

**MULTIGRADE ENGINE OIL PREPARED FROM FISCHER-TROPSCH
DISTILLATE BASE OIL**

CROSS REFERENCE TO RELATED APPLICATIONS

This Application claims priority from U.S. Provisional Application
No. 60/599,665 filed August 5, 2004.

This patent application also is related to co-pending U.S. Patent Application
Nos. 10/704,031 filed November 7, 2003, titled "Process for Improving the
Lubricating Properties of Base Oils Using a Fischer-Tropsch Derived Bottoms"
and 10/839,396 filed May 4, 2004, titled "Process for Improving the
Lubricating Properties of Base Oils Using Isomerized Petroleum Product" the
entire contents of both applications being incorporated herein by reference.

FIELD OF THE INVENTION

The disclosure herein relates to a multigrade engine oil prepared from a
Fischer-Tropsch distillate base oil that is capable of meeting the specifications
for ILSAC GF-3 or GF-4 and the SAE J300 revised June 2001 requirements
for MRV TP-1 prepared by blending the Fischer-Tropsch base oil with a pour
point depressing base oil blending component and an additive package
meeting ILSAC GF-3 or GF-4 requirements.

In a first aspect, there is provided a multigrade engine oil meeting the
specifications for SAE J300 revised June 2001 requirements, said engine oil
comprising:

- (a) between about 15 to about 94.5 wt% of a hydroisomerized
distillate Fischer-Tropsch base oil characterized by
 - (i) a kinematic viscosity between about 2.5 and about 8 cSt at
100°C, (ii) at least about 3 wt% of the molecules having

cycloparaffin functionality, and (iii) a ratio of weight percent molecules with monocycloparaffin functionality to weight percent of molecules with multicycloparaffin functionality greater than about 15;

- (b) between about 0.5 to about 20 wt% of a pour point depressing base oil-blending component prepared from an hydroisomerized bottoms material having an average degree of branching in the molecules between about 5 and about 9 alkyl-branches per 100 carbon atoms and wherein not more than 10 wt% boils below about 900°F; and
- (c) between about 5 to about 30 wt% of an additive package designed to meet the specifications for ILSAC GF-3.

In a second aspect, there is provided a process for preparing a multigrade engine oil meeting the specifications for SAE J300 revised June 2001 requirements which comprises:

- (a) hydroisomerizing a waxy Fischer-Tropsch base oil in an isomerization zone in the presence of a hydroisomerization catalyst and hydrogen under pre-selected conditions determined to provide a hydroisomerized Fischer-Tropsch base oil product;
- (b) recovering from the isomerization zone a hydroisomerized Fischer-Tropsch base oil product;

- (c) distilling the hydroisomerized Fischer-Tropsch base oil product recovered from the isomerization zone under distillation conditions pre-selected to collect a distillate Fischer-Tropsch base oil characterized by (i) a kinematic viscosity between about 2.5 and about 8 cSt at 100°C, (ii) at least about 3 wt% of the molecules having cycloparaffin functionality, and (iii) a ratio of weight percent molecules with monocycloparaffin functionality to weight percent of molecules with multicycloparaffin functionality greater than about 15;
- (d) blending the distillate Fischer-Tropsch base oil with (i) a pour point depressing base oil blending component prepared from an hydroisomerized bottoms material having an average degree of branching in the molecules between about 5 and about 9 alkyl-branches per 100 carbon atoms and wherein not more than 10 wt% boils below about 900°F and (ii) an additive package designed to meet the specifications for ILSAC GF-3 in the proper proportions to yield a multigrade engine oil meeting the specifications for SAE J300 revised June 2001.

BACKGROUND OF THE INVENTION

Engine oils are finished crankcase lubricants intended for use in automobile engines and diesel engines and consist of two general components; a lubricating base oil and additives. Lubricating base oil is the major constituent in these finished lubricants and contributes significantly to the properties of the engine oil. In general, a few lubricating base oils are used to manufacture

1 a variety of engine oils by varying the mixtures of individual lubricating base
2 oils and individual additives.
3
4 Numerous governing organizations, including Original Equipment
5 Manufacturers (OEM's), the American Petroleum Institute (API),
6 Association des Constructeurs d' Automobiles (ACEA), the American Society
7 of Testing and Materials (ASTM), International Lubricant Standardization and
8 Approval Committee (ILSAC), and the Society of Automotive Engineers
9 (SAE), among others, define the specifications for lubricating base oils and
10 engine oils. Increasingly, the specifications for engine oils are calling for
11 products with excellent low temperature properties, high oxidation stability,
12 and low volatility. Currently, only a small fraction of the base oils
13 manufactured today are able to meet these demanding specifications.
14
15 Lubricating base oils are petroleum derived or synthetic hydrocarbons having
16 a viscosity of about 2.5 cSt or greater at 100°C, preferably about 4 cSt or
17 greater at 100 C; a pour point of about 9 C or less, preferably about -15 C or
18 less; and a VI (viscosity index) that is usually about 90 or greater, preferably
19 about 100 or greater. Premium base oils will have a VI of at least 120.
20 Lubricating base oils intended for preparing finished lubricants should have a
21 Noack volatility no greater than current conventional Group I or Group II light
22 neutral oils.
23
24 The term "base oil" refers to a hydrocarbon product having the above
25 properties prior to the addition of additives. Base oils are generally recovered
26 from the higher boiling fractions recovered from the vacuum distillation
27 operation. They may be prepared from either petroleum-derived or from
28 syncrude-derived feedstocks. "Additives" are chemicals which are added to
29 improve certain properties in the finished lubricant so that it meets the
30 minimum performance standards for the grade of the finished lubricant. For
31 example, additives added to the engine oils may be used to improve stability
32 of the lubricant, lower its viscosity, raise the viscosity index, and control

1 deposits. Additives are expensive and may cause miscibility problems in the
2 finished lubricant. For these reasons, it is generally desirable to lower the
3 additive content of the engine oils to the minimum amount necessary to meet
4 the appropriate requirements.

5
6 There are two principal categories of engine oil additives: DI additive
7 packages (Detergent Inhibitor additive packages) and VI improvers (Viscosity
8 Index improvers). DI additive packages serve to suspend oil contaminants
9 and combustion by-products as well as to prevent oxidation of the oil with the
10 resultant formation of varnish and sludge deposits. VI improvers modify the
11 viscometric characteristics of lubricants by reducing the rate of thinning with
12 increasing temperature and the rate of thickening with low temperatures. VI
13 improvers thereby provide enhanced performance at low and high
14 temperatures. In many multigrade engine oil applications VI improvers have to
15 be used with DI additive packages. Engine oil additive packages are available
16 from additive suppliers. Additive packages are formulated such that, when
17 they are blended with a base oil or base oil blend having the desired
18 properties, the resulting engine oil is likely to meet a specified engine oil
19 service category. Specific engine oil service categories that are used, or being
20 developed, today include ILSAC GF-3, ILSAC GF-4, API CI-4, and
21 API PC-10.

22
23 The minimum specifications for the various viscosity grades of engine oils is
24 established by SAE J300 standards as revised in June 2001. Base oils
25 prepared from products made by the Fischer-Tropsch synthesis reaction are
26 characterized by a very low sulfur content and excellent stability making them
27 excellent candidates for blending into high quality finished lubricants.
28 Unfortunately, finished lubricants blended from Fischer-Tropsch derived base
29 oils generally display poor low temperature properties, particularly low
30 temperature pumpability. Consequently, Fischer-Tropsch derived base oils
31 have had difficulty passing the stringent mini-rotary viscometer (MRV) TP-1
32 viscosity specifications under SAE J300 as revised 2001.

1 ILSAC GF-3 refers to an engine oil service category of automotive gasoline
2 engines. This specification became official on July 1, 2001. ILSAC GF-4 refers
3 to a new engine oil service category of automotive gasoline engines that was
4 approved on January 8, 2004. It became official on July 1, 2004. This
5 category introduces new sulfur limits measured by standard test method
6 ASTM D 1552. The maximum sulfur limit for 0W-XX and 5W-XX oils is
7 0.5 wt%. The maximum sulfur limit for 10W-XX oils is 0.7 wt%. An engine oil
8 meeting GF-4 requirements will also meet GF-3 requirements, but an engine
9 oil meeting GF-3 requirements may not meet the requirements for a GF-3
10 engine oil.

11

12 A multigrade engine oil refers to an engine oil that has viscosity/temperature
13 characteristics which fall within the limits of two different SAE numbers in
14 SAE J300. The present invention is directed to the discovery that multigrade
15 engine oils meeting the specifications under SAE J300 as revised 2001,
16 including the MRV TP-1 viscosity specifications, may be prepared from
17 Fischer-Tropsch base oils having a defined cycloparaffin functionality when
18 they are blended with a pour point depressing base oil blending component
19 and an additive package.

20

21 As used in this disclosure the word "comprises" or "comprising" is intended as
22 an open-ended transition meaning the inclusion of the named elements, but
23 not necessarily excluding other unnamed elements. The phrase "consists
24 essentially of" or "consisting essentially of" is intended to mean the exclusion
25 of other elements of any essential significance to the composition. The phrase
26 "consisting of" or "consists of" is intended as a transition meaning the
27 exclusion of all but the recited elements with the exception of only minor
28 traces of impurities.

1 BRIEF DESCRIPTION OF THE INVENTION

2

3 The present invention is directed to a multigrade engine oil meeting the

4 specifications for SAE J300 revised June 2001, said engine oil comprising

5 (a) between about 15 to about 94.5 wt% of a hydroisomerized distillate

6 Fischer-Tropsch base oil characterized by (i) a kinematic viscosity between

7 about 2.5 and about 8 cSt at 100°C, (ii) at least about 3 wt% of the molecules

8 having cycloparaffin functionality, and (iii) a ratio of weight percent molecules

9 with monocycloparaffin functionality to weight percent of molecules with

10 multicycloparaffin functionality greater than about 15; (b) between about 0.5 to

11 about 20 wt% of a pour point depressing base oil blending component

12 prepared from an hydroisomerized bottoms material having an average

13 degree of branching in the molecules between about 5 and about

14 9 alkyl-branches per 100 carbon atoms and wherein not more than 10 wt%

15 boils below about 900°F; and (c) between about 5 to about 30 wt% of an

16 additive package designed to meet the specifications for ILSAC GF-3. Using

17 the present invention, multigrade engine oils may be prepared meeting the

18 specifications for SAE viscosity grade 0W-XX, 5W-XX, or 10W-XX engine oil,

19 wherein XX represents the integer 20, 30, or 40. A multigrade engine oil

20 meeting the specifications for SAE 0W-20 may be prepared according to the

21 present invention.

22

23 The present invention is also directed to a process for preparing a multigrade

24 engine oil meeting the specifications for SAE J300 revised June 2001 which

25 comprises (a) hydroisomerizing a waxy Fischer-Tropsch base oil in an

26 isomerization zone in the presence of a hydroisomerization catalyst and

27 hydrogen under pre-selected conditions determined to provide a

28 hydroisomerized Fischer-Tropsch base oil product; (b) recovering from the

29 isomerization zone a hydroisomerized Fischer-Tropsch base oil product;

30 (c) distilling the hydroisomerized Fischer-Tropsch base oil product recovered

31 from the isomerization zone under distillation conditions pre-selected to collect

32 a distillate Fischer-Tropsch base oil characterized by (i) a kinematic viscosity

1 between about 2.5 and about 8 cSt at 100°C, (ii) at least about 3 wt% of the
2 molecules having cycloparaffin functionality, and (iii) a ratio of weight percent
3 molecules with monocycloparaffin functionality to weight percent of molecules
4 with multicycloparaffin functionality greater than about 15; (d) blending the
5 distillate Fischer-Tropsch base oil with (i) a pour point depressing base oil
6 blending component prepared from an hydroisomerized bottoms material
7 having an average degree of branching in the molecules between about 5 and
8 about 9 alkyl-branches per 100 carbon atoms and wherein not more than
9 10 wt% boils below about 900°F and (ii) an additive package designed to
10 meet the specifications for ILSAC GF-3 in the proper proportions to yield a
11 multigrade engine oil meeting the specifications for SAE J300 revised
12 June 2001. Preferably the hydroisomerized distillate base oil fraction is also
13 hydrofinished prior to the blending step (c) to reduce both any aromatics and
14 olefins present to a low level.

15

16 The pour point depressing base oil blending component may be prepared
17 from the bottoms fraction from either a petroleum-derived or a
18 Fischer-Tropsch derived product. If the pour point depressing base oil
19 blending component is an isomerized petroleum derived bottoms product, it
20 preferably will have an average molecular weight of at least 600. If the pour
21 point depressing base oil blending component is a hydroisomerized
22 Fischer-Tropsch derived bottoms product, it will preferably have a molecular
23 weight between about 600 and about 1,100.

DETAILED DESCRIPTION OF THE INVENTION

The SAE J300 specifications (revised June 2001) for engine oil are detailed in Table 1 below.

Table 1*

SAE Viscosity Grade	High Temperature High Shear Rate Viscosity at 150°C (cP), Min	Viscosity (cP) at Temperature (°C), Max		Kinematic Viscosity mm ² /s (cSt) at 100°C	
		CCS	MRV TP-1 w/ No Yield Stress	Min	Max
0W	--	6,200 at -35	60,000 at -40	3.8	--
5W	--	6,600 at -30	60,000 at -35	3.8	--
10W	--	7,000 at -25	60,000 at -30	4.1	--
15W	--	7,000 at -20	60,000 at -25	5.6	--
20W	--	2,500 at -15	60,000 at -20	5.6	--
25W	--	13,000 at -10	60,000 at -15	9.3	--
20	2.6	--	--	5.6	< 9.3
30	2.9	--	--	9.3	< 12.5
40	2.9 (0W-40, 5W-40 and 10W-40 grades) 3.7 (15W-40, 20W-40 and 25W-40 grades)	--	--	12.5	< 16.3
50	3.7	--	--	16.3	< 21.9
60	3.7	--	--	21.9	< 26.1

*Notes 1cP = 1centipoise = 1mPa.s. This dynamic viscosity can be converted as follows: Dynamic Viscosity = Density x Kinematic Viscosity.

High Temperature High Shear Rate Viscosity is determined at 106 s⁻¹ by ASTM D 4683, ASTM D 4741, or ASTM D 5481.

Cold Cranking Simulator Viscosity (CCS Vis) is determined by ASTM D 5293.

Mini-Rotary Viscometer (MRV) TP-1 Viscosity is determined by ASTM D 4684.
Kinematic Viscosity is determined by ASTM D 445.

Analytical Methods

Kinematic viscosity described in this disclosure was measured by ASTM D 445-01.

1 The cold-cranking simulator viscosity (CCS VIS) is a test used to measure the
2 viscometric properties of lubricating base oils under low temperature and high
3 shear. The test method to determine CCS VIS is ASTM D 5293-02. Results
4 are reported in centipoise, cP. CCS VIS has been found to correlate with
5 low temperature engine cranking. Specifications for maximum CCS VIS are
6 defined for automotive engine oils by SAE J300 revised June 2001 as set out
7 in Table 1, above.

8
9 High temperature high shear rate viscosity (HTHS) is a measure of a fluid's
10 resistance to flow under conditions resembling highly-loaded journal bearings
11 in fired internal combustion engines, typically 1 million s⁻¹ at 150°C. HTHS is
12 a better indication of how an engine operates at high temperature with a given
13 lubricant than the kinematic low shear rate viscosities at 100°C. The HTHS
14 value directly correlates to the oil film thickness in a bearing. SAE J300
15 June 2001 (see Table 1) contains the current specifications for HTHS
16 measured by ASTM D 4683, ASTM D 4741, or ASTM D 5481. An SAE 20
17 viscosity grade engine oil, for example, is required to have a maximum HTHS
18 of 2.6 centipoise (cP).

19
20 Mini-Rotary Viscometer (MRV TP-1) test is related to the mechanism of
21 pumpability and is a low shear rate measurement that measured by standard
22 test method ASTM D 4684. Slow sample cooling rate is the key feature of the
23 method. A sample is pretreated to have a specified thermal history which
24 includes warming, slow cooling, and soaking cycles. The MRV TP-1
25 measures an apparent yield stress, which, if greater than a threshold value,
26 indicates a potential air-binding pumping failure problem. Above a certain
27 viscosity (currently defined as 60,000 cP by SAE J300 June 2001), the oil
28 may be subject to pumpability failure by a mechanism called "flow limited"
29 behavior. An SAE 10W oil, for example, is required to have a maximum
30 viscosity of 60,000 cP at -30°C with no yield stress. This method also
31 measures an apparent viscosity under shear rates of 1 to 50 s⁻¹.

1 In addition to meeting the requirements for SAE J300 (revised June 2001),
2 multigrade engine oils of the present invention may be formulated to meet the
3 ILSAC GF-3 specifications, as well as the more stringent GF-4 specifications.
4 Both GF-3 and GF-4 require a minimum Noack volatility value of 15. However,
5 preferably the Noack volatility value of the finished lubricant will be 10 or less.
6 Noack volatility as specified in ILSAC GF-3 and GF-4 uses standard test
7 method ASTM D 5800. According to this method Noack is defined as the
8 mass of oil, expressed in weight percent, which is lost when the oil is heated
9 at 250°C and 20 mmHg (2.67 kPa; 26.7 mbar) below atmospheric in a test
10 crucible through which a constant flow of air is drawn for 60 minutes. A more
11 convenient method for calculating Noack volatility and one which correlates
12 well with ASTM D 5800 uses a thermo gravimetric analyzer test (TGA) by
13 ASTM D 6375.

14

15 Pour point refers to the temperature at which the sample will begin to flow
16 under carefully controlled conditions. In this disclosure, where pour point is
17 given, unless stated otherwise, it has been determined by standard analytical
18 method ASTM D 5950 or its equivalent. VI may be determined by using
19 ASTM D 2270-93 (1998) or its equivalent. Molecular weight may be
20 determined by ASTM D 2502, ASTM D 2503, or other suitable method. For
21 use in association with this invention, molecular weight is preferably
22 determined by ASTM D 2503-02. As used herein, an equivalent analytical
23 method to the standard reference method refers to any analytical method
24 which gives substantially the same results as the standard method.

25

26 The branching properties of the pour point depressing base oil blending
27 component of the present invention was determined by analyzing a sample of
28 oil using carbon-13 NMR according to the following seven-step process.
29 References cited in the description of the process provide details of the
30 process steps. Steps 1 and 2 are performed only on the initial materials from
31 a new process.

- 1) Identify the CH branch centers and the CH₃ branch termination points using the DEPT Pulse sequence (Doddrell, D.T.; D.T. Pegg; M.R. Bendall, Journal of Magnetic Resonance 1982, 48, 323ff).
- 2) Verify the absence of carbons initiating multiple branches (quaternary carbons) using the APT pulse sequence (Patt, S.L.; J.N. Shoolery, Journal of Magnetic Resonance 1982, 46, 535ff).
- 3) Assign the various branch carbon resonances to specific branch positions and lengths using tabulated and calculated values (Lindeman, L.P., Journal of Qualitative Analytical Chemistry 43, 1971 1245ff; Netzel, D.A., et.al., Fuel, 60, 1981, 307ff).

Examples:

Branch	NMR Chemical Shift (ppm)
2-methyl	22.5
3-methyl	19.1 or 11.4
4-methyl	14.0
4+methyl	19.6
Internal ethyl	10.8
Propyl	14.4
Adjacent methyls	16.7

- 4) Quantify the relative frequency of branch occurrence at different carbon positions by comparing the integrated intensity of its terminal methyl carbon to the intensity of a single carbon (= total integral/number of carbons per molecule in the mixture). For the unique case of the 2-methyl branch, where both the terminal and the branch methyl occur at the same resonance position, the intensity was divided by two before doing the frequency of branch occurrence calculation. If the 4-methyl branch fraction is calculated and tabulated, its contribution to the 4+methyls must be subtracted to avoid double counting.

- 1 5) Calculate the average carbon number. The average carbon number
2 may be determined with sufficient accuracy for lubricant materials by
3 dividing the molecular weight of the sample by 14 (the formula weight
4 of CH₂).
5
- 6 6) The number of branches per molecule is the sum of the branches
7 found in step 4.
8
- 9 7) The number of alkyl branches per 100 carbon atoms is calculated from
10 the number of branches per molecule (step 6) x 100/average carbon
11 number.
12
- 13 Measurements can be performed using any Fourier Transform NMR
14 spectrometer. Preferably, the measurements are performed using a
15 spectrometer having a magnet of 7.0T or greater. In all cases, after
16 verification by Mass Spectrometry, UV or an NMR survey that aromatic
17 carbons were absent, the spectral width was limited to the saturated carbon
18 region, about 0 to 80 ppm vs. TMS (tetramethylsilane). Solutions of 15 to
19 25 wt% in chloroform-d₁ were excited by 45° pulses followed by a 0.8 second
20 acquisition time. In order to minimize non-uniform intensity data, the proton
21 decoupler was gated off during a 10 second delay prior to the excitation pulse
22 and on during acquisition. Total experiment times ranged from 11 to
23 80 minutes. The DEPT and APT sequences were carried out according to
24 literature descriptions with minor deviations described in the Varian or Bruker
25 operating manuals.
26
- 27 DEPT is Distortionless Enhancement by Polarization Transfer. DEPT does not
28 show quaternaries. The DEPT 45 sequence gives a signal all carbons bonded
29 to protons. DEPT 90 shows CH carbons only. DEPT 135 shows CH and CH₃
30 up and CH₂ 180° out of phase (down). APT is Attached Proton Test. It allows
31 all carbons to be seen, but if CH and CH₃ are up, then quaternaries and CH₂
32 are down. The sequences are useful in that every branch methyl should have

1 a corresponding CH. And the methyls are clearly identified by chemical shift
2 and phase. Both are described in the references cited. The branching
3 properties of each sample were determined by C-13 NMR using the
4 assumption in the calculations that the entire sample was iso-paraffinic.
5 Corrections were not made for n-paraffins or naphthenes, which may have
6 been present in the oil samples in varying amounts. The naphthenes content
7 may be measured using Field Ionization Mass Spectroscopy (FIMS).

8
9 FIMS analysis was conducted by placing a small amount (about 0.1 mg.) of
10 the base oil to be tested in a glass capillary tube. The capillary tube was
11 placed at the tip of a solids probe for a mass spectrometer, and the probe was
12 heated from about 50°C to 600°C at 100°C per minute in a mass
13 spectrometer operating at about 10⁻⁶ torr. The mass spectrometer used was a
14 Micromass Time-of-Flight mass spectrometer. The emitter was a
15 Carbotec 5um emitter designed for FI operation. A constant flow of
16 pentafluorochlorobenzene, used as lock mass, was delivered into the mass
17 spectrometer via a thin capillary tube. Response factors for all compound
18 types were assumed to be 1.0, such that weight percent was given directly
19 from area percent.

20
21 Since petroleum derived hydrocarbons and Fischer-Tropsch derived
22 hydrocarbons comprise a mixture of varying molecular weights having a wide
23 boiling range, this disclosure will refer to the 10% boiling point of the
24 boiling range of the pour point depressing base oil blending component. The
25 10% boiling point refers to that temperature at which 10 wt% of the
26 hydrocarbons present in the pour point depressing base oil blending
27 component will vaporize at atmospheric pressure. Only the 10% boiling point
28 is used when referring to the pour point depressing base oil blending
29 component, since it is generally derived from a bottoms fraction which makes
30 the upper boiling limit irrelevant for the purposes of defining the material. For
31 samples having a boiling range above 1000°F, the boiling range distributions
32 in this disclosure were measured using the standard analytical method

1 ASTM D 6352 or its equivalent. For samples having a boiling range below
2 1000°F, the boiling range distributions in this disclosure were measured using
3 the standard analytical method ASTM D 2887 or its equivalent.

4 5 **Hydroisomerization**

6
7 Hydroisomerization is intended to improve the cold flow properties of the
8 Fischer-Tropsch base oil by the selective addition of branching into the
9 molecular structure. Hydroisomerization is also used to prepare the pour point
10 depressing base oil blending component. Hydroisomerization ideally will
11 achieve high conversion levels of the wax to non-waxy iso-paraffins while at
12 the same time minimizing the conversion by cracking. Preferably, the
13 conditions for hydroisomerization in the present invention are controlled such
14 that the conversion of the compounds boiling above about 700°F in the wax
15 feed to compounds boiling below about 700°F is maintained between about
16 10 wt% and 50 wt%, preferably between 15 wt% and 45 wt%.

17
18 According to the present invention, hydroisomerization is conducted using a
19 shape selective intermediate pore size molecular sieve. Hydroisomerization
20 catalysts useful in the present invention comprise a shape selective
21 intermediate pore size molecular sieve and optionally a catalytically active
22 metal hydrogenation component on a refractory oxide support. The phrase
23 "intermediate pore size," as used herein means an effective pore aperture in
24 the range of from about 3.9 to about 7.1 Å when the porous inorganic oxide is
25 in the calcined form. The shape selective intermediate pore size
26 molecular sieves used in the practice of the present invention are generally
27 1-D 10-, 11- or 12-ring molecular sieves. The preferred molecular sieves of
28 the invention are of the 1-D 10-ring variety, where 10-(or 11-or 12-) ring
29 molecular sieves have 10 (or 11 or 12) tetrahedrally-coordinated atoms
30 (T-atoms) joined by an oxygen atom. In the 1-D molecular sieve, the 10-ring
31 (or larger) pores are parallel with each other, and do not interconnect. Note,
32 however, that 1-D 10-ring molecular sieves which meet the broader definition

1 of the intermediate pore size molecular sieve but include intersecting pores
2 having 8-membered rings may also be encompassed within the definition of
3 the molecular sieve of the present invention. The classification of intrazeolite
4 channels as 1-D, 2-D and 3-D is set forth by R.M. Barrer in Zeolites,
5 Science and Technology, edited by F.R. Rodrigues, L.D. Rollman and
6 C. Naccache, NATO ASI Series, 1984 which classification is incorporated in
7 its entirety by reference (see particularly page 75).

8
9 Preferred shape selective intermediate pore size molecular sieves used for
10 hydroisomerization are based upon aluminum phosphates, such as SAPO-11,
11 SAPO-31, and SAPO-41. SAPO-11 and SAPO-31 are more preferred, with
12 SAPO-11 being most preferred. SM-3 is a particularly preferred shape
13 selective intermediate pore size SAPO, which has a crystalline structure
14 falling within that of the SAPO-11 molecular sieves. The preparation of SM-3
15 and its unique characteristics are described in U.S. Patent Nos. 4,943,424
16 and 5,158,665. Also preferred shape selective intermediate pore size
17 molecular sieves used for hydroisomerization are zeolites, such as ZSM-22,
18 ZSM-23, ZSM-35, ZSM-48, ZSM-57, SSZ-32, offretite, and ferrierite. SSZ-32
19 and ZSM-23 are more preferred.

20
21 A preferred intermediate pore size molecular sieve is characterized by
22 selected crystallographic free diameters of the channels, selected crystallite
23 size (corresponding to selected channel length), and selected acidity.
24 Desirable crystallographic free diameters of the channels of the molecular
25 sieves are in the range of from about 3.9 to about 7.1 Å, having a maximum
26 crystallographic free diameter of not more than 7.1 and a minimum
27 crystallographic free diameter of not less than 3.9 Å. Preferably the maximum
28 crystallographic free diameter is not more than 7.1 Å and the minimum
29 crystallographic free diameter is not less than 4.0 Å. Most preferably the
30 maximum crystallographic free diameter is not more than 6.5 Å and the
31 minimum crystallographic free diameter is not less than 4.0 Å. The
32 crystallographic free diameters of the channels of molecular sieves are

1 published in the "Atlas of Zeolite Framework Types", Fifth Revised Edition,
2 2001, by Ch. Baerlocher, W.M. Meier, and D.H. Olson, Elsevier, pp. 10-15,
3 which is incorporated herein by reference.

4
5 A particularly preferred intermediate pore size molecular sieve, which is useful
6 in the present process is described, for example, in U.S. Patent
7 Nos. 5,135,638 and 5,282,958, the contents of which are hereby incorporated
8 by reference in their entirety. In U.S. Patent No. 5,282,958, such an
9 intermediate pore size molecular sieve has a crystallite size of no more than
10 about 0.5 microns and pores with a minimum diameter of at least about 4.8 Å
11 and with a maximum diameter of about 7.1 Å.

12
13 The catalyst has sufficient acidity so that 0.5 grams thereof when positioned in
14 a tube reactor converts at least 50% of hexadecane at 370°C, a pressure of
15 1200 psig, a hydrogen flow of 160 ml/min, and a feed rate of 1 ml/hr. The
16 catalyst also exhibits isomerization selectivity of 40% or greater (isomerization
17 selectivity is determined as follows: $100 \times (\text{weight percent branched } C_{16} \text{ in product}) / (\text{weight percent branched } C_{16} \text{ in product} + \text{weight percent } C_{13} \text{ in product})$ when used under conditions leading to 96% conversion of normal
18 hexadecane (n-C₁₆) to other species.

19
20
21
22 Such a particularly preferred molecular sieve may further be characterized by
23 pores or channels having a crystallographic free diameter in the range of from
24 about 4.0 Å to about 7.1 Å, and preferably in the range of 4.0 to 6.5 Å. The
25 crystallographic free diameters of the channels of molecular sieves are
26 published in the "Atlas of Zeolite Framework Types", Fifth Revised Edition,
27 2001, by Ch. Baerlocher, W.M. Meier, and D.H. Olson, Elsevier, pp. 10-15,
28 which is incorporated herein by reference.

29
30 If the crystallographic free diameters of the channels of a molecular sieve are
31 unknown, the effective pore size of the molecular sieve can be measured
32 using standard adsorption techniques and hydrocarbonaceous compounds of

1 known minimum kinetic diameters. See Breck, Zeolite Molecular Sieves, 1974
2 (especially Chapter 8); Anderson et al., J. Catalysis 58, 114 (1979); and
3 U.S. Patent No. 4,440,871, the pertinent portions of which are incorporated
4 herein by reference. In performing adsorption measurements to determine
5 pore size, standard techniques are used. It is convenient to consider a
6 particular molecule as excluded if does not reach at least 95% of its
7 equilibrium adsorption value on the molecular sieve in less than about
8 10 minutes ($p/p_0 = 0.5$ at 25°C). Intermediate pore size molecular sieves will
9 typically admit molecules having kinetic diameters of 5.3 to 6.5 Å with little
10 hindrance.

11

12 Hydroisomerization catalysts useful in the present invention comprise a
13 catalytically active hydrogenation metal. The presence of a catalytically active
14 hydrogenation metal leads to product improvement, especially VI and stability.
15 Typical catalytically active hydrogenation metals include chromium,
16 molybdenum, nickel, vanadium, cobalt, tungsten, zinc, platinum, and
17 palladium. The metals platinum and palladium are especially preferred, with
18 platinum most especially preferred. If platinum and/or palladium is used, the
19 total amount of active hydrogenation metal is typically in the range of 0.1 to
20 5 wt% of the total catalyst, usually from 0.1 to 2 wt%, and not to exceed
21 10 wt%.

22

23 The refractory oxide support may be selected from those oxide supports,
24 which are conventionally used for catalysts, including silica, alumina,
25 silica-alumina, magnesia, titania and combinations thereof.

26

27 The conditions for hydroisomerization will be tailored to achieve a
28 Fischer-Tropsch derived lubricant base oil fraction comprising greater than
29 5 wt% molecules with cycloparaffinic functionality, and a ratio of
30 weight percent of molecules with monocycloparaffinic functionality to
31 weight percent of molecules with multicycloparaffinic functionality of greater
32 than 15.

1 The conditions for hydroisomerization will depend on the properties of feed
2 used, the catalyst used, whether or not the catalyst is sulfided, the desired
3 yield, and the desired properties of the lubricant base oil. Conditions under
4 which the hydroisomerization process of the current invention may be carried
5 out include temperatures from about 550°F to about 775°F (288°C to about
6 413°C), preferably 600°F to about 750°F (315°C to about 399°C), more
7 preferably about 600°F to about 700°F (315°C to about 371°C); and pressures
8 from about 15 to 3,000 psig, preferably 100 to 2,500 psig. The
9 hydroisomerization dewaxing pressures in this context refer to the hydrogen
10 partial pressure within the hydroisomerization reactor, although the hydrogen
11 partial pressure is substantially the same (or nearly the same) as the total
12 pressure. The liquid hourly space velocity during contacting is generally from
13 about 0.1 to 20 hr⁻¹, preferably from about 0.1 to about 5 hr⁻¹. Hydrogen is
14 present in the reaction zone during the hydroisomerization process, typically
15 in a hydrogen to feed ratio from about 0.5 to 30 MSCF/bbl (thousand standard
16 cubic feet per barrel), preferably from about 1 to about 10 MSCF/bbl.
17 Hydrogen may be separated from the product and recycled to the reaction
18 zone. Suitable conditions for performing hydroisomerization are described in
19 U.S. Patent Nos. 5,282,958 and 5,135,638, the contents of which are
20 incorporated by reference in their entirety.

21

22 **Hydrofinishing**

23

24 Hydrofinishing operations are intended to improve the UV stability and color of
25 the products. It is believed this is accomplished by saturating the double
26 bonds present in the hydrocarbon molecule which also reduces the amount of
27 both aromatics and olefins to a low level. In the present invention,
28 hydroisomerized distillate base oil is preferably sent to a hydrofinisher prior to
29 the blending step. A general description of the hydrofinishing process may be
30 found in U.S. Patent Nos. 3,852,207 and 4,673,487. As used in this disclosure
31 the term UV stability refers to the stability of the lubricating base oil or other
32 products when exposed to ultraviolet light and oxygen. Instability is indicated

1 when a visible precipitate forms or darker color develops upon exposure to
2 ultraviolet light and air which results in a cloudiness or floc in the base oil.
3 Lubricating base oils used in the present invention generally will require UV
4 stabilization before they are suitable for use in the manufacture of commercial
5 lubricating oils.

6
7 In the present invention the total pressure in the hydrofinishing zone will be
8 above 500 psig, preferably above 1,000 psig, and most preferably will be
9 above 1,500 psig. The maximum total pressure is not critical to the process,
10 but due to equipment limitations the total pressure will not exceed 3,000 psig
11 and usually will not exceed about 2,500 psig. Temperature ranges in the
12 hydrofinishing reactor are usually in the range of from about 300°F (150°C) to
13 about 700°F (370°C), with temperatures of from about 400°F (205°C) to about
14 500°F (260°C) being preferred. The LHSV is usually within the range of from
15 about 0.2 to about 2.0, preferably 0.2 to 1.5 and most preferably from about
16 0.7 to 1.0. Hydrogen is usually supplied to the hydrofinishing reactor at a rate
17 of from about 1,000 to about 10,000 SCF per barrel of feed. Typically the
18 hydrogen is fed at a rate of about 3,000 SCF per barrel of feed.

19
20 Suitable hydrofinishing catalysts typically contain a Group VIII noble metal
21 component together with an oxide support. Metals or compounds of the
22 following metals are contemplated as useful in hydrofinishing catalysts include
23 ruthenium, rhodium, iridium, palladium, platinum, and osmium. Preferably the
24 metal or metals will be platinum, palladium or mixtures of platinum and
25 palladium. The refractory oxide support usually consists of silica-alumina,
26 silica-alumina-zirconia, and the like. Typical hydrofinishing catalysts are
27 disclosed in U.S. Patent Nos. 3,852,207; 4,157,294; and 4,673,487.

28

29 **The Hydroisomerized Distillate Fischer-Tropsch Base Oil**

30

31 The separation of Fischer-Tropsch products is generally conducted by either
32 atmospheric or vacuum distillation or by a combination of atmospheric and

1 vacuum distillation. Atmospheric distillation is typically used to separate the
2 lighter distillate fractions, such as naphtha and middle distillates, from a
3 bottoms fraction having an initial boiling point above about 700°F to about
4 750°F (about 370°C to about 400°C). At higher temperatures thermal cracking
5 of the hydrocarbons may take place leading to fouling of the equipment and to
6 lower yields of the heavier cuts. Vacuum distillation is typically used to
7 separate the higher boiling material, such as the distillate base oil fraction
8 used in the present invention.

9
10 As used in this disclosure, the term "distillate fraction" or "distillate" refers to a
11 side stream product recovered either from an atmospheric fractionation
12 column or from a vacuum column as opposed to the "bottoms" which
13 represents the residual higher boiling fraction recovered from the bottom of
14 the column.

15
16 The hydroisomerized distillate Fischer-Tropsch base oil used in the invention
17 typically will contain very low sulfur, high VI, and excellent cold flow
18 properties. Following the hydroisomerization step, the hydroisomerized
19 distillate base oil is usually hydrofinished, which in addition to improving the
20 UV stability of the base oil, also reduces the aromatics to a low level;
21 preferably the aromatics will comprise less than about 0.3 wt%. Following the
22 hydrofinishing step, the base oil will also contain low olefins; preferably in
23 amounts below the detection level by long duration carbon-13 NMR.

24
25 Generally, the Fischer-Tropsch base oils will have a minimum kinematic
26 viscosity at 100°C of at least 2.5 cSt, preferably at least 3 cSt and more
27 preferably at least 4 cSt, with an upper limit of about 8 cSt. The
28 Fischer-Tropsch base oil will have a pour point below 20°C, preferably below
29 -12°C, and a VI that is usually greater than 90, preferably greater than 100,
30 even more preferably greater than 120.

1 The number of molecules of the hydroisomerized distillate Fischer-Tropsch
2 base oil having cycloparaffinic functionality will be at least 5 wt%; preferably
3 the number of molecules having cycloparaffinic functionality will be at least
4 about 10 wt%. The hydroisomerized Fischer-Tropsch base oil will also have a
5 ratio of weight percent of molecules with monocycloparaffinic functionality to
6 weight percent of molecules with multicycloparaffinic functionality of greater
7 than about 15, preferably greater than about 50. Both the total cycloparaffinic
8 functionality and the ratio of monocycloparaffinic functionality to
9 multicycloparaffinic functionality present in the base oil may be controlled by
10 carefully selecting the operating conditions of the hydroisomerization step.
11

12 The viscosity index of the hydroisomerized distillate Fischer-Tropsch base oil
13 will preferably be equal to or greater than a value calculated by the equation:
14

$$15 \quad \quad \quad VI = 28 \times \ln(\text{kinematic viscosity at } 100^{\circ}\text{C}) + 95$$

16

17 Wherein: VI represents viscosity index

18 Ln represents the natural log.

19

20 The cold cranking simulator viscosity at -35°C of the hydroisomerized distillate
21 Fischer-Tropsch base oil preferably will be equal to or less than a value
22 calculated by the equation:
23

$$24 \quad \quad \quad \text{CCS VIS}(-35^{\circ}\text{C}) = 38 \times (\text{kinematic viscosity at } 100^{\circ}\text{C})^3$$

25

26 Wherein: CCS VIS(-35°C) represents cold cranking simulator
27 viscosity at -35°C .

1 Even more preferably the cold cranking simulator viscosity at -35°C of the
2 hydroisomerized distillate Fischer-Tropsch base oil will be equal to or less
3 than a value calculated by the equation:

$$\text{CCS VIS}(-35^{\circ}\text{C}) = 38 \times (\text{kinematic viscosity at } 100^{\circ}\text{C})^{2.8}$$

4
5
6
7 Wherein: CCS VIS(-35°C) represents cold cranking simulator
8 viscosity at -35°C.

9 10 **The Pour Point Depressing Base Oil Blending Component**

11
12 The pour point depressing base oil blending component is usually prepared
13 from the high boiling bottoms fraction remaining in the vacuum tower after
14 distilling off the lower boiling base oil fractions. It will have a molecular weight
15 of at least 600. It may be prepared from either a Fischer-Tropsch derived
16 bottoms or a petroleum derived bottoms. The bottoms is hydroisomerized to
17 achieve an average degree of branching in the molecule between about 5 and
18 about 9 alkyl-branches per 100 carbon atoms. Following hydroisomerization
19 the pour point depressing base oil blending component should have a pour
20 point between about -20°C and about 20°C, usually between about -10°C and
21 about 20°C. The molecular weight and degree of branching in the molecules
22 are particularly critical to the proper practice of the invention.

23
24 In the case of Fischer-Tropsch syncrude, the pour point depressing base oil
25 blending component is prepared from the waxy fraction that is normally a solid
26 at room temperature. The waxy fraction may be produced directly from the
27 Fischer-Tropsch syncrude or it may be prepared from the oligomerization of
28 lower boiling Fischer-Tropsch derived olefins. Regardless of the source of the
29 Fischer-Tropsch wax, it must contain hydrocarbons boiling above about 950°F
30 in order to produce the bottoms used in preparing the pour point depressing
31 base oil blending component. In order to improve the pour point and VI, the
32 wax is hydroisomerized to introduce favorable branching into the molecules.

1 The hydroisomerized wax will usually be sent to a vacuum column where the
2 various distillate base oil cuts are collected. In the case of Fischer-Tropsch
3 derived base oil, these distillate base oil fractions may be used for the
4 hydroisomerized Fischer-Tropsch distillate base oil. The bottoms material
5 collected from the vacuum column comprises a mixture of high boiling
6 hydrocarbons which are used to prepare the pour depressing base oil
7 blending component. In addition to hydroisomerization and fractionation, the
8 waxy fraction may undergo various other operations, such as, for example,
9 hydrocracking, hydrotreating, and hydrofinishing. The pour point depressing
10 base oil blending component of the present invention is not an additive in the
11 normal use of this term within the art, since it is really only a high boiling base
12 oil fraction.

13

14 The pour point depressing base oil blending component will have a pour point
15 that is at least 3°C higher than the pour point of the hydroisomerized
16 Fischer-Tropsch distillate base oil. It has been found that when the
17 hydroisomerized bottoms as described in this disclosure is used to reduce the
18 pour point of the blend, the pour point of the blend will be below the pour point
19 of both the pour point depressing base oil blending component and the
20 hydroisomerized distillate Fischer-Tropsch base oil. Therefore, it is not
21 necessary to reduce the pour point of the bottoms to the target pour point of
22 the engine oil. Accordingly, the actual degree of hydroisomerization need not
23 be as high as might otherwise be expected, and the hydroisomerization
24 reactor may be operated at lower severity with less cracking and less yield
25 loss. It has been found that the bottoms should not be over hydroisomerized
26 or its ability to act as a pour point depressing base oil blending component will
27 be compromised. Accordingly, the average degree of branching in the
28 molecules of the Fischer-Tropsch bottoms should fall within the range of from
29 about 5 to about 9 alkyl branches per 100 carbon atoms.

30

31 A pour point depressing base oil blending component derived from a
32 Fischer-Tropsch feedstock will have an average molecular weight between

1 about 600 and about 1,100, preferably between about 700 and about 1,000.
2 The kinematic viscosity at 100°C will usually fall within the range of from about
3 8 cSt to about 22 cSt. The 10% boiling point of the boiling range of the
4 bottoms typically will fall between about 850°F and about 1050°F. Generally,
5 the higher molecular weight hydrocarbons are more effective as pour point
6 depressing base oil blending components than the lower molecular weight
7 hydrocarbons. Typically, the molecular weight of the pour point depressing
8 base oil blending component will be 600 or greater. Consequently, higher cut
9 points in the fractionation column which result in a higher boiling bottoms
10 material are usually preferred when preparing the pour point depressing base
11 oil blending component. The higher cut point also has the advantage of
12 producing a higher yield of the distillate base oil fractions.

13

14 It has also been found that by solvent dewaxing the hydroisomerized bottoms
15 material at a low temperature, generally -10°C or less, the effectiveness of the
16 pour point depressing base oil blending component may be enhanced. The
17 waxy product separated during solvent dewaxing from the bottoms has been
18 found to display improved pour point depressing properties provided the
19 branching properties remain within the limits of the invention. The oily product
20 recovered after the solvent dewaxing operation while displaying some pour
21 point depressing properties is less effective than the waxy product.

22

23 In the case of being petroleum-derived, the basic method of preparation is
24 essentially the same as already described above. Particularly preferred for
25 preparing a petroleum derived pour point depressing base oil blending
26 component is bright stock containing a high wax content. Bright stock
27 constitutes a bottoms fraction which has been highly refined and dewaxed.
28 Bright stock is a high viscosity base oil which is named for the SUS viscosity
29 at 210°F. Typically petroleum derived bright stock will have a viscosity above
30 180 cSt at 40°C, preferably above 250 cSt at 40°C, and more preferably
31 ranging from 500 to 1,100 cSt at 40°C. Bright stock derived from Daqing
32 crude has been found to be especially suitable for use as the pour point

1 depressing base oil blending component of the present invention. The bright
2 stock should be hydroisomerized and may optionally be solvent dewaxed.
3 Bright stock prepared solely by solvent dewaxing has been found to be much
4 less effective as a pour point depressing base oil blending component.

5
6 The petroleum derived pour point depressing base oil blending component
7 preferably will have a paraffin content of at least about 30 wt%, more
8 preferably at least 40 wt%, and most preferably at least 50 wt%. The boiling
9 range of the pour point depressing base oil blending component should be
10 above about 950°F (510°C). The 10% boiling point should be greater than
11 about 1050°F (565°C) with a 10% point in excess of 1150°F (620°C) being
12 preferred. The average degree of branching in the molecules of the pour point
13 depressing base oil blending component preferably will fall within the range of
14 from about 6 to about 8 alkyl-branches per 100 carbon atoms.

15

16 **Additive Package**

17

18 Additive packages are intended to provide additives which provide desirable
19 properties, such as, anti-fatigue, anti-wear, and extreme pressure properties,
20 to the finished lubricant. The additive package which is blended into
21 the multigrade engine oil should be designed to meet ILSAC GF-3 or
22 GF-4 specifications. The specifications for GF-4 are similar to those for
23 GF-3, although GF-4 requirements are more difficult to meet in certain
24 tests. Therefore, any multigrade engine oil which meets GF-4
25 specifications will meet GF-3 as well. However, the reverse is not true. That
26 is to say, not all multigrade engine oils which meet GF-3 specifications
27 will pass GF-4. A number of commercial suppliers are available which
28 offer GF-3 and GF-4 additive packages on the market. Two specific
29 examples of commercially available GF-3 additive packages are
30 Lubrizol LZ20000 (The Lubrizol Corporation) and Oloa 55006A
31 (Chevron Oronite Company LLC). Although the commercially available
32 additive packages are proprietary, U.S. Patent Nos. 6,500,786 and 6,730,638

1 describe formulations intended to meet ILSAC GF-4 requirements for an
2 additive package.
3
4 Zinc dialkyldithiophosphates (ZDDP) is an anti-wear additive which is a
5 common component present in commercial additive packages. However,
6 ZDDP gives rise to ash, which contributes to particulate matter in automotive
7 exhaust emissions, and regulatory agencies are seeking to reduce emissions
8 of zinc into the environment. In addition, phosphorus, also a component of
9 ZDDP, is suspected of limiting the service life of the catalytic converters that
10 are used on cars to reduce pollution. It is desirable to limit the particulate
11 matter and pollution formed during engine use for toxicological and
12 environmental reasons, but it is also important to maintain undiminished the
13 anti-wear properties of the lubricating oil. In view of the shortcoming of the
14 known zinc and phosphorus containing additives, efforts have been made to
15 reduce the amount of zinc and phosphorus present in the additive packages.
16 Preferably, additive packages used in preparing the multigrade engine oils of
17 the present invention will contain less than about 1.00 wt% zinc, expressed as
18 elemental metal. The additive package will also preferably contain less than
19 about 0.90 wt% phosphorus, expressed as elemental metal.

20

21 **The Multigrade Engine Oil**

22

23 A commercial multigrade engine oil refers to an engine oil that has
24 viscosity/temperature characteristics which fall within the limits of two different
25 SAE numbers in SAE J300 (see Table 1) and also meets either the
26 ILSAC GF-3 or GF-4 requirements, plus an API service category, such as SL
27 (for gasoline-powered vehicles) or CI-4 (for diesel-powered vehicles). Europe
28 has its own specification system, although they do incorporate some
29 North American tests. The rest of the world mostly uses the North American
30 system to some degree, although obsolete API service categories abound in
31 developing countries. A multigrade engine oil within the scope of the present
32 invention comprises between about 15 and about 94.5 wt% of the

1 hydroisomerized distillate Fischer-Tropsch base oil, between about 0.5 to
2 about 20 wt% of the pour point depressing base oil blending component, and
3 between about 5 to about 30 wt% of the additive package. Generally, the
4 multigrade engine oil blends of the invention will contain sufficient pour point
5 depressing base oil blending component to reduce the pour point of the
6 hydroisomerized distillate Fischer-Tropsch base oil by at least 2°C. In
7 addition, the multigrade engine oil may optionally also contain other
8 components or additives. For example, the multigrade engine oil may also
9 contain from about 5 wt% to about 70 wt% of a polymerized olefin selected
10 from at least one of a polyalphaolefin base oil, a polyinternalolefin base oil, or
11 a mixture of polyalphaolefin and polyinternalolefin base oils. However, usually
12 additional pour point depressants and/or viscosity index improvers are not
13 necessary in formulations prepared according to this invention.

14

15 In blending the multigrade engine oil of the invention the order in which the
16 various components are blended is not important. For example, when it is
17 stated that sufficient pour point depressing base oil blending component
18 should be present to reduce the pour point of the hydroisomerized distillate
19 Fischer-Tropsch base oil by at least 2°C, it is not intended to intimate that the
20 pour point depressing base oil blending component and the hydroisomerized
21 distillate base oil must be blended together first and then the additive package
22 blended in next. The intent is that the ratio of pour point depressing base oil
23 blending component and hydroisomerized distillate Fischer-Tropsch base oil
24 in the final blend should be such that if the two components were blended
25 together without the additive package, the pour point of the hydroisomerized
26 distillate Fischer-Tropsch base oil would be reduced by at least 2°C. The
27 actual order in which the components are blended is irrelevant.

28

29 Multigrade engine oils within the scope of the invention may be formulated to
30 meet the specifications for SAE viscosity grade 0W-XX, 5W-XX, or 10W-XX
31 engine oil, wherein XX represents the integer 20, 30, or 40. Formulations
32 meeting the specifications for SAE viscosity grade 0W-20 have been

1 successfully prepared using the present invention. This requires that the
2 MRV TP-1 of the formulation must have a result of 60,000 cP at -40°C with no
3 yield stress. Likewise, multigrade engine oils within the scope of the invention
4 may be formulated with an MRV TP-1 result of 60,000 at temperatures of
5 -35°C and -30°C, respectively. Formulations with an MVR TP-1 result at -40°C
6 of 30,000 and 15,000 are also possible.

7
8 In order to meet the ILSAC GF-3 and GF-4 requirements a Noack volatility
9 value of 15 as measured by standard test method ASTM D 5800 is
10 necessary. Due to the low volatility of Fischer-Tropsch materials used in the
11 formulations of the invention, Noack volatility values of 10 or less may be
12 achieved.

13
14 The present invention may be further illustrated by the following example
15 which is not intended, however, to represent a limitation on the scope of the
16 invention.

EXAMPLE

Two Fischer-Tropsch waxes were made with either iron-based or cobalt-based Fischer-Tropsch catalyst. They had the properties shown in Table 2:

Table 2

Fischer-Tropsch Catalyst	Fe-Based	Co-Based
Total Nitrogen and Sulfur, ppm	less than 10	less than 25
Oxygen by Neutron Activation, wt%	0.15	0.69
Oil Content, D 721, wt%	<0.8	6.68
Total Normal Paraffin, wt% by GC	92.15	83.72
D 6352 SIMDIST (wt%), °F		
T0.5	784	129
T5	853	568
T10	875	625
T20	914	674
T30	941	717
T40	968	756
T50	995	792
T60	1013	827
T70	1031	873
T80	1051	914
T90	1081	965
T95	1107	1005
T99.5	1133	1090

Four different Fischer-Tropsch derived products were made by hydroisomerizing the Fischer-Tropsch waxes from Table 2 over Pt/SAPO-11 on an alumina support. Two of the products were made from the iron-based Fischer-Tropsch wax and two were made from the cobalt-based Fischer-Tropsch wax. The full range broad boiling isomerized wax products were subsequently separated by vacuum distillation. The properties of these four fractions are summarized in Table 3. FT-4.4 and FT-4.5 were hydroisomerized Fischer-Tropsch derived lubricant base oil distillate fractions and FT-8.0 and FT-9.8 were bottoms fractions. Note that the FT-9.8 had the

1 10% boiling point in its boiling range greater than 900°F and had a pour point
 2 between about -15°C and about 20°C.

3

4

Table 3

Sample Properties	FT-4.4	FT-4.5	FT-8.0	FT-9.8
	Base Oil - Distillate Fractions		Distillate Bottoms	
FT Wax	Co-Based	Fe-Based	Co-Based	Fe-Based
Viscosity at 100°C, cSt	4.415	4.524	7.953	9.830
Viscosity Index	147	149	165	163
Pour Point, °C	-12	-17	-12	-12
CCS Vis @ -35°C, cP	2,079	2,090	13,627	28,850
SIMDIST (wt%), °F				
5	743	716	824	911
10 / 30	753/726	732/792	830/877	921/936
50	823	843	919	971
70 / 90	868/929	883/917	977/1076	999/1050
95	949	929	1120	1074
FIMS Analysis, wt%				
Paraffins	85.0	89.4	70.2	81.3
Monocycloparaffins	14.0	10.4	28.0	16.4
Multicycloparaffins	1.0	0.2	1.8	2.3
Total	100.0	100.0	100.0	100.0
Methyl Branches per 100 Carbons				6.63
N-Paraffins by GC, wt%				Less than 2

5

6 Note that FT-9.8 meets the properties of the pour point depressing base oil
 7 blending component used to prepare blends of this invention. It has the
 8 preferred amount of methyl branching, n-paraffin composition, CCS VIS,
 9 10% boiling point, and pour point. FT-8 does not meet the properties of the
 10 pour point reducing base oil blending component of this invention. It has a
 11 10% boiling point well below 900°F.

12

13 Three different multigrade engine oil formulations were made using the
 14 Fischer-Tropsch derived base oils described above. The components of each
 15 of these engine oil formulations are shown in Table 4.

1

Table 4

Component, wt%	Engine Oil 1	Comparative Engine Oil 2	Comparative Engine Oil 3
SAE Grade	0W-20	0W-20	5W-20
FT-4.4	0	53.74	15.34
FT-4.5	79.83	0	0
FT-8	0	35.61	74.01
FT-9.8	8.87	0	0
GF-3 Additive #1	11.30	0	0
GF-3 Additive #2	0	10.35	10.35
PAMA PPD	0	0.30	0.30
TOTAL	100.00	100.00	100.00

2

3 Comparative Engine Oils 2 and 3 contained a polyalkyl methacrylate (PAMA)
 4 pour point depressant, while Engine Oil 1 did not. None of the examples
 5 contained additional viscosity index improver, other than what may have been
 6 present in incidental amounts in the GF-3 additive packages.

7

8 The viscometric properties of these three engine oil formulations are
 9 summarized in Table 5.

10

11

Table 5

Properties	Engine Oil 1	Comparative Engine Oil 2	Comparative Engine Oil 3
Viscosity at 100 °C	6.67	7.09	8.89
Pour Point, °C	-43	-43	Not tested
MRV TP-1 @-40 °C	12,400	71,156	Not tested
Yield Stress	None	None	
MRV TP-1 @-35 °C	Not tested	Not tested	176,400
Yield Stress			80
Noack Volatility, Wt%	9.0	Not tested	Not tested

12

13 Note the extremely low MRV TP-1 viscosity of Engine Oil 1. This result was
 14 surprising considering the engine oil formulation was made using a high
 15 viscosity bottoms product which would not be expected to have good low
 16 temperature properties. The results are especially surprising considering that
 17 no pour point depressant or viscosity index improver was added to the
 18 formulation. These excellent low temperature properties are believed to be
 19 related to (a) the high boiling point and particular branching properties of the

- 1 pour point reducing base oil blending component, and (b) the desirable
- 2 properties of the hydroisomerized Fischer-Tropsch lubricant base oil that were
- 3 blended into the engine oil formulation.

1 WHAT IS CLAIMED IS:

2

3 1. A multigrade engine oil meeting the specifications for SAE J300
4 revised June 2001 requirements, said engine oil comprising:

5

6 (a) between about 15 to about 94.5 wt% of a hydroisomerized
7 distillate Fischer-Tropsch base oil characterized by
8 (i) a kinematic viscosity between about 2.5 and about 8 cSt at
9 100°C, (ii) at least about 3 wt% of the molecules having
10 cycloparaffin functionality, and (iii) a ratio of weight percent
11 molecules with monocycloparaffin functionality to weight percent
12 of molecules with multicycloparaffin functionality greater than
13 about 15;

14

15 (b) between about 0.5 to about 20 wt% of a pour point depressing
16 base oil blending component prepared from an hydroisomerized
17 bottoms material having an average degree of branching in the
18 molecules between about 5 and about 9 alkyl-branches per
19 100 carbon atoms and wherein not more than 10 wt% boils
20 below about 900°F; and

21

22 (c) between about 5 to about 30 wt% of an additive package
23 designed to meet the specifications for ILSAC GF-3.

24

25 2. The multigrade engine oil of claim 1 wherein the additive package is
26 designed to meet the specifications for ILSAC GF-4.

27

28 3. The multigrade engine oil of claim 1 wherein the additive package
29 contains less than about 1.00 wt% zinc expressed as elemental metal.

- 1 4. The multigrade engine oil of claim 1 wherein the additive package
2 contains less than about 0.90 wt% phosphorus expressed as elemental
3 metal.
4
- 5 5. The multigrade engine oil of claim 1 meeting the specifications for
6 SAE viscosity grade 0W-XX, 5W-XX, or 10W-XX engine oil, wherein
7 XX represents the integer 20, 30, or 40.
8
- 9 6. The multigrade engine oil of claim 5 meeting the specifications for
10 SAE viscosity grade 0W-20.
11
- 12 7. The multigrade engine oil of claim 1 having a MRV TP-1 result of less
13 than 60,000 cP at -30°C.
14
- 15 8. The multigrade engine oil of claim 7 having a MRV TP-1 result of less
16 than 60,000 cP at -35°C.
17
- 18 9. The multigrade engine oil of claim 8 having a MRV TP-1 result of less
19 than 60,000 cP at -40°C.
20
- 21 10. The multigrade engine oil of claim 9 having a MRV TP-1 result of less
22 than 30,000 cP at -40°C.
23
- 24 11. The multigrade engine oil of claim 10 having a MRV TP-1 result of less
25 than 15,000 cP at -40°C.
26
- 27 12. The multigrade engine oil of claim 1 having a Noack volatility value of
28 about 15% or less.
29
- 30 13. The multigrade engine oil of claim 12 having a Noack volatility value of
31 about 10% or less.

- 1 14. The multigrade engine oil of claim 1 wherein the hydroisomerized
2 distillate Fischer-Tropsch base oil is characterized by at least about
3 10 wt% of the molecules having cycloparaffin functionality.
4
- 5 15. The multigrade engine oil of claim 1 wherein hydroisomerized distillate
6 Fischer-Tropsch base oil is characterized by the ratio of weight percent
7 of molecules with monocycloparaffin functionality to weight percent of
8 molecules with multicycloparaffin functionality of greater than about 50.
9
- 10 16. The multigrade engine oil of claim 1 wherein the hydroisomerized
11 distillate base oil contains less than about 0.3 wt% aromatics.
12
- 13 17. The multigrade engine oil of claim 1 wherein the hydroisomerized
14 distillate base oil contains olefins in an amount which is undetectable
15 by long duration carbon-13 NMR.
16
- 17 18. The multigrade engine oil of claim 1 wherein the pour point depressing
18 base oil blending component is derived from an isomerized
19 Fischer-Tropsch derived bottoms product having a molecular weight
20 between about 600 and about 1,100.
21
- 22 19. The multigrade engine oil of claim 1 wherein the pour point depressing
23 base oil blending component is an isomerized petroleum derived
24 bottoms product having an average molecular weight of at least 600.
25
- 26 20. The multigrade engine oil of claim 1 wherein the pour point depressing
27 base oil blending component has an average degree of branching in
28 the molecules between about 6 and about 8 alkyl-branches per
29 100 carbon atoms.
30
- 31 21. The multigrade engine oil of claim 1 further comprising from about
32 5 wt% to about 70 wt% of a polymerized olefin selected from at least

- 1 one of a polyalphaolefin base oil, a polyinternalolefin base oil, or a
2 mixture of polyalphaolefin and polyinternalolefin base oils.
3
- 4 22. The multigrade engine oil of claim 1 containing no additional pour point
5 depressant additive or viscosity index improver.
6
- 7 23. A process for preparing a multigrade engine oil meeting the
8 specifications for SAE J300 revised June 2001 requirements which
9 comprises:
10
- 11 (a) hydroisomerizing a waxy Fischer-Tropsch base oil in an
12 isomerization zone in the presence of a hydroisomerization
13 catalyst and hydrogen under pre-selected conditions determined
14 to provide a hydroisomerized Fischer-Tropsch base oil product;
15
16
- 17 (b) recovering from the isomerization zone a hydroisomerized
18 Fischer-Tropsch base oil product;
19
- 20 (c) distilling the hydroisomerized Fischer-Tropsch base oil product
21 recovered from the isomerization zone under distillation
22 conditions pre-selected to collect a distillate Fischer-Tropsch
23 base oil characterized by (i) a kinematic viscosity between about
24 2.5 and about 8 cSt at 100°C, (ii) at least about 3 wt% of the
25 molecules having cycloparaffin functionality, and (iii) a ratio of
26 weight percent molecules with monocycloparaffin functionality to
27 weight percent of molecules with multicycloparaffin functionality
28 greater than about 15;
29
- 30 (d) blending the distillate Fischer-Tropsch base oil with (i) a pour
31 point depressing base oil blending component prepared from an
32 hydroisomerized bottoms material having an average degree of

1 branching in the molecules between about 5 and about
2 9 alkyl-branches per 100 carbon atoms and wherein not more
3 than 10 wt% boils below about 900°F and (ii) an additive
4 package designed to meet the specifications for ILSAC GF-3 in
5 the proper proportions to yield a multigrade engine oil meeting
6 the specifications for SAE J300 revised June 2001.

7

8 24. The process of claim 23 including the additional step of hydrofinishing
9 the hydroisomerized Fischer-Tropsch base oil product wherein
10 aromatics comprise no more than 0.3 wt% of the hydroisomerized
11 Fischer-Tropsch base oil and the amount of olefins are undetectable by
12 long duration carbon-13 NMR.

13

14 25. The process of claim 23 wherein the distillate Fischer-Tropsch base oil
15 has a viscosity index equal to or greater than the viscosity index
16 calculated by the equation:

17

$$18 \qquad \qquad \qquad VI = 28 \times \ln(\text{kinematic viscosity at } 100^{\circ}\text{C}) + 95$$

19

20 Wherein: VI represents viscosity index

21 Ln represents the natural log.

22

23 26. The process of claim 23 wherein the distillate Fischer-Tropsch base oil
24 has a cold cranking simulator viscosity at -35°C equal to or less than a
25 value calculated by the equation:

26

$$27 \qquad \qquad \qquad \text{CCS VIS}(-35^{\circ}\text{C}) = 38 \times (\text{kinematic viscosity at } 100^{\circ}\text{C})^3$$

28

29 Wherein: CCS VIS(-35°C) represents cold cranking simulator
30 viscosity at -35°C.

31

- 1 27. The process of claim 26 wherein the distillate Fischer-Tropsch base oil
2 has a cold cranking simulator viscosity at -35°C equal to or less than a
3 value calculated by the equation:
4
5 $CCS\ VIS(-35^{\circ}C) = 38 \times (\text{kinematic viscosity at } 100^{\circ}C)^{2.8}$
6
7 Wherein: CCS VIS(-35°C) represents cold cranking simulator
8 viscosity at -35°C.
- 9 28. The process of claim 23 wherein the pour point depressing base oil
10 blending component has a molecular weight of at least 600.
11
- 12 29. The process of claim 23 wherein the pour point depressing base oil
13 blending component has an average degree of branching in the
14 molecules between about 6 and about 8 alkyl-branches per 100 carbon
15 atoms.
16
- 17 30. The process of claim 23 wherein sufficient pour point depressing base
18 oil blending component is blended into the multigrade engine oil to
19 lower the pour point of the distillate Fischer-Tropsch base oil by at least
20 2°C.
21
- 22 31. The process of claim 23 wherein the additive package is designed to
23 meet the specifications for ILSAC GF-4.
24
- 25 32. The process of claim 23 wherein the distillate Fischer-Tropsch base oil
26 is blended with the pour point depressing base oil blending component
27 and additive package in the proper proportions to yield a multigrade
28 engine oil having a MRV TP-1 result of less than 60,000 cP at -30°C.
29
- 30 33. The process of claim 32 wherein the distillate Fischer-Tropsch base oil
31 is blended with the pour point depressing base oil blending component

- 1 and additive package in the proper proportions to yield a multigrade
2 engine oil having a MRV TP-1 result of less than 60,000 cP at -35°C.
3
- 4 34. The process of claim 33 wherein the distillate Fischer-Tropsch base oil
5 is blended with the pour point depressing base oil blending component
6 and additive package in the proper proportions to yield a multigrade
7 engine oil having a MRV TP-1 result of less than 60,000 cP at -40°C.
8
- 9 35. The process of claim 34 wherein the distillate Fischer-Tropsch base oil
10 is blended with the pour point depressing base oil blending component
11 and additive package in the proper proportions to yield a multigrade
12 engine oil having a MRV TP-1 result of less than 30,000 cP at -40°C.
13
- 14 36. The process of claim 35 wherein the distillate Fischer-Tropsch base oil
15 is blended with the pour point depressing base oil blending component
16 and additive package in the proper proportions to yield a multigrade
17 engine oil having a MRV TP-1 result of less than 15,000 cP at -40°C.