40 or greater isomerization selectivity
10 ratio as defined in U.S. Patent No. 5,282,958 at 96% hexadecane conversion.
11 Specific examples of molecular sieves which can be used include ZSM-12,
12 ZSM-21, ZSM-22, ZSM-23, ZSM-35, ZSM-38, ZSM-48, ZSM-57, SSZ-32,
13 SSZ-35, Ferrierite, L-type zeolite, SAPO-11, SAPO-31, SAPO-41, MAPO-11
14 and MAPO-31.

15

16 Optionally, the resulting isomerized products are hydrogenated. After
17 hydrogenation, which typically is a mild hydrofinishing step, the resulting lube
18 oil product is highly paraffinic and has excellent lubricating properties.
19 Hydrofinishing is done after isomerization. Hydrofinishing is well known in the
20 art. Typical reaction conditions include temperatures ranging from about
21 190°C to about 340°C and pressures of from about 400 psig to about
22 3000 psig, at space velocities (LHSV) of from about 0.1 to about 20, and
23 hydrogen recycle rates of from about 400 to about 1500 SCF/bbl.

24

25 The hydrofinishing step is beneficial in preparing an acceptably stable
26 lubricating oil. Lubricant oils that do not receive the hydrofinishing step may
27 be unstable in air and light and tend to form sludges.

28

29 The process will be readily understood by referring to the flow diagram in the
30 figure. In the flow scheme contained in the figure, the process of the present
31 invention is practiced in batch operation. However, it is possible to practice

1 the present invention in continuous operation. The reaction scheme shown in
2 the figure permits many optional stages in which isomerization and/or
3 hydrogenation of the various reactants and products can occur. Each of
4 these optional stages is indicated below.

5
6 Box 10 is a reactor that reacts syngas in the presence of an appropriate
7 Fischer-Tropsch catalyst to form Fischer-Tropsch products. These products
8 are fractionally distilled (Box 20), forming a relatively low molecular weight
9 fraction which is sent to a separate reactor (Box 60) for molecular averaging,
10 a desired fraction which is isolated in Box 50, and a relatively high molecular
11 weight fraction which is also sent to a reactor (Box 60) for molecular
12 averaging. Following molecular averaging, the reaction mixture is fractionally
13 distilled (Box 20), where the desired product is isolated in Box 40, and the
14 relatively high and low molecular weight fractions are optionally sent back to
15 the molecular averaging stage (Box 60).

16
17 Between the distillation stage and the storage and/or molecular averaging
18 stages, the fractions can be isomerized (Box 30) and/or hydrotreated (Box
19 40). After the desired fractions are all obtained and stored in Box 40, they can
20 be isomerized (Box 30) and/or hydrotreated (Box 50). The unprocessed
21 material in the desired molecular weight range is a hydrocarbon which can be
22 isomerized to form a lube base oil. The lube base oil can be blended with
23 additives (Box 70) to form the lube oil composition. Each of the isomerization
24 stages is optional, but it is preferred that isomerization occur at least once in
25 the overall process.

26
27 While the present invention has been described with reference to specific
28 embodiments, this application is intended to cover those various changes and
29 substitutions that may be made by those skilled in the art without departing
30 from the spirit and scope of the appended claims.

1 WHAT IS CLAIMED IS:

2

3 1. A process for preparing a hydrocarbon in the lube base oil range, the
4 process comprising;

5

6 (a) combining a fraction with an average molecular weight below a
7 target molecular weight with a fraction with average molecular
8 weight above a target molecular weight in a suitable proportion
9 such that, when the molecular weights of the fractions are
10 averaged, the average molecular weight is the desired molecular
11 weight for a lube base oil;

12

13 (b) subjecting the fractions to molecular averaging to provide a product
14 with a desired molecular weight; and

15

16 (c) isolating the product.

17

18 2. The process of claim 1, wherein the fraction with an average molecular
19 weight below a target molecular weight and/or the fraction with average
20 molecular weight above a target molecular weight are prepared via a
21 Fischer-Tropsch process.

22

23 3. The process of claim 1, wherein the fraction with an average molecular
24 weight below a target molecular weight and/or the fraction with average
25 molecular weight above a target molecular weight are obtained via
26 distillation of crude oil, provided that the fraction does not include
27 appreciable amounts of olefins, saturated and partially saturated cyclic
28 compounds or heteroatoms.

29

30 4. The process of claim 1, wherein the product is isolated via fractional
31 distillation.

32

- 1 5. The process of claim 1, further comprising isomerization of the resulting
2 product.
3
- 4 6. The process of claim 1, further comprising hydrotreating the resulting
5 product.
6
- 7 7. The process of claim 4, wherein after the product is isolated, at least a
8 portion of the relatively high and/or relatively low molecular weight
9 fractions are recycled.
10
- 11 8. The process of claim 5, wherein the fraction with the desired molecular
12 weight is combined with a lube oil additive selected from the group
13 consisting of lubricants, emulsifiers, wetting agents, densifiers, fluid-loss
14 additives, viscosity modifiers, corrosion inhibitors, oxidation inhibitors,
15 friction modifiers, demulsifiers, anti-wear agents, dispersants,
16 anti-foaming agents, pour point depressants, detergents, and rust
17 inhibitors.
18
- 19 9. The process of claim 1, wherein one or more of the fractions are
20 hydrotreated to remove the heteroatoms, olefins, and/or saturated and
21 partially saturated cyclic compounds prior to the molecular averaging
22 reaction.
23
- 24 10. The process of claim 1, wherein the relatively low molecular weight
25 fraction is isomerized prior to the molecular averaging step.
26
- 27 11. The process of claim 5, wherein the pour point of the product is less than
28 10°C.
29
- 30 12. The process of claim 5, wherein the pour point of the product is less than
31 0°C.

- 1 13. The process of claim 5, wherein the pour point of the product is less than
2 -15°C.
3
- 4 14. The process of claim 5, wherein the pour point of the product is between
5 -15 and -40°C.
6
- 7 15. The process of claim 5, wherein the viscosity index of the product is
8 greater than 100.
9
- 10 16. The process of claim 5, wherein the viscosity index of the product is
11 greater than 140.
12
- 13 17. The process of claim 5, wherein the viscosity index of the product is
14 greater than 150.
15
- 16 18. The process of claim 5, wherein the kinematic viscosity of the product is
17 about 3 centipoises or more.
18
- 19 19. The process of claim 5, wherein the kinematic viscosity of the product is
20 about 4 centipoises or more.
21
- 22 20. The process of claim 1, wherein the fraction with an average molecular
23 weight below that of the desired product is roughly a C₂₀ fraction.
24
- 25 21. The process of claim 1, wherein the fraction with an average molecular
26 weight above that of the desired product is roughly a C₄₀ fraction.
27
- 28 22. The process of claim 1, wherein the desired average molecular weight is
29 approximately C₃₀.
30

- 1 23. The process of claim 1, wherein the fraction with the desired molecular
2 weight has a boiling point in the range of between 650°F and 1200°F.
3
- 4 24. The process of claim 1, wherein the fraction with the desired molecular
5 weight has a boiling point in the range of between 700°F and 1100°F.
6
- 7 25. A process for preparing a hydrocarbon in the lube base oil range, the
8 process comprising;
9
- 10 (a) performing Fischer-Tropsch synthesis on syngas to provide a
11 product stream;
12
- 13 (b) fractionally distilling the product stream and isolating fractions;
14
- 15 (c) storing a fraction with a suitable molecular weight for use in
16 preparing a lube oil composition (a "target molecular weight");
17
- 18 (d) combining a fraction an average molecular weight below the target
19 molecular weight with a fraction with average molecular weight
20 above the target molecular weight in a suitable proportion such
21 that, when the molecular weights of the fractions are averaged, the
22 average molecular weight is approximately that of the target
23 molecular weight;
24
- 25 (e) subjecting the fractions in step (d) to molecular averaging to
26 provide a product with a desired molecular weight; and
27
- 28 (f) fractionally distilling the product and isolating the fraction with the
29 target molecular weight.
30

- 1 26. The process of claim 25, further comprising combining at least a portion
2 of the fractions in steps (c) and (f) and isomerizing them to form a lube
3 base oil.
4
- 5 27. The process of claim 25, further comprising hydrotreating the product.
6
- 7 28. The process of claim 25, further comprising blending the product with
8 one or more additional lube base oils.
9
- 10 29. The process of claim 25, further comprising isolating fractions with
11 relatively high and low molecular weights and recycling at least a portion
12 of these fractions.
13
- 14 30. The process of claim 25, wherein the fraction with an average molecular
15 weight below a target molecular weight and/or the fraction with average
16 molecular weight above a target molecular weight are obtained via
17 distillation of crude oil, provided that the fraction does not include
18 appreciable amounts of olefins, saturated and partially saturated cyclic
19 compounds or heteroatoms, wherein the feed to the molecular averaging
20 step is hydrotreated prior to molecular averaging.
21
- 22 31. The process of claim 26, further comprising blending the product with
23 one or more lube oil additives selected from the group consisting of
24 lubricants, emulsifiers, wetting agents, densifiers, fluid-loss additives,
25 viscosity modifiers, corrosion inhibitors, oxidation inhibitors, friction
26 modifiers, demulsifiers, anti-wear agents, dispersants, anti-foaming
27 agents, pour point depressants, detergents, and rust inhibitors.
28
- 29 32. A lube base oil composition prepared by:
30
- 31 (a) performing Fischer-Tropsch synthesis on syngas to provide a
32 product stream;

- 1 (b) fractionally distilling the product stream and isolating fractions;
- 2
- 3 (c) storing a fraction with a suitable molecular weight for use in
- 4 preparing a lube oil composition (a "target molecular weight");
- 5
- 6 (d) combining a fraction an average molecular weight below the target
- 7 molecular weight with a fraction with average molecular weight
- 8 above the target molecular weight in a suitable proportion such
- 9 that, when the molecular weights of the fractions are averaged, the
- 10 average molecular weight is approximately that of the target
- 11 molecular weight;
- 12
- 13 (e) subjecting the fractions in step (d) to molecular averaging to
- 14 provide a product with a desired molecular weight;
- 15
- 16 (f) fractionally distilling the product and isolating the fraction with the
- 17 target molecular weight; and
- 18
- 19 (g) isomerizing the product to reduce the pour point.
- 20
- 21 33. The product of claim 32, further comprising combining at least a portion
- 22 of the fractions in steps (c) and (f) and isomerizing them to form a lube
- 23 base oil.
- 24
- 25 34. The product of claim 32, wherein the product includes hydrocarbons in
- 26 the range of between C₂₀ and C₅₀ which include a degree of
- 27 isomerization typical of that observed in catalytic dewaxing or isomeric
- 28 dewaxing processes.

1/1

FIGURE 1

