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(54) Title: BIODEGRADABLE HIGH PERFORMANCE HYDROCARBON BASE OILS

(57) Abstract

Discloses novel biodegradable high performance hydrocarbon base oils useful as lubricants in engine oil and industrial compositions, and process for their manufacture. A waxy, or paraffinic feed, particularly a Fischer-Tropsch wax, is reacted over a dual function catalyst to produce hydroisomerization and hydrocraking reactions, at 700 °F+ conversion levels ranging from about 20 to 50 wt.%, preferably about 25-40 wt.%, sufficient to produce a crude fraction, e.g., a C_5-1050 °F+ crude fraction, containing 700 °F+ isoparaffins having from about 6.0 to about 7.5 methyl branches per 100 carbon atoms in the molecule. The methyl paraffins containing crude fraction is topped via atmospheric distillation to produce a bottoms fraction having an initial boiling point between about 650 °F and 750 °F which is then solvent dewaxed, and the dewaxed oil is then fractionated under high vacuum to produce biodegradable high performance hydrocarbon base oils.

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BIODEGRADABLE HIGH PERFORMANCE HYDROCARBON BASE OILS

1. Field of the Invention

This invention relates to biodegradable high performance hydrocarbon base oils, suitable as engine oil and industrial oil compositions. In particular, it relates to lubricant base oil compositions, and process for making such compositions by the hydroisomerization/hydrocracking of paraffinic waxes, suitably Fischer-Tropsch waxes.

2. Background

It is well known that very large amounts of lubricating oils, e.g., engine oils, transmission oils, gear box oils, etc., find their way into the natural environment, accidentally and even deliberately. These oils are capable of causing much environmental harm unless they are acceptably biodegradable. For this reason there is increasing emphasis in this country, and abroad, to develop and employ high performance lubricant base oils which are environmentally friendly, or substantially biodegradable on escape or release into the environment.

Few hydrocarbon base oils are environmentally friendly though their qualities as lubricants may be unchallenged. The literature stresses the superior biodegradability of ester based lubricants, natural and synthetic, over hydrocarbon based products. However there is little or no emphasis on performance. Few references are found relating to the biodegradability of hydrocarbon lubricants. Ethyl Petroleum Additives's EP 468 109A however does disclose the biodegradability of lubricating oils containing at least 10 volume percent of a "biodegradable liquid hydrocarbon of lubricating viscosity formed by oligomerization of a 1-alkene hydrocarbon having 6 to 20 carbon atoms in the molecule and hydrogenation of the resultant oligomer."

Apparently hydrogenated oligomers of this type have unexpectedly high biodegradability, particularly those having at least 50 volume percent dimer, trimer and/or tetramer. Ethyl Petroleum Additive's EP 558 835 A1 discloses lubricating oils having similar polyalphaolefin, PAO, components. However, both references point out performance debits for the synthetic and natural ester oils, such as low oxidative stability at high temperatures and poor hydrolytic stability. British Petroleum's FR 2675812 discloses the production of biodegradable PAO hydrocarbons base oils by dewaxing a hydrocracked base oil at low temperatures.

There is a clear need for biodegradable high performance hydrocarbon base oils useful as engine oil and industrial oil, or lubricant compositions which are at least equivalent to the polyalphaolefins in quality, but have the distinct advantage of being more biodegradable.

3. Summary of the Invention

This invention, which supplies these and other needs, accordingly relates to biodegradable high performance paraffinic lubricant base oils, and process for the production of such compositions by the hydrocracking and hydroisomerization of paraffinic, or waxy hydrocarbon feeds, especially Fischer-Tropsh waxes or reaction products, all or at least a portion of which boils above 700°F, i.e., 700°F+. The waxy feed is first contacted, with hydrogen, over a dual functional catalyst to produce hydroisomerization and hydrocracking reactions sufficient to convert at least about 20 percent to about 50 percent, preferably from about 25 percent to about 40 percent, on a once through basis based on the weight of the 700°F+ feed, or 700°F+ feed component, to 700°F- materials, and produce 700°F+ materials rich in methyl-paraffins. This resultant crude product, which contains both 700°F- and 700°F+ materials, characterized generally as a C_5-1050°F+ crude fraction, is first topped via atmospheric distillation to produce a lower boiling fraction the upper end of which boils between about 650°F and 750°F, e.g., 700°F, and a higher boiling, or bottoms fraction having an initial boiling point ranging between about 650°F and 750°F, e.g., 700°F, and an upper end or final boiling point of about 1050°F+, e.g., a 700°F+ fraction. The lower boiling fraction, e.g., the 700°F- fraction, from the distillation is a non-lube, or fuel fraction.

At these conversion levels, the hydroisomerization/hydrocracking reactions converts a significant amount of the waxy, or paraffinic feed to 700°F+ methyl-paraffins, i.e., isoparaffins containing one or more methyl groups in the molecule, with minimal formation of branches of carbon number greater than 1; i.e., ethyl, propyl, butyl or the like. The 700°F+ bottoms fractions so-treated contain 700°F+ isoparaffins having from about 6.0 to about 7.5 methyl branches per 100 carbon atoms, preferably from about 6.5 to about 7.0 methyl branches per 100 carbon atoms, in the molecule. These isoparaffins, contained in a mixture with other materials, provide a product from which high performance, highly biodegradable lube oils can be obtained.

The higher boiling bottoms fractions, e.g., the 700°F+ bottoms fraction containing the methyl-paraffins, or crude fraction, is dewaxed in a conventional solvent dewaxing step to remove n-paraffins, and the recovered dewaxed product, or dewaxed oil, is fractionated under vacuum to produce paraffinic lubricating oil fractions of different viscosity grades, including hydrocarbon oil fractions suitable as high performance engine oils and engine lubricants which, unlike most hydrocarbon base oils, are biodegradable on release or escape into the environment. In terms of their performance they are unsurpassed by the PAO lubricants, and are superior thereto in terms of their biodegradability.

4. Detailed Description

The feed materials that are isomerized to produce the lube base stocks, and lubricants with the catalyst of this invention are waxy feeds, i.e., C_5+, preferably having an initial boiling point above about 350°F (117°C), more preferably above about 550°F (288°C), and contain a major amount of components boiling above 700°F (370°C). The feed may be obtained either from a Fischer-Tropsch process which produces substantially normal paraffins, or from petroleum derived slack waxes.

Slack waxes are the by-products of dewaxing operations where a diluent such as propane or a ketone (e.g., methylethyl ketone, methyl isobutyl ketone) or other diluent is employed to promote wax crystal growth, the wax being removed from the base oil by filtration or other suitable means. The slack waxes are generally paraffinic in nature, boil above about 600°F (316°C), preferably in the range of 600°F (316°C) to about 1050°F (566°C), and may contain from about 1 to about 35 wt.% oil. Waxes with low oil contents, e.g., 5-20 wt.% are preferred; however, waxy distillates or raffinates containing 5-45% wax may also be used as feeds. Slack waxes are usually freed of polynuclear aromatics and hetero-atom compounds by techniques known in the art; e.g., mild hydrotreating as described in U.S. Patent No. 4,900,707, which also reduces sulfur and nitrogen levels preferably to less than 5 ppm and less than 2 ppm, respectively. Fischer-Tropsch waxes are preferred feed materials, having negligible amounts of aromatics, sulfur and nitrogen compounds. The Fischer-Tropsch liquid, or wax, is characterized as the product of a Fischer-Tropsh process wherein a synthetic gas, or mixture of hydrogen and carbon monoxide, is processed at elevated temperature over a supported catalyst comprised of a Group VIII metal, or metals, of the Periodic Table of The Elements (Sargent-Welch Scientific Company, Copyright 1968), e.g., cobalt, ruthenium, iron, etc. The Fischer-Tropsch wax contains C_5+, preferably C_{10}+, more preferably C_{20}+ paraffins. A distillation showing the fractional make up (±10 wt.% for each fraction) of a typical Fischer-Tropsch process liquid feedstock is as follows:

Boiling Temperature Range	Wt.% of Fraction
IBP - 320°F	13
320 - 500°F	23
500 - 700°F	19
700 - 1050°F	34
1050°F+	11
	100

The wax feed is contacted, with hydrogen, at hydrocracking/ hydroisomerization conditions over a bifunctional catalyst, or catalyst containing a metal, or metals, hydrogenation component and an acidic oxide support component active in producing both hydrocracking and hydroisomerization reactions. Preferably, a fixed bed of the catalyst is contacted with the feed at conditions which convert about 20 to 50 wt.%, preferably about 25 to 40 wt.%, of the 700°F components of the feed to 700°F- materials and produce a lower boiling fraction having an upper end boiling point between about 650°F and 750°F, e.g., 700°F, and a higher boiling, or bottoms fraction having an initial boiling point between about 650°F and 750°F, e.g., 700°F, the higher boiling fraction that remains containing high quality blending components for the production of high performance biodegradable base oils. In general, the hydrocracking/ hydroisomerization reaction is conducted by contacting the waxy feed over the catalyst at a controlled combination of conditions which produce these levels of conversion; i.e., by selection of temperatures ranging from about 400°F to about 850°F, preferably from about 500°F to about 700°F, pressures ranging generally from about 100 pounds per square inch gauge (psig) to about 1500 psig, preferably from about 300 psig to about 1000 psig, hydrogen treat gas rates ranging from about 1000 SCFB to about 10,000 SCFB, preferably from about 2000 SCFB to about 5000 SCFB, and space velocities ranging generally from about 0.5 LHSV to about 10 LHSV, preferably from about 0.5 LHSV to about 2.0 LHSV.

The active metal component of the catalyst is preferably a Group VIII metal, or metals, of the Periodic Table Of The Elements (Sargent-Welch Scientific Company Copyright 1968) in amount sufficient to be catalytically active for hydrocracking and hydroisomerization of the waxy feed. The catalyst may also contain, in addition to the Group VIII metal, or metals, a Group IB and/or a Group VIB metal, or metals, of the Periodic Table. Generally, metal concentrations range from about 0.05 percent to about 20 percent, based on the total weight of the catalyst (wt.%), preferably from about 0.1 wt. percent to about 10 wt. percent. Exemplary of such metals are such non-noble Group VIII metals as nickel and cobalt, or mixtures of these metals with each other or with other metals, such as copper, a Group IB metal, or molybdenum, a Group VIB metal. Palladium and platinum are exemplary of suitable Group VIII noble metals. The metal, or metals, is incorporated with the support component of the catalyst by known methods, e.g., by impregnation of the support with a solution of a suitable salt or acid of the metal, or metals, drying and calcination.

The catalyst support is constituted of metal oxide, or metal oxides, components at least one component of which is an acidic oxide active in producing olefin cracking and hydroisomerization reactions. Exemplary oxides include silica, silica-alumina, clays, e.g., pillared clays, magnesia, titania, zirconia, halides, e.g., chlorided alumina, and the like. The catalyst support is preferably constituted of silica and alumina, a particularly preferred support being constituted of up to about 35 wt.% silica, preferably from about 2 wt.% to about 35 wt.% silica, and having the following pore-structural characteristics:

Pore Radius, Å	Pore Volume
0-300	>0.03 ml/g
100-75,000	<0.35 ml/g
0-30	<25% of the volume of the pores with 0-300 Å radius
100-300	<40% of the volume of the pores with 0-300 Å radius

The base silica and alumina materials can be, e.g., soluble silica containing compounds such as alkali metal silicates (preferably where $Na_2O:SiO_2$ = 1:2 to 1:4), tetraalkoxy silane, orthosilic acid ester, etc.; sulfates, nitrates, or chlorides of aluminum alkali metal aluminates; or inorganic or organic salts of alkoxides or the like. When precipitating the hydrates of silica or alumina from a solution of such starting materials, a suitable acid or base is added and the pH is set within a range of about 6.0 to 11.0. Precipitation and aging are carried out, with heating, by adding an acid or base under reflux to prevent evaporation of the treating liquid and change of pH. The remainder of the support producing process is the same as those commonly employed, including filtering, drying and calcination of the support material. The support may also contain small amounts, e.g., 1-30 wt.%, of materials such as magnesia, titania, zirconia, hafnia, or the like.

Support materials and their preparation are described more fully in U.S. Patent No. 3,843,509 incorporated herein by reference. The support materials generally have a surface area ranging from about 180-400 m^2/g, preferably 230-375 m^2/g, a pore volume generally of about 0.3 to 1.0 ml/g, preferably about 0.5 to 0.95 ml/g, bulk density of generally about 0.5-1.0 g/ml, and a side crushing strength of about 0.8 to 3.5 kg/mm.

The hydrocracking/hydroisomerization reaction is conducted in one or a plurality of reactors connected in series, generally from about 1 to about 5 reactors; but preferably the reaction is conducted in a single reactor. The waxy hydrocarbon feed, e.g., Fischer-Tropsch wax, preferably one boiling above about 700°F, or has a large amount of 700°F+ hydrocarbon components, is fed, with hydrogen, into the reactor, a first reactor of the series, to contact a fixed bed of the catalyst at hydrocracking/hydro-isomerization reaction conditions to hydrocrack, hydroisomerize and convert at least a portion of the waxy feed to products which include after further work up high quality oils and lube blending components.

The following examples are illustrative of the more salient features of the invention. All parts, and percentages, are given in terms of weight unless otherwise specified.

Examples 1-9

A mixture of hydrogen and carbon monoxide synthesis gas (H_2:CO 2.11-2.16) was converted to heavy paraffins in a slurry Fischer-Tropsch reactor. A titania supported cobalt rhenium catalyst was utilized for the Fischer-Tropsch reaction. The reaction was conducted at 422-428°F, 287-289 psig, and the feed was introduced at a linear velocity of 12 to 17.5 cm/sec. The alpha of the Fischer-Tropsch synthesis step was 0.92. The paraffinic Fischer-Tropsch product was isolated in three nominally different boiling streams; separated by utilizing a rough flash. The three boiling fractions which were obtained were: 1) a C_5-500°F boiling fraction, i.e., F-T cold separator liquids; 2) a 500-700°F boiling fraction, i.e., F-T hot separator liquids; and 3) a 700°F+ boiling fraction, i.e., a F-T reactor wax.

A series of base oils were prepared in runs made by hydrocracking and isomerizing the 700°F+ Fischer-Tropsch reactor wax feedstock, with hydrogen, at different levels of conversion over a silica exhanced cobalt-moly-nickel catalyst (CoO, 3.6 wt.%; MoO_3, 16.4 wt.%; NiO, 0.66 wt.%; on a reactors; but preferably the reaction is conducted in a single reactor. The waxy hydrocarbon feed, e.g., Fischer-Tropsch wax, preferably one boiling above about 700°F, or has a large amount of 700°F+ hydrocarbon components, is fed, with hydrogen, into the reactor, a first reactor of the series, to contact a fixed bed of the catalyst at hydrocracking/hydro-isomerization reaction conditions to hydrocrack, hydroisomerize and convert at least a portion of the waxy feed to products which include after further work up high quality oils and lube blending components.

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TABLE 1

CONVERSION TO 700°F-, wt.%

	30	35	45	50	58	67	80
Operating Conditions							
Temperature, °F	681.9	689	705.2	701.5	709.7	707.1	711.4
Space Velocity, LHSV	0.42	0.50	0.50	0.45	0.50	0.43	0.44
Pressure, psig	--	--	1000	--	--	--	--
H_2 Treat Rate, SCF/B	--	--	2500	--	--	--	--
Yields (wt.% recovery)							
C_1-C_4	1.17	0.73	1.73	2.11	2.14	2.43	3.70
C_5-320°F	5.48	3.11	9.68	9.75	9.48	14.93	23.10
320-550°F	10.43	10.11	17.82	17.92	22.87	25.20	27.04
550-700°F	20.48	23.94	21.88	24.63	27.81	28.01	30.21
700°F+	62.44	62.11	48.89	45.59	37.70	29.43	15.93
15/5 Composite Distillation (wt.%)							
IBP-650°F	32.25	26.71	37.46	44.26	48.35	59.80	67.77
650°F+	67.75	73.29	62.54	55.74	51.65	40.20	32.23

A 650°F+ bottom fraction was recovered from the products obtained from each of the runs by atmospheric distillation, and then again fractionated under high vacuum to produce several viscosity grades of lubricant, viz. 60N, 100N, 175N and about 350-400N. The residual products were then subjected to solvent dewaxing to remove waxy hydrocarbons and lower the pour point to about -18°C (32°F).

For each viscosity grade, the dewaxing conditions were held constant so that the effect of conversion level on dewaxing could be evaluated. The dewaxing conditions for 100N and 175N viscosity grades at the 30%, 50%, 67% and 80% conversion levels are given in Table 2.

Table 2
Dewaxing Conditions[1]

	Viscosity Grade	
	100N	175N
30% Conversion		
Solvent:Oil Ratio	3:1	3:1
Filter Temp, °C	-21	-21
Pour Pt, °C	-18	-18
50% Conversion		
Solvent:Oil Ratio	3:1	3:1
Filter Temp, °C	-21	-21
Pour Pt, °C	-21	-21
67% Conversion		
Solvent:Oil Ratio	3:1	3:1
Filter Temp, °C	-21	-21
Pour Pt, °C	-15	-18
80% Conversion		
Solvent:Oil Ratio	3:1	3:1
Filter Temp, °C	-21	-21
Pour Pt, °C	-24	-24

[1] All dewaxings employed 100% methylisobutylketone, MIBK.

The physical properties, yields of dewaxed oil, DWO, and corresponding dry wax contents (both as wt.% on waxy feed) for each dewaxing in terms of the 100N and 175N viscosity grades at specific levels of conversion are given in Table 3.

TABLE 3
DEWAXED BASE OIL PHYSICAL PROPERTIES
VISCOSITY GRADES

	30% Conversion		50% Conversion		67% Conversion		80% Conversion	
	100N	175N	100N	175N	100N	175N	100N	175N
Dewaxed Oil Yield/Dry Wax Content (wt.% on waxy feed)	80.7/17.6	75.3/21.4	93.0/6.6	91.1/7.7	97/2.4	92/5.2	98/2.0 96.3/1.7	
Pour/Cloud Pt., °C	-18/-14	-18/-14	-21/-14	-21/-17	-15/-7	-18/-14	-24/-21	-24/-21
Density @ 15°C, kg/dm	0.8143	0.8218	0.8153	0.8229	0.8147	0.8231	0.8160	0.8234
Refractive Index @ 20°C								
Viscosity, cSt								
@ 40°C	15.59	26.96	16.28	29.14	15.90	28.76	16.71	18.94
@ 100°C	3.81	5.59	3.86	5.77	3.77	5.68	3.85	5.61
Viscosity Index	141	153	133	145	129	143	124	136
GCD,°C								
IBP	346	380	343	390	347	394	351	393
5%	369	408	367	418	369	419	370	416
50%	426	471	424	473	421	469	421	466
95%	486	535	488	531	479	524	478	523
FBP	522	567	528	565	515	558	513	559

Nuclear magnetic resonance (NMR) branching densities for 100N base oils produced at 30%, 50%, 67%, and 80% levels, respectively, are given in Table 4. It will be observed that the lower levels of methyl branching occurs at the lower conversion levels; with the biodegradability of the oil increasing at the lower levels of conversion. Compositions of highest biodegradability are thus produced at the 30 wt.% level of conversion, and the next highest biodegradability compositions are produced at the 50 wt.% conversion level.

Table 4

100N Base Oil, ^{13}CNMR Branching Densities

------% Conversion------

Base Oil	30	50	67	80
V.I.	141	133	129	124
Per 100 Carbons Methyl Groups (CH_3^-)	6.8	7.5	7.5	7.8

It is also found that the viscosity index, VI, decreases with increasing level of conversion for each specific viscosity grade. This is because base oils prepared at higher conversion levels tend to be more highly branched and consequently have lower viscosity indexes. For the 100N base oils, the VI ranges from 141 to 118. For the 175N oils, the corresponding VI range is 153 to 136, respectively. The 175N base oils have VIs which are also comparable to the commercial ETHYLFLO 166 which has a VI of 143. The VI of the 100N viscosity grade is comparable to the commercial ETHYLFLO 164 which has a VI of 125. For purposes of comparison, certain physical properties of the commercial 100N ETHYLFLO 164 and 175N ETHYLFLO 166 are presented in Table 5.

Table 5

ETHYLFLO™ 164

(Lot 200-128)

Viscosity at 100°C, cSt	3.88
Viscosity at 40°C, cSt	16.9
Viscosity at -40°C, cSt	2450
Viscosity Index	125
Pour Point, °C	-70
Flash Point (D-92), °C	217
NOACK volatility, %	11.7
CEC-L-33-T-82	30%

ETHYLFLO™ 166
(Lot 200-122)

Viscosity at 100°C, cSt	5.98
Viscosity at 40°C, cSt	30.9
Viscosity at -40°C, cSt	7830
Pour Point, °C	-64
Flash Point (D-92), °C	235
NOACK VOLATILITY, %	6.1
Viscosity Index	143
CEC-L-33-T-82	29%

To determine the biodegradability of the DWO base stocks, and lubricant compositions, tests were conducted in accordance with CEC-L-33-T-82, a test method developed by the Coordinating European Council (CEC) and reported in "Biodegradability Of Two-Stroke Cycle Outboard Engine Oils In Water: Tentative Test Method" pp 1-8 and incorporated herein by reference. The test measures the decrease in the amount of a substrate due to microbial action. It has been shown, as measured by CEC-L-33-T-82 that the DWO base stocks, and lubricant compositions produced in accordance with this invention are of biodegradability above about 50%, and 10 are generally above about 50% to about 90%, and higher, biodegradable.

Examples 10-13

The CEC-L-33-T-82 test was run to observe the biodegradation of the following samples over a 21 day period, to wit:

Samples:

A: Base Oil 100N, 30 wt.% Conv. - 1.5133 g/100 mL FREON
B: Base Oil 100N, 50 wt.% Conv. - 1.4314 g/100 mL FREON
C: Base Oil 100N, 67 wt.% Conv. - 1.5090 g/100 mL FREON
D: Base Oil 100N, 80 wt.% Conv. - 1.5388 g/100 mL FREON
X: VISTONE A30 - 1.4991 g/100 mL FREON
(Positive Calibration Material)

Each of the tests were conducted using a FREON solvent, and the stock solutions used were standard as required by the test procedure.

The inoculum used was non-filtered primary effluent from the Pike Brook Treatment Plant in Bellemead, New Jersey. The inoculum was determined to have between 1 x 10^4 and 1 x 10^5 colony forming units/mL (CFU/mL) by Easicult-TCC dip slides.

Triplicate test systems for all test materials and Vistone A30 were prepared and analyzed on day zero for parent material concentration. All extractions were performed as described in the test procedure. The analyses were performed on the Nicolet Model 205 FT-IR. Triplicate test systems for samples B through X, in addition to poisoned systems of each sample were placed on orbital shakers and continuously agitated at 150 rpm in total darkness at 25± 0°C until day twenty-one. On day twenty-one the samples were analyzed for residual parent material. Sample "A" was also evaluated at the day seven interval to determine removal rate along with the above mentioned samples. Triplicate systems for "A" were prepared, extracted and analyzed after seven, fourteen and twenty-one days of incubation.

RESULTS

100N BASE OILS		
SAMPLE Level of Conversion	% BIODEGRADATION (21 DAYS)	STANDARD DEVIATION, SD
A: Base Oil 30 wt.%	84.62	1.12
B: Base Oil 50 wt.%	77.95	0.86
C: Base Oil 67 wt.%	73.46	1.01
D: Base Oil 80 wt.%	73.18	2.34
E. ETHYLFLO 164	30.00	0.54
X: VISTONE A30	98.62	1.09

[1] Based on analysis of triplicate inoculated test systems and triplicate poisoned test systems.

RATE STUDY SAMPLE A		
DAY	% BIODEGRADATION	SD
7	76.15	2.74
14	82.82	2.37
21	84.62	1.12

Examples 14-16

The CEC-L-33-T-82 test was run to observe the biodegradation of the following test materials over a 21 day period.

Samples:
A:[1] Base Oil 175N, 30 wt.% Conv. - 1.58 g/100 mL FREON
B:[2] Base Oil 175N, 50 wt.% Conv. - 1.09 g/100 mL FREON
C:[1] Base Oil 175N, 80 wt.% Conv. - 1.43 g/100 mL FREON
X:[1] VISTONE A30 - 1.5 g/100 mL FREON
(Positive Calibration Material)

[1] 500 µL used to dose test systems to achieve ≈7.5 mg loading of test material.
[2] 750 µL used to dose test systems to achieve ≈7.5 mg loading of test material.

Each of the tests were conducted using a FREON solvent, and the stock solutions used were standard as required by the test procedure.

The inoculum was non-filtered primary effluent from the Pike Brook Treatment Plant in Bellemead, New Jersey. The inoculum was determined to have between 1 x 10^4 and 1 x 10^5 colony forming units/mL (CFU/mL) by Easicult-TCC dip slides.

Triplicate test systems for all test materials and Vistone A30 were prepared and analyzed on day zero for parent material concentration. All extractions were performed as described in the test procedure. The analyses were performed on the Nicolet Model 205 FT-IR. Triplicate test systems for samples A through X, in addition to poisoned systems of each sample were placed inside environmental chambers and continuously agitated at 150 rpm in total darkness at 25 ± 0°C until day twenty-one. On day twenty-one the samples were analyzed for residual parent material.

RESULTS

175N BASE OILS		
SAMPLE	% BIODEGRADATION (21 DAYS)[1]	SD
A: Base Oil	76.93	1.452
B: Base Oil	62.01	1.379
C: Base Oil	51.04	1.657
G. ETHYLFLO 166	29.0	
X: VISTONE A30	85.31	0.408

[1] Based on analysis of triplicate inoculated test systems and triplicate poisoned test systems.

These data show that two different 100N oils were of biodegradability approaching 75%, and two different 100N oils were of biodegradability well above 75%; one approximating 85%. The Blue Angels in Germany, defines "readily biodegradable" as >80% in the CEC-L-33-T-82 test. The three 175N oils that were demonstrated had biodegradability values ranging between about 51% to about 77%.

The DWO base stocks, and lubricant compositions due to their high paraffinic content, >97.5 Vol.%, are also suitable as feedstocks for medicinal grade white oils. The following is exemplary.

Example 18

A dewaxed 60N base oil was subjected to mild hydrofining over a Ni-Mn-$MoSO_4$ bulk catalyst to produce an 80 wt.% level of conversion (i.e., 240°C, 600° psi H_2, 0.25 LHSV). The product readily passed the diagnostic "hot acid test" for medicinal grade white oils.

It is apparent that various modifications and changes can be made without departing the spirit and scope of this invention.

CLAIMS:

1. A process for the production of a biodegradable high performance hydrocarbon base oil useful as a lubricant in engine oil and industrial oil compositions, which comprises

contacting a 700°F+ paraffinic feed, or paraffinic feed containing 700°F+ components, with hydrogen, over a dual functional catalyst to produce hydroisomerization and hydrocracking reactions and 700°F+ conversion levels ranging from about 20 percent to about 50 percent, on a once through basis based on the weight of 700°F+ components of the feed, and a crude fraction containing 700°F+ materials rich in methyl paraffins,

topping said crude fraction via atmospheric distillation to produce a residual bottoms fraction the initial boiling point of which boils between about 650°F and about 750°F,

dewaxing said bottoms fraction with a solvent, and recovering a dewaxed oil, and

fractionating said dewaxed oil with a vacuum to recover said biodegradable high performance hydrocarbon base oil.

2. The process of Claim 1 wherein the paraffinic feed is a Fischer-Tropsch wax, or Fischer-Tropsch reaction product.

3. The process of Claim 1 wherein the catalyst is comprised of a Group VIII metal, or metals, supported on a particulate refractory inorganic oxide carrier.

4. The process of Claim 3 wherein the catalyst is comprised of a Group IB or Group VIB metal, or metals, or both a Group IB and Group VIB metal, or metals, in addition to the Group VIII metal, or metals.

5. The process of Claim 4 wherein the concentration of the metal, or metals, ranges from about 0.1 percent to about 20 percent, based on the total weight of the catalyst, the Group IB metal is copper, the Group VIB metal is molybdenum, and the Group VIII metal is palladium, platinum, nickel, or cobalt.

6. The process of Claim 1 wherein the crude fraction that is produced by the hydroisomerization/hydrocracking reactions produces 700°F+ materials rich in isoparaffins having from about 6.0 to about 7.5 methyl branches per 100 carbon atoms in the molecule.

7. The process of Claim 6 wherein the 700°F+ materials that are produced are rich in isoparaffins having from about 6.5 to about 7.0 methyl branches per 100 atoms in the molecules.

8. The process of Claim 1 wherein the 700°F+ level of conversion of the paraffinic feed ranges from about 25 percent to about 40 percent.

9. The process of Claim 1 wherein one or more viscosity grades of lubricant are produced from the solvent dewaxed oil by vacuum fractionation, and at least one of the fractions is hydrofined sufficiently to pass the diagnostic hot acid test to produce a medicinal grade white oil.

10. As a composition of matter, a biodegradable high performance hydrocarbon base oil useful as an engine oil component or engine oil produced in accordance with the process described by any of Claims 1 through 8.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/18427

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C10G67/04 C10G45/58

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

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

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 365 390 A (CHEVRON) 23 January 1968 see the whole document	1,3-10
Y		2
Y	EP 0 323 092 A (EXXON) 5 July 1989 see the whole document	2
X	EP 0 225 053 A (MOBIL OIL) 10 June 1987 see page 10-06-87; claims 1-10	1-10
X	EP 0 321 307 A (ESSO) 21 June 1989 see claims 1-10	1-10

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

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

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Date of the actual completion of the international search	Date of mailing of the international search report
8 April 1997	14.04.97

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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