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Remarks:

This application was filed on 23.11.2004 as a divisional application to the application mentioned under INID code 62.

- (54) Use of polyalfaolefins (pao) derived from 1-dodecene or 1-tetradecene to imrove thermal stability of engine oils in internal combustion engines
- (57) The present invention relates to compositions of automotive engine oils using synthetic polyalphaole-fins derived from olefins other than 1-decene, especially 1-dodecene, to improve engine oil performance, as

demonstrated by the severe Volkswagen T-4, Volkswagen TDI, and Sequence IIIE tests.

Description

FIELD OF THE INVENTION

[0001] The present invention relates to compositions of automotive engine oils using synthetic poly alpha olefins derived from olefins other than 1-decene, especially 1-dodecene and 1-tetradecene, to improve engine oil performance, as demonstrated by the severe Volkswagen T-4, Volkswagen TDI, and Sequence IIIE tests.

BACKGROUND OF THE INVENTION

[0002] Today's automobiles tend to have smaller, more demanding engines operating at higher temperatures. Thus, the engine oil has to function in an increasingly severe environment while meeting fuel economy demands. Besides changes in the additive package, increasingly synthetic base oils are being used instead of conventional mineral oils. Of the synthetic oils, poly alpha olefins (PAO) are among the most popular.

[0003] PAO is manufactured by oligomerization of linear alpha olefin followed by hydrogenation to remove unsaturated moleties and fractionation to obtain the desired product slate. 1-decene is the most commonly used alpha olefin in the manufacture of PAO, but 1-dodecene and 1-tetradecene can also be used. PAO's are commonly categorized by the numbers denoting the approximate viscosity in centistokes of the PAO at 100°C. It is known that PAO 2, PAO 2.5, PAO 4, PAO 5, PAO 6, PAO 7, PAO 8, PAO 9 and PAO 10 and combinations thereof can be used in engine oils. The most common of these are PAO 4, PAO 6 and PAO 8.

[0004] Conventionally, base oils of lubricating viscosity used in motor oil compositions may be mineral oil or synthetic oils of viscosity suitable for use in the crankcase of an internal combustion engine. Crankcase base oils ordinarily have a viscosity of about 1300 cSt at 0°F (-18°C) to 24 cSt at 210°F (99°C). The base oils may be derived from synthetic or natural sources. Mineral oil for use as the base oil in this invention includes paraffinic, naphthenic and other oils that are ordinarily used in lubricating oil compositions. Synthetic oils include both hydrocarbon synthetic oils and synthetic esters.

[0005] Although the common 1-decene based PAO 4, 6 and 8 offer better performance than mineral oil based engine oils, they encounter difficulties when subjected to the severe PV 1449, CEC L-78-T-96 and Sequence IIIE tests. The PV 1449 and Sequence IIIE tests evaluate fully formulated engine oils with respect to high temperature oxidative stability and piston deposits. The CEC L-78-T-96 test evaluates fully formulated engine oils with respect to piston cleanliness and piston ring sticking. The PV 1449 and CEC L-78-T-96 tests will be referred to hereinafter as the Volkswagen T-4 and TDI engine tests, respectively.

[0006] It has been found to be difficult to blend an engine oil of the desired 0W30 viscosity grade based on PAO 4 and 6 that successfully completes the TDI test. Repeatedly, it was found that too low oil pressure caused the engine to fail from 2 to 8 hours before the end of the test. In the T-4 test, it was found that the increase in engine oil viscosity resulting in engine failure during the test was related to oil oxidation stability and volatility. To pass the T-4 test, it was found that the PAO 4/6 based engine all requires large quantities of expensive anti-oxidants. The other way to obtain PAO 4/6 based oil which passes the T-4 test is to use an expensive fully synthetic oil.

[0007] The Volkswagen T-4 and TDI tests have recently become an important measure of engine lubrication oil quality under very severe conditions. The Sequence IIIE test is analogous to a T-4 test but is specifically developed for U.S. built engines. The T-4 and Sequence IIIE tests are for gasoline engines and the TDI test is for diesel engines. They replicate the severe engine conditions put on motor lubrication oil by sustained, very high speed driving, as on the German Autobahn. What is needed is a PAO based oil which is able to successfully complete severe engine tests such as the Volkswagen T-4 and TDI tests and the Sequence IIIE test without having to use large quantities of anti-oxidants or a fully synthetic oil.

[0008] Surprisingly, it has been found that lubrication oils based on alpha olefins having at least 12 carbons, for example, 1-dodecene, and that have approximate viscosities at 100°C of from 3.5 to 8.5 centistokes successfully pass the T-4 and TDI tests with PAO based oil weight percentages much lower than previously achieved. This represents a major development in the search for an economical lubrication oil that is well suited for modem driving conditions.

SUMMARY OF THE INVENTION

[0009] In one embodiment, the present invention relates to the use of PAO derived from 1-dodecene or 1-tetradecene as the base oil, or a component of the base oil, of an engine oil for the purpose of improving the high temperature stability of the engine oil when compared with the use of a 1-decene derived PAO.

[0010] In another embodiment, the present invention relates to the use of PAO derived from 1-dodecene or 1-tetradecene as the base oil, or a component of the base oil, of an engine oil comprised of base oil, dispersants, detergents, oxidation inhibitors, foam inhibitors, anti-wear agents and at least one viscosity index improver, for the purpose of

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improving the high temperature stability of the engine oil to least the point at which the engine oil is able to pass the VW T-4, VW TDI, or Sequence IIIE tests.

[0011] In a preferred embodiment of either of the above embodiments, the base oil is from 15 to 85% of the engine oil and at least 15% of the base oil is derived from 1-dodecene or 1-tetradecene.

[0012] In another preferred embodiment of the above embodiments, the PAO is from 50 to 85% of the base oil for 0W-xx SAE viscosity grade oils where xx = 20-50, is from 15 to 50% of the base oil for 5W-xx SAE viscosity grade oils where xx = 20-50, or is from 5 to 35% of the base oil for 10W-xx SAE viscosity grade oils where xx = 20-50.

[0013] In still another embodiment, the present invention relates to an engine oil having a SAE viscosity grade of 0W-xx where xx denotes 20-40 comprised of from 15 to 85% base oil having from 50 to 85% PAO at least 15% of which is derived from 1-dodecene or 1-tetradecene, from 0 to 20% of at least one ashless dispersant: from 0 to 30% of detergent; from 0 to 5% of at least one anti-wear agent; from 0 to 10% of at least one oxidation inhibitor; from 0 to 1% of at least one foam inhibitor, and from 0 to 20% of at least one viscosity index improver.

[0014] In yet another embodiment, the present invention relates to an engine oil having a SAE viscosity grade of 5W-xx where xx denotes 20-40 comprised of from 15 to 85% base oil having from 15 to 50% PAO at least 15% of which is derived from 1-dodecene or 1-tetradecene, from 0 to 20% of at least one ashless dispersant; from 0 to 30% of detergent; from 0 to 5% of at least one anti-wear agent; from 0 to 10% of at least one oxidation inhibitor; from 0 to 1% of at least one foam inhibitor, and from 0 to 20% of at least one viscosity index improver.

[0015] In still another embodiment, the present invention relates to an engine oil having a SAE viscosity grade of 10W-xx where xx denotes 20-50 comprised of from 15 to 85% base oil having from 5 to 35% PAO at least 15% of which is derived from 1-dodecene or 1-tetradecene, from 0 to 20% of at least one ashless dispersant; from 0 to 30% of detergent; from 0 to 5% of at least one anti-wear agent; from 0 to 10% of at least one oxidation inhibitor; from 0 to 1% of at least one foam inhibitor, and from 0 to 20% of at least one viscosity index improver.

[0016] In a preferred embodiment of any of the above embodiments, the PAO derived from 1-dodecene or 1-tetradecene has an approximate viscosity at 100°C of from 3.5 to 9.5 centistokes.

[0017] In a more preferred embodiment of the above embodiment, the PAO derived from 1-dodecene or 1-tetradecene has an approximate viscosity at 100°C of approximately 5 centistokes or approximately 7 centistokes.

BRIEF DESCRIPTION OF THE DRAWINGS

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[0018] In order to assist the understanding of this invention, reference will now be made to the appended drawings. The drawings are exemplary only, and should not be construed as limiting the invention.

[0019] Figure 1 is a graph comparing the absolute and relative T-4 viscosity increases in PAO 6 and PAO 5/7 based motor oil in an experiment the conditions of which are described in Example 5.

[0020] Figure 2 is a graph comparing the absolute and relative T-4 viscosity increases in PAO 4, PAO 5 and PAO 6 based motor oil in an experiment the conditions of which are described in Example 6.

DETAILED DESCRIPTION OF THE INVENTION

[0021] In its broadest aspect, the present invention involves improving thermal oxidative stability of engine oil by using PAO derived from a 1-dodecene or 1-tetradecene as a base oil.

[0022] The difficulties encountered with the use!of PAO based on 1-decene as feedstock can be avoided by the use instead of PAO 5 and 7 based on 1-dodecene or 1-tetradecene.

[0023] It has also been found that PAO 5/7 offers superior oxidation stability during use in comparison to PAO 4/6. As the examples below show, such improved oxidation stability is found in both gasoline (T-4) and diesel (TDI) engines (especially direct injection diesels). Furthermore, the superior oxidation stability qualities are shown in both fully synthetic as well as semi-synthetic engine oils, which are a mixture of PAO's and mineral oils.

[0024] PAO 5/7 has also been shown to be superior over PAO 4/6/8 in PSA TU3M high temperature gasoline tests and Sequence IIIE high temperature oxidation tests.

ADDITIVE COMPONENTS

[0025] The following additive components are examples of some components that can be favorably employed in the present invention. These examples of additives are provided to illustrate the present invention, but they are not intended to limit it:

(1) Metal detergents: sulfurized or unsulfurized alkyl or alkenyl phenates, alkyl or alkenyl aromatic sulfonates, sulfurized or unsulfurized metal salts of multi-hydroxy alkyl or alkenyl aromatic compounds, alkyl or alkenyl hydroxy aromatic sulfonates, sulfurized or unsulfurized alkyl or alkenyl naphthenates, metal salts of alkanoic acids, metal

salts of an alkyl or alkenyl multi-acid, metal salts of an alkyl salicylic acid, carboxylates, overbased detergents and chemical and physical mixtures thereof.

(2) Ashless dispersants: alkenyl succinimides, alkenyl succinimides modified with other organic compounds, and alkenyl succinimides modified with boric acid, alkenyl succinic ester.

(3) Oxidation inhibitors:

- (a) Phenol type oxidation inhibitors: 4,4'-methylenebis (2,6-di-tert-butylphenol), 4,4'-bis(2,6-di-tert-butylphenol), 4,4'-bis(2-methyl-6-tert-butylphenol), 2,2'-(methylenebis (4-methyl-6-tert-butyl-phenol), 4,4'-butylidenebis(3-methyl-6-tert-butylphenol), 4,4'-isopropylidenebis(2,6-di-tert-butylphenol), 2,2'-methylnebis(4-methyl-6-nonylphenol), 2,2'-isobutylidene-bis(4,6-dimethylphenol), 2,2'-methylenebis(4-methyl-6-cyclohaxylphenol), 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,4-dimethyl-6-tert-butyl-phenol, 2,6-di-tert-4-(N,N' dimethylaminomethylphenol), 4,4'-thiobis(2-methyl-6-tert-butylphenol), 2,2'-thiobis(4-methyl-6-tert-butylphenol), bis(3-methyl-4-hydroxy-5-tert-butylbenzyl)-sulfide, and bis (3,5-di-tert-butyl-4-hydroxybenzyl).
- (b) Diphenylamine type oxidation inhibitor: alkylated diphenylamine, phenyl-1-naphthylamine, and alkylated 1-naphthylamine.
- (c) Other types: metal dithiocarbamate (e.g., zinc dithiocarbamate), and methylenebis (dibutyldithiocarbamate).
- (4) Rust inhibitors (Anti-rust agents):
 - (a) Nonionic polyoxyethylene surface active agents: polyoxyethylene lauryl ether, polyoxyethylene higher alcohol ether, polyoxyethylene nonylphenyl ether, polyoxyethylene octylphenyl ether, polyoxyethylene octyl stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene sorbitol monostearate, polyoxyethylene sorbitol mono-oleate, and polyethylene glycol monooleate.
 - (b) Other compounds: stearic acid and other fatty acids, dicarboxilic acids, metal soaps, fatty acid amine salts, metal salts of heavy sulfonic acid, partial carboxylic acid ester of polyhydric alcohol, and phosphoric ester.
- (5) Demulsifiers: addition product of alkylphenol and ethyleneoxide, polyoxyethylene alkyl ether, and polyoxyethylene sorbitan ester.
- (6) Extreme pressure agents (EP agents): zinc dithiophosphates, zinc dithiocarbamates, zinc dialkyldithiophosphate (primary alkyl type & secondary alkyl type), zinc diaryl dithiophosphate, sulfurized oils, diphenyl sulfide, methyl trichlorostearate, chlorinated naphthalene, fluoroalkylpolysiloxane, and lead naphthenate.
- 40 (7) Friction modifiers: fatty alcohol, fatty acid, amine, borated ester, and other esters.
 - (8) Multifunctional additives: sulfurized oxymolybdenum dithiocarbamate, sulfurized oxymolybdenum organo phosphoro dithioate, oxymolybdenum monoglyceride, oxymolybdenum diethylate amide, amine-molybdenum complex compound, and sulfur-containing molybdenum complex compound.
 - (9) Viscosity index improvers: polymethacrylate type polymers, ethylenepropylene copolymers, styrene-isoprene copolymers, hydrated styrene-isoprene copolymers, polyisobutylene, and dispersant type viscosity index improvers.
- (10) Pour point depressants: polymethyl methacrylate.
 - (11) Foam inhibitors: alkyl methacrylate polymers and dimethyl silicone polymers.
 - [0026] In one embodiment, an engine lubricating oil composition would contain:
 - (a) a major part of a base oil of lubricating viscosity, wherein the base oil comprises 1-dodecene and/or 1-tetra-decene-derived polyalphaolefins;

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- (b) 0% to 20% of at least one ashless dispersant;
- (c) 0% to 30% of the detergent;
- 5 (d) 0% to 5% of at least one zinc dithiophosphate;
 - (e) 0% to 10% of at least one oxidation inhibitor;
 - (f) 0% to 1% of at least one foam inhibitor; and
 - (g) 0% to 20% of at least one viscosity index improver.

[0027] In a further embodiment, an engine lubricating oil composition is produced by blending a mixture of the above components. The lubricating oil composition produced by that method might have a slightly different composition than the initial mixture, because the components may interact. The components can be blended in any order and can be blended as combinations of components.

ADDITIVE CONCENTRATES

20 [0028] Additive concentrates are also included within the scope of this invention. The concentrates of this invention comprise the compounds or compound mixtures of the present invention, with at least one of the additives disclosed above. Typically, the concentrates contain sufficient organic diluent to make them easy to handle during shipping and storage.

[0029] From 20% to 80% of the concentrate is organic diluent. Suitable organic diluents which can be used include for example, solvent refined 100N, i.e., Cit-Con 100N, and hydrotreated 100N, i.e., RLOP 100N, and the like. The organic diluent preferably has a viscosity of from about 1 to about 20 cSt at 100°C.

EXAMPLES

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[0030] The invention will be further illustrated by following examples, which set forth particularly advantageous method embodiments. While the Examples are provided to illustrate the present invention, they are not Intended to limit it. [0031] Examples 1 through 4 cover bench test data obtained in the proprietary MAO 92 oxidation bench test. In this test, air is bubbled through an oil sample at elevated temperature. The oil sample contains an oxidation catalyst. The viscosity of the oil at 40°C is measured at regular intervals until 1000 cSt is reached. The time to reach this value is a measure of the stability. The longer the time, the better the oxidation stability. The MAO 92 oxidation test has a repeatability of 7 hours.

EXAMPLE 1

[0032] A fully formulated engine oil was prepared, containing an additive package comprised of 6% dispersant, 71.5 mmol detergent, 15.5 mmol zinc dithiophosphate, 0.55% supplementary additives, 2.0% VII, 34.8% Esso 145N, 20.55% Esso 600N and 15% PAO 5 and 15% PAO 7. This oil was subjected to the MAO 92 oxidation test, the result being 125 hours.

45 COMPARATIVE EXAMPLE 2

[0033] As a comparison, a similar engine oil as described in Example 1 was prepared. However, the 15% PAO 5 and 15% PAO 7 were replaced by 30% PAO 6. The result of the oxidation test was only 100 hours.

50 EXAMPLE 3

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[0034] The experiment of Example 1 was repeated using an additive package comprised of 6% dispersant, 71.5 mmol detergent, 15.5 mmol zinc dithiophosphate, 0.55% supplementary additives, 2.0% VII, 52% PAO 5 and 33.3% PAO 7. The result in the oxidation test is 162 hours.

COMPARATIVE EXAMPLE 4

[0035] As a comparison to Example 3, the PAO 5 and 7 were replaced by 11.1% PAO 4 and 74.2% PAO 6. The result

in the oxidation test, 152 hours, was poor in comparison to the oil of Example 3.

EXAMPLE 5

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[0036] The oils of Example 1 and Comparative Example 2 were subjected to the bench tests used to mimic the viscosity increase of the VW T-4 engine test. The lower the absolute and relative viscosity increase, the better the test result. As can be seen in Figure 1, the oil based on PAO 5/7 is far superior to the oil based on PAO 6.

TABLE 1

Oil code	OIL 10	OIL 11
Additive package	AP7	AP7
PAO 5		15
PAO 6	30	
PAO 7		15
Calculated T-4 viscosity (cSt)	756.6	201.8
Calculated T-4 viscosity increase (%)	819.0	189.7

EXAMPLE 6

[0037] A fully formulated engine oil was prepared containing an additive package comprised of 6% dispersant, 87 mmol detergent, 19 mmol zinc dithiophosphate and 0.35% supplementary additives, 10.3% VII and 30% PAO 5, the balance made up by mineral base stock. Two similar engine oils were prepared but the 30% PAO 5 was replaced by 30% PAO 4 and 30% PAO 6, respectively. These three oils were subjected to the bench tests used to mimic the viscosity increase of the VWT-4 engine test. The lower the absolute and relative viscosity increase, the better the test result. As can be seen in Figure 2, the oil based on PAO 5 is far superior to the oils based on PAO 4 and PAO 6.

TABLE 2

Oil code	OIL 13	OIL 12	OIL 14
Additive package	AP4	AP4	AP4
PAO 5	30		
PAO 4		30	
PAO 6			30
Calculated T-4 viscosity (cSt)	99.4	258.2	154.3
Calculated T-4 viscosity increase (%)	10.5	212	79.5

EXAMPLE 6

[0038] A fully formulated engine oil was prepared containing an additive package comprised of 6.5% dispersant, 98 mmol detergent, 5.5 mmol zinc dithiophosphate and 1.8% supplementary additives, 4.0% VI improver and the balance a 57.6/42.4 mixture of PAO 4 and PAO 6. This oil was run in the VW TDI engine. The test was aborted after 52 hours, i.e., 8 hours before reaching the end-of-test, as result of iow oil pressure due to a lack of engine oil remaining in the sump. [0039] A VW TDI test was conducted on a 1.9 liter turbo charged, intercooled DI diesel type engine. The engine tested has power of 81 kW at 4150 rpm's. There are 4 cylinders in the engine measuring 79.5 x 95.5 mm (b x s). EGR is not activated in the engine and the oil charge is 4.5 liters. The test procedure had a 5 hour run-in step, a 3 hour power curve step, and a 2 hour flushing step.

[0040] These steps were followed by a 60 hour cycling step which had two stages: stage 1, the idling stage; and stage 2, the full load stage. One cycle takes three hours and the cycle was repeated 20 times (20 x 3 hrs.). Further facts about the cycling stage are given in Table 3 below.

TABLE 3

CEC L-78-T-96 (TDI) Engine Test Test Conditions					
Stage 1 Stage 2					
Duration (minutes)	30	150			
Speed (rpm) Idle 4150					
Oil Temperature (°C) 40 145					
Coolant Temperature (°C)	30	90			
Boost Air Temperature (°C)	30	60			

15 COMPARATIVE EXAMPLE 7

[0041] As a comparison to Example 6, the PAO 4 and 6 were replaced by 8.6% PAO 5 and 91.4% PAO 7. The oil successfully completed the 60 hour VW TDI engine test.

20 EXAMPLE 8

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[0042] T-4 bench tests and engine tests were performed on oil compositions containing various additives, including viscosity index improvers and various proportions of PAO 4, PAO 5, PAO 6, PAO 7, PAO 8 and mineral stock. Tables 4A through 4D show the T-4 bench test and engine test results as well as the MAO 92 results for the compositions. These results show the correlation between the engine test results and the bench test model for both the absolute viscosity at end-of test (EOT) and also for the relative viscosity increase. Both are requirements for the T-4 test. [0043] The Engine Test Conditions for conducting the VW T-4 test are given below in Table 4. The total test had a duration of 262 hours (10 hours run-in, + 2 hours power curve, + 2 hours flushing, + 48 x PNK cycles = 48 x 4 = 192 hrs, + 56 hrs N cycle \rightarrow 262 hours). The test oil charge was 5 liters with no oil top-up allowed. Of the various test requirements, the limits on viscosity increase are the most difficult to achieve. Both rotative viscosity increase as well as absolute viscosity increase at EOT are limited. The limits are as follows: EOT Viscosity at 40°C <200 cSt. [0044] EOT Viscosity increase <130%.

TABLE 4A

TABLE 4A				
Oil Code	OIL 1	OIL 2	OIL 3	
Additive Package	AP1	AP 2	AP3	
dispersant (wt%)	n.a.	5	6.75	
detergent (mmol)	n.a.	84	70	
-zinc dithiophosphate (mmol)	n.a.	18	18	
-supplementary additives (wt%)	n.a.	1.6	0.93	
VI Improver (%)	n.a.	4.7	10.5	
VI Improver		polymethylacrylate type polymers (PMA)	ethylene propylene copolymers (OCP)	
PAO 4	n.a.			
PAO 5	n.a.			
PAO 6	n.a.	62.1	25	
PAO 7	n.a.			
PAO 8	n.a.	20		
Mineral Stock (%)	n.a.		50.6	

TABLE 4A (continued)

Mineral Stock	n.a. full synth.		Group 1
TGA (°C)	336.8	342.5	312.5
MAO 92-visc. at 100 H (cSt)	69.3	125.9	180.1
MAO 92-visc. increase at 100 H (%)	-9.8	65.9	87.1
Calculated VW T-4 viscosity increase (cSt)	107.8	114.1	302.8
Calculated VW T-4 viscosity increase (%)	47.9	55.3	264.0
Act. T-4 visc. increase (cSt)	134.2	107.0	450.9
Act. T-4 visc. increase (%)	74.5	41.0	368.5

TABLE 4B

	TABLE 4B		
Oil Code	OIL4	OIL5	OIL6
Additive Package	AP2	AP4	AP5
dispersant (wt%)	5	6	6.5
detergent (mmol)	84	87	98
-zinc dithiophosphate (mmol)	18	19	15.5
-supplementary additives (wt%)	1.6	0.35	1.8
VI Improver (%)	6.2	9	6.3
VI Improver	OCP	OCP	Styrene isoprene copolymers (StyrIP)
PAO 4			45.5
PAO 5			
PAO 6	21.8	23.5	13.1
PAO 7			
PAO 8			
Mineral Stock (%)	58.8	55	20
Mineral Stock	Group I	Group I	Group II
TGA (°C)	316.2	318.7	320
MAO 92-visc. at 100 H (cSt)	1344.6	190.9	74
MAO 92-visc. increase at 100 H (%)	1326.5	108.7	32.3
Calculated VW T-4 viscosity increase (cSt)	1017.4	277.2	197.3
Calculated VW T-4 viscosity increase (%)	971.1	236.2	182.7
Act. T-4 visc. increase (cSt)	Too viscous to measure	335.4	151.7
Act. T-4 visc. increase (%)		268.0	171.2

TABLE 4C

	Oil Code	OIL7	OIL8	OIL9
5	Additive Package	AP5	AP5	AP6
	dispersant (wt%)	6.5	6.5	6
	detergent (mmol)	98	98	93
10	-zinc dithiophosphate (mmol)	15.5	15.5	19
	-supplementary additives (wt%)	1.8	1.8	1.6
	VI Improver (%)	5.2	5.0	5.0
15	VI Improver	StyrIP	StyrIP	StyrIP
	PAO 4	43	15.98	15.98
	PAO 5		63.92	63.92
	PAO 6	36.7		
20	PAO 7			
	PAO 8			
	Mineral Stock (%)			
25	Mineral Stock			
	TGA (°C)	314	353	355
20	MAO 92-visc. at 100 H (cSt)	53.8	51.1	-25.4
30	MAO 92-visc. increase at 100 H (%)	-1.3	50.5	-25.3
	Calculated VW T-4 viscosity increase (cSt)	215.5	12.9	-45.6
	Calculated VW T-4 viscosity increase (%)	202.1	-22.4	-80.2
35	Act. T-4 visc. increase (cSt)	118.0		
	Act. T-4 visc. increase (%)	108.0		

TABLE 4D

Oil Code	OIL10	OIL11
Additive Package	AP7	AP7
dispersant (wt%)	6	6
detergent (mmol)	71.5	71.5
-zinc dithiophosphate (mmol)	15.5	15.5
-supplementary additives (wt%)	0.55	0.55
VI Improver (%)	2.0	2.0
VI Improver	OCP	OCP
PAO 4		
PAO 5		15
PAO 6	30	

TABLE 4D (continued)

PAO 7		15
PAO 8		
Mineral Stock (%)	55.3	55.3
Mineral Stock	Group I	Group I
TGA (°C)	310	325
MAO 92-visc. at 100 H (cSt)	880	122
MAO 92-visc. increase at 100 H (%)	1000	99.7
Calculated VW T-4 viscosity increase (cSt)	756.6	201.8
Calculated VW T-4 viscosity increase (%)	819.0	189.7
Act. T-4 visc. increase (cSt)		
Act. T-4 visc. increase (%)		

TABLE 5

VW PV 1449 ENGINE TEST (T-4) Test Conditions						
PNK Cycles	Cycles Max Power P Max NO _x N Cold Idling K Max NO _x					
Duration	120 min	72 min	48 min	56 hrs		
RPM	4300	4300	900	4300		
Oil Sump Temp °C	133	130	40	130		
Coolant Temp °C	100	100	30	100		
Power kW	62	34	0	34		
Torque Nm	140	75	0	75		
Fuel Cons. kg/h	19.4	10.8	1.1	10.8		
Exh. Gas Temp °C	820	763	292	763		

TABLE 6

TABLE 0				
Oil Code	Oil 12	Oil 13	Oil 14	
ADDITIVE PACKAGE	AP4	AP4	AP4	
-dispersant (wt%)	6	6	6	
-detergent (mmol)	87	87	87	
-zinc dithiophosphate (mmol)	19	19	19	
-supplementary additives (wt%)	0.35	0.35	0.35	
VI IMPROVER (%)	10.4	10.3	10.7	
VI IMPROVER	OCP	OCP	OCP	
PAO 4	30			
PAO 5		30		
PAO 6			30	
PAO 7				

TABLE 6 (continued)

PAO 8			
MINERAL STOCK (%)	47.1	47.2	46.8
MINERAL STOCK	Gr. I/III	Gr. I/III	Gr. I/III

EXAMPLE 9

Bench Test Thermal Gravimetric Analysis (TGA) of PAO 5 and 7

Dispersant wt%

Detergent mmol

VII wt%

PAO 4/6 wt %

PAO 4/5 wt %

PAO 5/7 wt %

Mineralstock wt %

PAO 6 wt %

TGA (°C)

Zinc dithiophosphate mmol

Supplementary additives wt%

[0045] Bench test analysis was performed on four different samples of oil to find the TGA DPeak (i.e. the temperature at which the weight loss, due to both evaporation and oxidation, of the oil is the most important, which correlates with oil consumption). This test measures the weight variation of a sample as a function of temperature, under a nitrogen flow. At a certain temperature; defined as the DPeak, the weight loss is the most important. The exact DPeak value is determined as the maximum of the derivative curve. The repeatability of the TGA test is equal to 8°C. Table 7 shows the results.

TABLE 7

Test 2

6.5

98

15.5

1.8

5.2

15.98/63.92

353

Test 3

6

71.5

15.5

0.55

2.0

30

55.3 Esso

310

Test 4

6

71.5

15.5

0.55

2.0

30

55.3 Esso

325

Test 1

6.5

98

15.5

1.8

5.2

43/36.7

314

)	n	
•	v	

5

25

30

35

40

45

50

55

EXAMPLE 10

[0046] A fully formulated engine oil was prepared, containing 13.6% of an additive package, 6.9% VI Improver, 10% ester and 35% PAO 5 and 34.5% PAO 7. A Seq. IIIE test was run on this oil with a 1986 3.8 liter Buick V6 engine using leaded gasoline. The Initial oil fill is 5.3 liters. Total test duration is 64 hours. The engine speed is 3000 rpm with a load of 50.6 kW. The oil temperature is 149°C. The results of the test were as follows:

viscosity increase: -11%

- time to 375% vis. incr.: 87.3 hours

Aver. engine sludge: 9.7oil consumption, liter 0.67

[0047] As a comparison, a similar engine oil as described above was prepared. However, the 35% PAO 5 and 34.5% PAO 7 were replaced by 69.5% PAO 6. Again, a Seq. IIIE was run, resulting in:

viscosity increase: 1%

time to 375% vis. incr.: 85.8 hours

- Aver. engine sludge: 9.6

- oil consumption, liter 1.14

[0048] While the present invention has been described with reference to specific embodiments, this application is intended to cover those various changes and substitutions that may be made by those skilled in the art without departing from the spirit and scope of the appended claims.

10 Claims

15

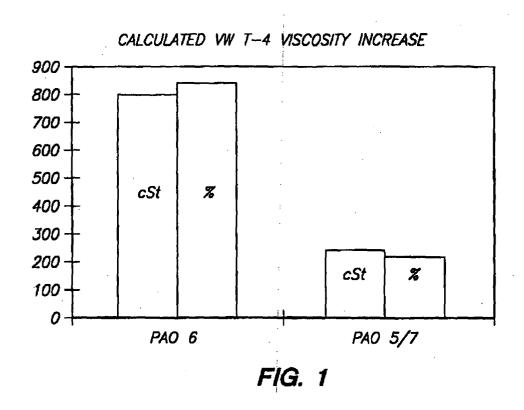
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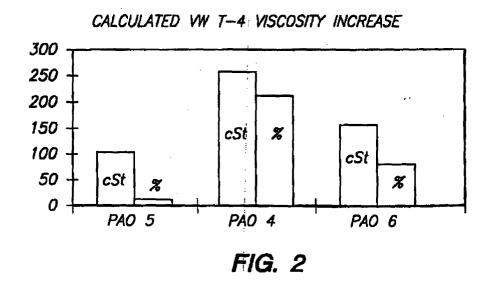
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- 1. The use, in an engine oil base oil, of a PAO base oil derived from 1-dodecene or 1-tetradecene having a viscosity of from 3.5 to 9.5 mm²s⁻¹, for the purpose of improving the high temperature stability of the engine oil as measured using the VW T-4 engine test when compared with the use of a 1-decene derived PAO.
- 2. The use according to claim 1, wherein the PAO is from 50 to 85% of the base oil for 0W-xx SAE viscosity grade oils where xx = 20-40.
- 3. The use according to claim 1, wherein the PAO is from 15 to 50% of the base oil for 5W-xx SAE viscosity grade oils where xx = 20-50.
 - **4.** The use according to claim 1, wherein the PAO is from 5 to 35% of the base oil for 10W-xx SAE viscosity grade oils where xx = 20-50.
- 5. The use according to any preceding claim, wherein the PAO derived from 1-dodecene or 1-tetradecene has a viscosity of from 5 to 9.5 mm²s⁻¹,
 - **6.** The use according to any preceding claim, wherein the PAO derived from 1-dodecene or 1-tetradecene has a viscosity at 100°C of no greater than 7 mm²s⁻¹.
 - 7. The use according claim 6, wherein the PAO derived from 1-dodecene or 1-tetradecene has a viscosity at 100°C of 5 mm²s⁻¹ or 7 mm²s⁻¹.
- 8. The use according to any one of the preceding claims, wherein the engine oil further comprises one or more additive selected from dispersants, detergents, oxidation inhibitors, foam inhibitors, anti-wear agents and viscosity index improvers.
 - **9.** The use according to any one of the preceding claims, wherein the high temperature stability of the engine oil is improved to at least the point at which the engine oil is able to pass the VW T-4 engine test.
 - **10.** An engine oil comprising a base oil, wherein the base oil comprises a PAO base oil derived from 1-dodecene or 1-tetradecene having a viscosity of from 3.5 to 9.5 mm²s⁻¹ and having improved high temperature stability of the engine oil as measured using the VW T-4 engine test when compared with the use of a 1-decene derived PAO.
- **11.** The engine oil according to claim 10, wherein the PAO is from 50 to 85% of the base oil for 0W-xx SAE viscosity grade oils where xx = 20-40.
 - **12.** The engine oil according to claim 10, wherein the PAO is from 15 to 50% of the base oil for 5W-xx SAE viscosity grade oils where xx = 20-50.
 - **13.** The engine oil according to claim 10, wherein the PAO is from 5 to 35% of the base oil for 10W-xx SAE viscosity grade oils where xx = 20-50.
 - **14.** The engine oil according to any one of claims 10 to 13, wherein the PAO derived from 1-dodecene or 1-tetradecene has a viscosity of from 5 to 9.5 mm²s⁻¹,
 - **15.** The engine oil according to any one of claims 10 to 14, wherein the PAO derived from 1-dodecene or 1-tetradecene has a viscosity at 100°C of no greater than 7 mm²s⁻¹.

	16.	The engine oil according claim 15, wherein the PAO derived from 1-dodecene or 1-tetradecene has a viscosity at 100°C of 5 mm ² s ⁻¹ or 7 mm ² s ⁻¹ .
5	17.	The engine oil according to any one of claims 10 to 16, further comprising a mineral oil.
5	18.	The engine oil according to any one of claims 10 to 17, further comprising one or more additive selected from dispersants, detergents, oxidation inhibitors, foam inhibitors, anti-wear agents and viscosity index improvers.
10	19.	The engine oil according to any one of claims 10 to 18, wherein the high temperature stability of the engine oil is improved to at least the point at which the engine oil is able to pass the VW T-4 engine test.
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EUROPEAN SEARCH REPORT

Application Number EP 04 02 7778

Category	Citation of document with indic	Relevant	CLASSIFICATION OF THE	
oulogo, y	of relevant passages	1	to claim	APPLICATION (Int.CI.7)
X	US 4 218 330 A (SHUBK 19 August 1980 (1980- * column 8, line 28 - examples 9,10 * * column 2, lines 12- * column 3, line 62 - * claims 3,8-11,13,14	08-19) column 9, line 21; 16,35-45 * column 4, line 29 *	1-19	C10M107/10 C10M111/04 C07C2/06
X	GB 2 307 243 A (ALBEM 21 May 1997 (1997-05- * page 4, paragraph 3 2; example 3 * * page 6, line 4 - pa * * page 1, line 27 - p * * page 4, line 27 - p * * page 6, line 1 - pa * * claims 4,5,7-10 *	21) B - page 5, paragraph age 6, line 7 * bage 2, line 32 * bage 5, line 11 *	1-19	
A	DATABASE WPI Section Ch, Week 9403 Derwent Publications Class A17, AN 94-0231 XP002068813 & JP 05 331483 A (TOM 14 December 1993 (1998) * abstract *	Ltd., London, GB; 31 IEN CORP)	1-19	TECHNICAL FIELDS SEARCHED (Int.CI.7)
A	GB 2 078 776 A (NIPPO LTD) 13 January 1982 * page 5; table 1 *		1-19	
A	GB 1 264 981 A (IFP) 23 February 1972 (197 * page 5; table 1 *	 (2-02-23) -/	1-19	
	The present search report has bee	n drawn up for all claims	_	
	Place of search	Date of completion of the search		Examiner
	Munich	7 February 2005	Per	rakis, N
X : parti Y : parti docu	TEGORY OF CITED DOCUMENTS cularly relevant if taken alone cularly relevant if combined with another ment of the same category nological background	T : theory or principl E : earlier patent do after the filing dat D : document cited i L : document cited fe	oument, but publice en the application or other reasons	
O : non-	written disclosure mediate document	& : member of the sa document	ame patent family	r, corresponding



EUROPEAN SEARCH REPORT

Application Number EP 04 02 7778

	DOCUMENTS CONSIDERE Citation of document with indication		Relevant	CLASSIFICATION OF THE
Category	of relevant passages	on, where appropriate,	to claim	APPLICATION (Int.CI.7)
A	US 3 763 244 A (L.R.SHU 2 October 1973 (1973-10 * column 2, line 10 - 1 * column 4, line 63 - 1 * column 7, line 57 - column 7, line 57 - column 7, line 57 - column 7 * column	0-02) line 36 * line 71 * column 8, line 20 *	1-19	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
	The present search report has been d	rawn up for all claims	_	
	Place of search Date of completion of the search			Examiner
	Munich	7 February 2005	Per	akis, N
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document		T: theory or princip E: earlier patent do after the filing de D: document cited L: document cited	ocument, but publis ate in the application for other reasons	shed on, or

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 04 02 7778

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

07-02-2005

US 4218330		date		Patent family member(s)		Publication date
	A	19-08-1980	CA DE FR GB JP JP JP	1104591 2925784 2429829 2024846 1354018 55005998 61021987	A1 A1 A ,B C A	07-07-19 03-01-19 25-01-19 16-01-19 24-12-19 17-01-19
GB 2307243	A	21-05-1997	CA EP JP JP NO WO US	2208641 0802963 11501971 3284219 973236 9718280 6071863	A1 T B2 A A1	22-05-19 29-10-19 16-02-19 20-05-20 11-07-19 22-05-19 06-06-20
JP 5331483	Α	14-12-1993	NONE			
GB 2078776	Α	13-01-1982	JP JP JP DE	1479192 56169630 63020278 3122078	A B	10-02-19 26-12-19 27-04-19 04-03-19
GB 1264981	A	23-02-1972	BE DE FR JP NL	729786 1906674 1601089 48027884 6902155	A1 A B	18-08-19 09-10-19 10-08-19 27-08-19 17-09-19
US 3763244	Α	02-10-1973	NONE			