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(19) **United States**(12) **Patent Application Publication**
Miller et al.(10) **Pub. No.: US 2014/0342960 A1**(43) **Pub. Date: Nov. 20, 2014**(54) **BASE OIL BLEND UPGRADING PROCESS
WITH A DIESTER BASE OIL TO YIELD
IMPROVED COLD FLOW PROPERTIES AND
LOW NOACK**(71) Applicants: **Stephen Joseph Miller**, San Francisco,
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16, 2013.**Publication Classification**(51) **Int. Cl.**
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CPC **C10M 105/36** (2013.01); **C10M 2207/2805**
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USPC **508/496**(57) **ABSTRACT**

The present invention is generally directed to diester-based base oils and base oil blends with improved cold flow properties and improved Noack. The diesters employed have a number a performance benefits in lubricant applications—among them: biodegradability, extreme temperature performance, oxidative stability, solubility for additives and deposit and sludge precursors, flash and fire points. However, ester usage in lubricants has been quite limited due to their high cost. We utilize new proprietary diesters, structurally different from traditional diesters, which are made from fatty acids and alpha olefins in simple processing steps, yet feature performance similar to more traditional lubricant esters.

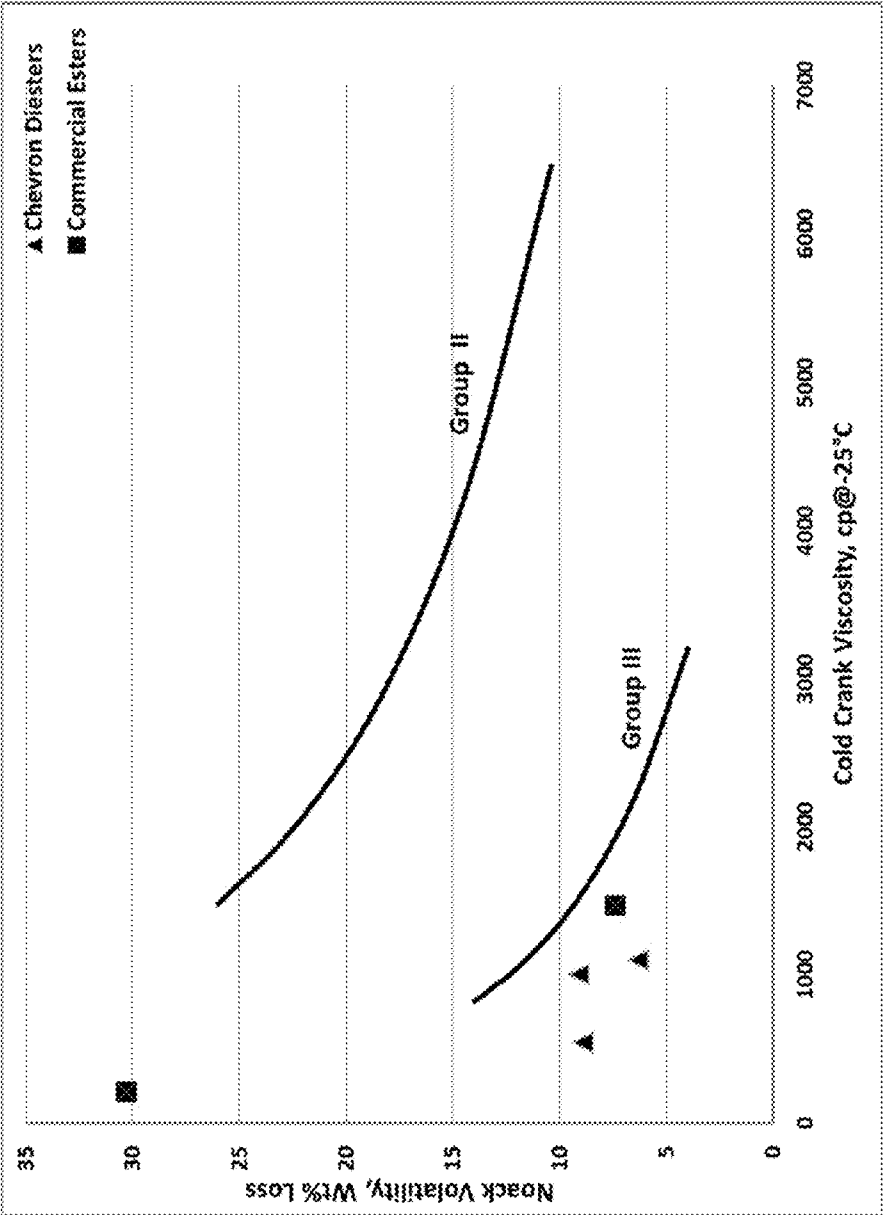


Figure 1

BASE OIL BLEND UPGRADING PROCESS WITH A DIESTER BASE OIL TO YIELD IMPROVED COLD FLOW PROPERTIES AND LOW NOACK

FIELD OF THE INVENTION

[0001] The present invention relates to a process for improving a starting base oil or starting base oil blend by replacing portions of a starting base oil or starting base oil blend with a diester with suitable properties to improve the cold flow properties and lower the volatility relative to the starting base oil or starting base oil blend. The present invention relates to base oil or base oil blends comprising a diester with suitable properties to improve the cold flow properties and lower the volatility of a starting base oil or starting base oil blend.

BACKGROUND OF THE INVENTION

[0002] Esters have been used as lubricating oils for over 50 years. They are used in a variety of applications ranging from jet engines, refrigeration and motor oils. In fact, esters were the first synthetic crankcase motor oils in automotive applications. However, esters gave way to polyalphaolefins (PAOs) due to the lower cost of PAOs and their formulation similarities to mineral oils. In full synthetic motor oils, however, esters are almost always used in combination with PAOs to balance the effect on seals, additives solubility, volatility reduction, and energy efficiency improvement by enhanced lubricity. In this aspect, novel diester-based multi-grade engine oil compositions comprising PAOs have been described in commonly-assigned U.S. patent application Ser. No. 12/548,191; filed Aug. 26, 2009.

[0003] Ester-based lubricants, in general, have excellent lubrication properties due to the polarity of the ester molecules of which they are comprised. The polar ester groups of such molecules adhere to positively-charged metal surfaces creating protective films which slow down the wear and tear of the metal surfaces. Such lubricants are less volatile than the traditional lubricants and tend to have much higher flash points and much lower vapor pressures. Ester lubricants are excellent solvents and dispersants, and can readily solvate and disperse the degradation by-products of oils. Therefore, they greatly reduce sludge buildup. While ester lubricants are stable to thermal and oxidative processes, the ester functionalities give microbes a handle to do their biodegrading more efficiently and more effectively than their mineral oil-based analogues. Therefore, there exists an opportunity to employ an alternative blending component that reduces volatility at a reduced cost and with other advantages not afforded with PAO.

[0004] In view of the foregoing, a simpler, more efficient method of generating diester-based multi-grade engine oils would be extremely useful, particularly wherein such methods utilize renewable raw materials in combination with converting low value Fischer-Tropsch (FT) olefins and alcohols to high value diester base oils.

[0005] Novel diester-based lubricant compositions and their corresponding syntheses have been described in commonly-assigned U.S. Pat. No. 7,871,967 B2; issued Jan. 18, 2011. The synthetic routes described in this patent application comprise and/or generally proceed through the following sequence of reaction steps: (1) epoxidation of an olefin to

form an epoxide; (2) conversion of the epoxide to form a diol; and (3) esterification of the diol to form a diester.

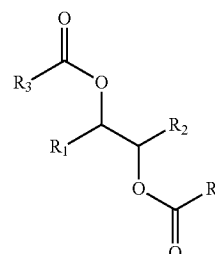
[0006] Moreover, novel diester-based lubricant compositions and their corresponding syntheses have been described in commonly-assigned U.S. Pat. No. 7,867,959 B2; issued Jan. 11, 2011. The synthetic routes described in this patent application comprise and/or generally proceed through the following sequence of reaction steps: (1) epoxidation of an olefin to form an epoxide; (2) directly esterifying the epoxide with a carboxylic acid to form a diester species.

[0007] The specifications for lubricating base oils and engine oils are calling for products with excellent low temperature properties, high oxidation stability, and low volatility. Currently, only a small fraction of the base oils manufactured today are able to meet these demanding specifications.

[0008] Accordingly, there is need for base oils and base oil blends, which have improved low volatility, excellent cold flow properties and improved fuel economy to meet today's stringent performance requirements.

SUMMARY OF THE INVENTION

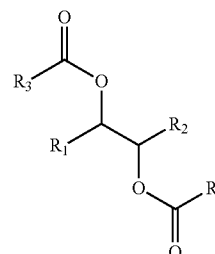
[0009] In one embodiment, the present invention is directed to a process for improving cold flow properties and lowering Noack in a starting base oil or starting base oil blend, comprising: replacing between about 5 to 60 wt % of a starting base oil or starting base oil blend with an equal quantity of a base oil comprising: a) a diester component, comprising a quantity of at least one diester species of Formula I:



I

[0010] wherein R_1 , R_2 , R_3 and R_4 are the same or independently selected from C_2 to C_{17} hydrocarbon groups, and wherein the process affords an upgraded base oil blend.

[0011] In one embodiment, the present invention is directed to a base oil blend comprising: a) a diester component, comprising a quantity of at least one diester species of Formula I:



I

[0012] wherein R_1 , R_2 , R_3 and R_4 are the same or independently selected from C_2 to C_{17} hydrocarbon groups; b) a

second base oil, and wherein the second base oil is a Group I base oil, Group II base oil or Group III base oil.

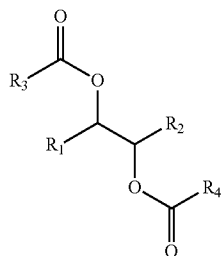
BRIEF DESCRIPTION OF THE DRAWINGS

[0013] FIG. 1 is a chart illustrates the Noack and CCS Viscosity of the diesters of the present invention as compared to the current commercial esters as presented in Table 6 and other Group II and III bases oils.

DETAILED DESCRIPTION OF THE INVENTION

[0014] In some embodiments, the present invention is directed to a process for improving cold flow properties and lowering Noack in a starting base oil or starting base oil blend, wherein improving cold flow properties, further comprises lowering CCS VIS (cold-cranking simulator apparent viscosity) at -25°C ., -30°C . or -35°C ., lowering pour point and lowering Noack.

[0015] In some embodiments, the present invention is directed to a process for improving cold flow properties and lowering Noack in a starting base oil or starting base oil blend, further comprising a process for lowering CCS Viscosity and lowering Noack in a starting base oil or starting base oil blend, comprising: replacing between about 5 to 60 wt % of a starting base oil or starting base oil blend with an equal quantity of a base oil comprising: a) a diester component, comprising a quantity of at least one diester species of Formula I:



I

[0016] wherein R_1 , R_2 , R_3 and R_4 are the same or independently selected from C_2 to C_{17} hydrocarbon groups, and wherein the process affords an upgraded base oil blend.

[0017] In some embodiments, the present invention is directed to a process for lowering CCS Viscosity and lowering Noack in a starting base oil or starting base oil blend, further comprising a diester component that comprises a mixture of isomers where R_1 and R_2 are independently different for each isomer.

[0018] In some embodiments, the present invention is directed to a process for lowering CCS Viscosity and lowering Noack in a starting base oil or starting base oil blend, wherein the base oil or base oil blend comprises a Group I base oil, Group II base oil or Group III base oil.

[0019] In some embodiments, the present invention is directed to a process for lowering CCS Viscosity and lowering Noack in a starting base oil or starting base oil blend, wherein the upgraded base oil blend comprises at least one of light neutral base oil, medium neutral base oil, Yubase 4, Yubase 6, 150R, 600R, 110RLV, 100R and 220R.

[0020] In some embodiments, the present invention is directed to a process for lowering CCS Viscosity and lowering Noack in a starting base oil or starting base oil blend,

wherein the diester component has a Noack Volatility between 6 and 10 wt %, a CCS Viscosity at -30°C . between about 700 and 2000 cP, a pour point less than -10°C ., a cloud point less than -10°C ., a kinematic viscosity at 100°C . between 2.5 to 6.5 centistokes, a VI greater than 110 and a BN Oxidator greater than 20 hours.

[0021] In some embodiments, the present invention is directed to a process for lowering CCS Viscosity and lowering Noack in a starting base oil or starting base oil blend, wherein the diester component has a Noack Volatility between 6 and 9 wt %, and a CCS Viscosity at -30°C . between about 800 and 1900 cP.

[0022] In some embodiments, the present invention is directed to a process for lowering CCS Viscosity and lowering Noack in a starting base oil or starting base oil blend, wherein the diester component has a Noack Volatility between 6 and 9 wt %, and a CCS Viscosity at -25°C . between about 400 and 1250 cP.

[0023] In some embodiments, the present invention is directed to a process for lowering CCS Viscosity and lowering Noack in a starting base oil or starting base oil blend, wherein the kinematic viscosity of the upgraded base oil blend at a temperature of 100°C . is between 3 to 5.5 centistokes.

[0024] In some embodiments, the present invention is directed to a process for lowering CCS Viscosity and lowering Noack in a starting base oil or starting base oil blend, wherein the upgraded base oil blend has a Pour Point and Cloud Point that are independently -12°C . or lower.

[0025] In some embodiments, the present invention is directed to a process for lowering CCS Viscosity and lowering Noack in a starting base oil or starting base oil blend, wherein the upgraded base oil blend has a CCS Viscosity at -30°C . less than 4,200 cP.

[0026] In some embodiments, the present invention is directed to a process for lowering CCS Viscosity and lowering Noack in a starting base oil or starting base oil blend, wherein the upgraded base oil blend has a CCS Viscosity at -35°C . less than 3,400 cP.

[0027] In some embodiments, the present invention is directed to a process for lowering CCS Viscosity and lowering Noack in a starting base oil or starting base oil blend, wherein the upgraded base oil blend has a CCS Viscosity at -25°C . less than 2,400 cP.

[0028] In some embodiments, the present invention is directed to a process for lowering CCS Viscosity and lowering Noack in a starting base oil or starting base oil blend, wherein the upgraded base oil blend has a Noack Volatility less than 15 wt %.

[0029] In some embodiments, the present invention is directed to a process for lowering CCS Viscosity and lowering Noack in a starting base oil or starting base oil blend, wherein R_1 and R_2 of Formula I are selected to have a combined carbon number of from 6 to 16 and R_3 and R_4 are selected to have a combined carbon number of from 10 to 34.

[0030] In some embodiments, the present invention is directed to a process for lowering CCS Viscosity and lowering Noack in a starting base oil or starting base oil blend, wherein R_1 and R_2 of Formula I are selected to have a combined carbon number of C_{16} , C_{14} or C_{12} and R_3 and R_4 are independently selected from the group consisting of C_{12} and a mixture of C_6 - C_{10} .

[0031] In some embodiments, the present invention is directed to a process for lowering CCS Viscosity and lowering Noack in a starting base oil or starting base oil blend, wherein the diester component is derived from a C_8 to C_{18} olefin and a C_6 to C_{14} carboxylic acid.

[0032] In some embodiments, the present invention is directed to a process for lowering CCS Viscosity and lowering Noack in a starting base oil or starting base oil blend, wherein the to upgraded base oil blend comprises quantities of at least two different diester isomers.

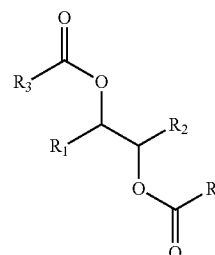
[0033] In some embodiments, the present invention is directed to a process for lowering CCS Viscosity and lowering Noack in a starting base oil or starting base oil blend, further comprising an upgraded base oil blend with about a 2 to 35% lower Noack Volatility as compared to the starting base oil or starting base oil blend.

[0034] In some embodiments, the present invention is directed to a process for lowering CCS Viscosity and lowering Noack in a starting base oil or starting base oil blend, further comprising an upgraded base oil blend with about a 2 to 35% lower CCS Viscosity at -35° or CCS Viscosity at -30° as compared to the starting base oil or starting base oil blend.

[0035] In some embodiments, the present invention is directed to a process for lowering CCS Viscosity and lowering Noack in a starting base oil or starting base oil blend, wherein the diester component has a molecular mass that is from at least about 340 a.m.u. to at most about 780 a.m.u.

[0036] In some embodiments, the present invention is directed to a process for lowering CCS Viscosity and lowering Noack in a starting base oil or starting base oil blend, wherein the diester component is selected from the group consisting of decanoic acid 2-decanoyloxy-1-hexyl-octyl ester and its isomers, tetradecanoic acid-1-hexyl-2-tetradecanoyloxy-octyl esters and its isomers, dodecanoic acid 2-dodecanoyloxy-1-hexyl-octyl ester and its isomers, hexanoic acid 2-hexanoyloxy-1-hexy-octyl ester and its isomers, octanoic acid 2-octanoyloxy-1-hexyl-octyl ester and its isomers, hexanoic acid 2-hexanoyloxy-1-pentyl-heptyl ester and isomers, octanoic acid 2-octanoyloxy-1-pentyl-heptyl ester and isomers, decanoic acid 2-decanoyloxy-1-pentyl-heptyl ester and isomers, decanoic acid-2-ecanoyloxy-1-pentyl-heptyl ester and its isomers, dodecanoic acid-2-dodecanoyloxy-1-pentyl-heptyl ester and isomers, tetradecanoic acid 1-penty-2-tetradecanoyloxy-heptyl ester and isomers, tetradecanoic acid 1-butyl-2-tetradecanoyloxy-hexy ester and isomers, dodecanoic acid-1-butyl-2-dodecanoyloxy-hexyl ester and isomers, decanoic acid 1-butyl-2-decanoyloxy-hexyl ester and isomers, octanoic acid 1-butyl-2-octanoyloxy-hexyl ester and isomers, hexanoic acid 1-butyl-2-hexanoyloxy-hexyl ester and isomers, tetradecanoic acid 1-propyl-2-tetradecanoyloxy-pentyl ester and isomers, dodecanoic acid 2-dodecanoyloxy-1-propyl-pentyl ester and isomers, decanoic acid 2-decanoyloxy-1-propyl-pentyl ester and isomers, octanoic acid 1-2-octanoyloxy-1-propyl-pentyl ester and isomers, hexanoic acid 2-hexanoyloxy-1-propyl-pentyl ester and isomers, and mixtures thereof.

[0037] In one embodiment, the present invention is directed to a base oil blend comprising: a) a diester component, comprising a quantity of at least one diester species of Formula I:



[0038] wherein R_1 , R_2 , R_3 and R_4 are the same or independently selected from C_2 to C_{17} hydrocarbon groups; b) a second base oil, and wherein the second base oil is a Group I base oil, Group II base oil or Group III base oil.

[0039] In some embodiments, the present invention is directed to a base oil blend, wherein the diester component comprises a mixture of isomers where R_1 and R_2 are different for each isomer.

[0040] In some embodiments, the present invention is directed to a base oil blend, further comprising, a third base oil.

[0041] In some embodiments, the present invention is directed to a base oil blend, wherein the diester component has a Noack Volatility between about 6 and 10 wt %, a pour point less than about -10° C., a cloud point less than about -10° C., a kinematic viscosity at 100° C. between about 2.5 to 6.5 centistokes, a VI greater than about 110 and a BN Oxidator greater than about 20 hours.

[0042] In some embodiments, the present invention is directed to a base oil blend, wherein the second base oil is light neutral base oil, medium neutral base oil, Yubase 4, Yubase 6, 150R, 600R, 110RLV, 220R or 100R.

[0043] In some embodiments, the present invention is directed to a base oil blend, wherein the third base oil is light neutral base oil, medium neutral base oil, Yubase 4, Yubase 6, 150R, 600R, 110RLV, 220R or 100R.

[0044] In some embodiments, the present invention is directed to a base oil blend, having: a) a viscosity index between about 110 to 140; b) a Noack volatility of less than about 16 wt %; c) a Pour Point less than about -12° C.; and d) a Cloud Point less than about -12° C.

[0045] In some embodiments, the present invention is directed to a base oil blend, wherein the kinematic viscosity at a temperature of 100° C. is between about 3 to 5.5 centistokes.

[0046] In some embodiments, the present invention is directed to a base oil blend, wherein the Pour Point and Cloud Point are independently about -20° C. or lower.

[0047] In some embodiments, the present invention is directed to a base oil blend, wherein the CCS Viscosity at -30° C. less than about 4,200 cP.

[0048] In some embodiments, the present invention is directed to a base oil blend, wherein the CCS Viscosity at -35° C. less than about 3,400 cP.

[0049] In some embodiments, the present invention is directed to a base oil blend, wherein the CCS Viscosity at -25° C. less than about 2,400 cP.

[0050] In some embodiments, the present invention is directed to a base oil blend, wherein the Noack Volatility less than about 15 wt %.

[0051] In some embodiments, the present invention is directed to a base oil blend, wherein R_1 and R_2 of Formula I

are selected to have a combined carbon number of from 6 to 16 and R_3 and R_4 are selected to have a combined carbon number of from 10 to 34.

[0052] In some embodiments, the present invention is directed to a base oil blend, wherein R_1 and R_2 of Formula I are selected to have a combined carbon number of C_{16} , C_{14} or C_{12} and R_3 and R_4 are independently selected from the group consisting of C_{12} and a mixture of C_6 - C_{10} .

[0053] In some embodiments, the present invention is directed to a base oil blend, wherein the diester component is derived from a C_8 to C_{18} olefin and a C_6 to C_{14} carboxylic acid.

[0054] In some embodiments, the present invention is directed to a base oil blend, wherein the diester component comprises quantities of at least two different diester isomers.

[0055] In some embodiments, the present invention is directed to a base oil blend, wherein the diester component has a molecular mass that is from at least about 340 a.m.u. to at most about 780 a.m.u.

[0056] In some embodiments, the present invention is directed to a base oil blend, wherein the diester component is selected from the group consisting of decanoic acid 2-decanoyloxy-1-hexyl-octyl ester and its isomers, tetradecanoic acid-1-hexyl-2-tetradecanoyloxy-octyl esters and its isomers, dodecanoic acid 2-dodecanoyloxy-1-hexyl-octyl ester and its isomers, hexanoic acid 2-hexanoyloxy-1-hexyloctyl ester and its isomers, octanoic acid 2-octanoyloxy-1-hexyl-octyl ester and its isomers, hexanoic acid 2-hexanoyloxy-1-pentyl-heptyl ester and isomers, octanoic acid 2-octanoyloxy-1-pentyl-heptyl ester and isomers, decanoic acid 2-decanoyloxy-1-pentyl-heptyl ester and isomers, decanoic acid-2-ecanoyloxy-1-pentyl-heptyl ester and its isomers, dodecanoic acid-2-dodecanoyloxy-1-pentyl-heptyl ester and isomers, tetradecanoic acid 1-penty-2-tetradecanoyloxy-heptyl ester and isomers, tetradecanoic acid 1-butyl-2-tetradecanoyloxy-hexyl ester and isomers, dodecanoic acid-1-butyl-2-dodecanoyloxy-hexyl ester and isomers, decanoic acid 1-butyl-2-decanoyloxy-hexyl ester and isomers, octanoic acid 1-butyl-2-octanoyloxy-hexyl ester and isomers, hexanoic acid 1-butyl-2-hexanoyloxy-hexyl ester and isomers, tetradecanoic acid 1-propyl-2-tetradecanoyloxy-pentyl ester and isomers, dodecanoic acid 2-dodecanoyloxy-1-propyl-pentyl ester and isomers, decanoic acid 2-decanoyloxy-1-propyl-pentyl ester and isomers, octanoic acid 1-2-octanoyloxy-1-propyl-pentyl ester and isomers, hexanoic acid 2-hexanoyloxy-1-propyl-pentyl ester and isomers, and mixtures thereof.

DEFINITIONS AND TERMS

[0057] The following terms will be used throughout the specification and will have the following meanings unless otherwise indicated.

[0058] The phrase “Group I Base Oil” contain less than 90 percent saturates and/or greater than 0.03 percent sulfur and have a viscosity index greater than or equal to 80 and less than 120 using the ASTM methods specified in Table E-1 of American Petroleum Institute Publication 1509.

[0059] The term “Group II Base Oil” refers to a base oil which contains greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and has a viscosity index greater than or equal to 80 and less than 120 using the ASTM methods specified in Table E-1 of American Petroleum Institute Publication 1509.

[0060] The term “Group II+ Base Oil” refers to a Group II base oil having a viscosity index greater than or equal to 110 and less than 120.

[0061] The term “Group III Base Oil” refers to a base oil which contains greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and has a viscosity index greater than or equal to 120 using the ASTM methods specified in Table E-1 of American Petroleum Institute Publication 1509.

[0062] The term “Fischer-Tropsch derived” means that the product, fraction, or feed originates from or is produced at some stage by a Fischer-Tropsch process.

[0063] The term “petroleum derived” means that the product, fraction, or feed originates from the vapor overhead streams from distilling petroleum crude and the residual fuels that are the non-vaporizable remaining portion. A source of the petroleum derived product, fraction, or feed can be from a gas field condensate.

[0064] The term “multi-grade engine oil” refers to an engine oil that has viscosity/temperature characteristics which fall within the limits of two different SAE numbers in SAE J300. The present invention is directed to the discovery that multi-grade engine oils meeting the specifications under SAE J300 as revised 2009, including the MRV viscosity specifications, may be prepared from Fischer-Tropsch base oils having a defined cycloparaffin functionality when they are blended with a pour point depressing base oil blending component and an additive package.

[0065] The term “light neutral base oil” refers to a base oil with a boiling range from about 700° F. to about 800° F., a kinematic viscosity at 100° C. from 4 cSt to about 5 cSt.

[0066] The term “medium neutral base oil” refers to a base oil with a boiling range from about 800° F. to about 900° F., a kinematic viscosity at 100° C. from 5 cSt to about 8 cSt.

[0067] Highly paraffinic wax means a wax having a high content of n-paraffins, generally greater than 40 wt %, but can be greater than 50 wt %, or even greater than 75 wt %, and less than 100 wt % or 99 wt %. Examples of highly paraffinic waxes include slack waxes, deoiled slack waxes, refined foots oils, waxy lubricant raffinates, n-paraffin waxes, NAO waxes, waxes produced in chemical plant processes, deoiled petroleum derived waxes, microcrystalline waxes, Fischer-Tropsch waxes, and mixtures thereof.

[0068] The term “derived from highly paraffinic wax” means that the product, fraction, or feed originates from or is produced at some stage by from a highly paraffinic wax.

[0069] Aromatics means any hydrocarbonaceous compounds that contain at least one group of atoms that share an uninterrupted cloud of delocalized electrons, where the number of delocalized electrons in the group of atoms corresponds to a solution to the Huckel rule of $4n+2$ (e.g., $n=1$ for 6 electrons, etc.). Representative examples include, but are not limited to, benzene, biphenyl, naphthalene, and the like.

[0070] Molecules with cycloparaffinic functionality mean any molecule that is, or contains as one or more substituents, a monocyclic or a fused multicyclic saturated hydrocarbon group. The cycloparaffinic group can be optionally substituted with one or more, such as one to three, substituents. Representative examples include, but are not limited to, cyclopropyl, cyclobutyl, cyclohexyl, cyclopentyl, cycloheptyl, decahydronaphthalene, octahydropentalene, (pentadecan-6-yl)cyclohexane, 3,7,10-tricyclohexylpentadecane, decahydro-1-(pentadecan-6-yl)naphthalene, and the like.

[0071] Molecules with monocycloparaffinic functionality mean any molecule that is a monocyclic saturated hydrocar-

bon group of three to seven ring carbons or any molecule that is substituted with a single monocyclic saturated hydrocarbon group of three to seven ring carbons. The cycloparaffinic group can be optionally substituted with one or more, such as one to three, substituents. Representative examples include, but are not limited to, cyclopropyl, cyclobutyl, cyclohexyl, cyclopentyl, cycloheptyl, (pentadecan-6-yl)cyclohexane, and the like.

[0072] Molecules with multicyclopaffinic functionality mean any molecule that is a fused multicyclic saturated hydrocarbon ring group of two or more fused rings, any molecule that is substituted with one or more fused multicyclic saturated hydrocarbon ring groups of two or more fused rings, or any molecule that is substituted with more than one monocyclic saturated hydrocarbon group of three to seven ring carbons. The fused multicyclic saturated hydrocarbon ring group often is of two fused rings. The cycloparaffinic group can be optionally substituted with one or more, such as one to three, substituents. Representative examples include, but are not limited to, decahydronaphthalene, octahydropentalene, 3,7,10-tricyclohexylpentadecane, decahydro-1-(pentadecan-6-yl)naphthalene, and the like.

[0073] Brookfield Viscosity: ASTM D2983-04a is used to determine the low-shear-rate viscosity of automotive fluid lubricants at low temperatures. The low-temperature, low-shear-rate viscosity of automatic transmission fluids, gear oils, torque and tractor fluids, and industrial and automotive hydraulic oils are frequently specified by Brookfield viscosities.

[0074] Kinematic viscosity is a measurement of the resistance to flow of a fluid under gravity. Many base oils, lubricant compositions made from them, and the correct operation of equipment depends upon the appropriate viscosity of the fluid being used. Kinematic viscosity is determined by ASTM D445-06. The results are reported in mm^2/s .

[0075] Viscosity index (VI) is an empirical, unitless number indicating the effect of temperature change on the kinematic viscosity of the oil. Viscosity index is determined by ASTM D2270-04.

[0076] Pour point is a measurement of the temperature at which a sample of base oil will begin to flow under carefully controlled conditions. Pour point can be determined as described in ASTM D5950-02. The results are reported in degrees Celsius. Many commercial base oils have specifications for pour point. When base oils have low pour points, the base oils are also likely to have other good low temperature properties, such as low cloud point, low cold filter plugging point, and low temperature cranking viscosity.

[0077] Noack volatility is usually tested according to ASTM D5800-05 Procedure B. A more convenient method for calculating Noack volatility and one which correlates well with ASTM D5800-05 is by using a thermogravimetric analyzer (TGA) test by ASTM D6375-05. TGA Noack volatility is used throughout the present disclosure unless otherwise stated.

[0078] The base oils of the lubricant composition as disclosed herein also have excellent viscometric properties under low temperature and high shear, making them very useful in multi-grade engine oils. The cold-cranking simulator apparent viscosity (CCS VIS) is a test used to measure the viscometric properties of base oils under low temperature and high shear. The test method to determine CCS VIS is ASTM D5293-02. Results are reported in $\text{mPa}\cdot\text{s}$. CCS VIS has been found to correlate with low temperature engine cranking.

Specifications for maximum CCS VIS are defined for automotive engine oils by SAE J300, revised in 2009. The maximum CCS VIS for a OW SAE Viscosity Grade engine oil is $6200 \text{ mPa}\cdot\text{s}$ at -35°C .

[0079] The phrase “improving cold flow properties” refers to one or more of lowering CCS VIS (cold-cranking simulator apparent viscosity) at -25°C , -30°C , or -35°C , lowering pour point and lowering Noack.

[0080] The Mini-Rotary Viscometer (MRV) test, ASTM D4684-07, which is related to the mechanism of pumpability, is a low shear rate measurement. Slow sample cooling rate is the method’s key feature. A sample is pretreated to have a specified thermal history which includes warming, slow cooling, and soaking cycles. The MRV measures an apparent yield stress, which, if greater than a threshold value, indicates a potential air-binding pumping failure problem. Above a certain viscosity (currently defined as $60,000 \text{ mPa}\cdot\text{s}$ by SAE J300 2009), the oil may be subject to pumpability failure by a mechanism called “flow limited” behavior. An SAE OW oil, for example, is required to have a maximum viscosity of $60,000 \text{ mPa}\cdot\text{s}$ at -40°C with no yield stress. This method also measures an apparent viscosity under shear rates of 1 to 50 s^{-1} .

[0081] High temperature high shear rate viscosity (HTHS) is a measure of a fluid’s resistance to flow under conditions resembling highly-loaded journal bearings in fired internal combustion engines, typically 1 million s^{-1} at 150°C . HTHS is a better indication of how an engine operates at high temperature with a given lubricant than the kinematic low shear rate viscosities at 100°C . The HTHS value directly correlates to the oil film thickness in a bearing. SAE J300 2009 contains the current specifications for HTHS measured by ASTM D4683, ASTM D4741, or ASTM D5481. An SAE 20 viscosity grade engine oil, for example, is required to have a minimum HTHS of $2.6 \text{ mPa}\cdot\text{s}$.

[0082] Scanning Brookfield Viscosity: ASTM D5133-05 is used to measure the low temperature, low shear rate, viscosity/temperature dependence of engine oils. The low temperature, low shear viscometric behavior of an engine oil determines whether the oil will flow to the sump inlet screen, then to the oil pump, then to the sites in the engine requiring lubrication in sufficient quantity to prevent engine damage immediately or ultimately after cold temperature starting. ASTM D5133-05, the Scanning Brookfield Viscosity technique, measures the Brookfield viscosity of a sample as it is cooled at a constant rate of $1^\circ \text{C}/\text{hour}$. Like the MRV, ASTM D5133-05 is intended to relate to the pumpability of an oil at low temperatures. The test reports the gelation point, defined as the temperature at which the sample reaches $30,000 \text{ mPa}\cdot\text{s}$. The gelation index is also reported, and is defined as the largest rate of change of viscosity increase from -5°C to the lowest test temperature. The latest API SM/ILSAC GF-4 specifications for passenger car engine oils require a maximum gelation index of 12.

[0083] “Lubricants,” as defined herein, are substances (usually a fluid under operating conditions) introduced between two moving surfaces so to reduce the friction and wear between them. Base oils used as motor oils are generally classified by the American Petroleum Institute as being mineral oils (Group I, II, and III) or synthetic oils (Group IV and V). See American Petroleum Institute (API) Publication Number 1509.

[0084] “Pour point,” as defined herein, represents the lowest temperature at which a fluid will pour or flow. See, e.g., ASTM International Standard Test Methods D 5950-96, D 6892-03, and D 97.

[0085] “Cloud point,” as defined herein, represents the temperature at which a fluid begins to phase separate due to crystal formation. See, e.g., ASTM Standard Test Methods D 5773-95, D 2500, D 5551, and D 5771.

[0086] “Centistoke,” abbreviated “cSt,” is a unit for kinematic viscosity of a fluid (e.g., a lubricant), wherein 1 centistoke equals 1 millimeter squared per second (1 cSt=1 mm²/s). See, e.g., ASTM Standard Guide and Test Methods D 2270-04, D 445-06, D 6074, and D 2983.

[0087] With respect to describing molecules and/or molecular fragments herein, “R_n,” where “n” is an index, refers to a hydrocarbon group, wherein the molecules and/or molecular fragments can be linear and/or branched.

[0088] As defined herein, “C_n,” where “n” is an integer, describes a hydrocarbon molecule or fragment (e.g., an alkyl group) wherein “n” denotes the number of carbon atoms in the fragment or molecule.

TABLE 1

Property	Test Method	YUBASE 4	YUBASE 6
Appearance	Visual	Bright & Clear	Bright & Clear
Specific Gravity, @15/4° C.	ASTM D 1298	0.8338	0.8423
Kinematic Viscosity, @40° C.	ASTM D 445	19.57	36.82
Kinematic Viscosity, @100° C.	ASTM D 445	4.23	6.52
Viscosity Index	ASTM D 2270	122	131
Noack Volatility, wt %	DIN 51581	15	7
Flash Point, ° C.	ASTM D 92	230	240
Pour Point, ° C.	ASTM D 97	-15	-15
Color	ASTM D 1500	L0.5	L0.5
Con. Carbon Residue, wt %	ASTM D 189	<0.01	<0.01
Copper Corrosion	ASTM D 130	1-a	1-a
Sulfur, ppm	ASTM D 2622	<10	<10
Total Acid No., mgKOH/g	ASTM D 664	0.01	0.01

[0093] The terms “100R, 150R, 220R, 600R and 110RLV” are base oils defined as presented in Table 2 shown below.

TABLE 2

Property	ASTM Method	100R	150R	220R	600R	110RLV
API Base Oil Category	API 1509 E 1.3	II	II	II	II	II(+)
Appearance	SM 360-99	Bright and Clear	Bright and Clear	Bright and Clear	Bright and Clear	Bright and Clear
Color	ASTM D 1500	L0.5	L0.5	L0.5	L0.5	L0.5
API Gravity, deg.	ASTM D 4052	34.4	33.4	31.9	31.2	35.4
Density, lb/gal	ASTM D 4052	7.1	7.15	7.22	7.28	7.06
Density, kg/l	ASTM D 4052	0.853	0.858	0.867	0.874	0.848
Specific Gravity, @ 60° F./60° F.	ASTM D 4052	0.853	0.858	0.867	0.874	0.848
Viscosity @ 40° C., cSt	ASTM D 445	20.3	30.9	43.7	108	21.1
Viscosity @ 100° C., cSt	ASTM D 445	4.1	5.3	6.6	12.2	4.4
Viscosity @ 100° F., SUS	ASTM D 2161	107	153	214	590	113
Viscosity Index	ASTM D 2270	102	107	102	103	118
CCS @ -20° C., cP	ASTM D 5293	N/A	1750	3400	N/A	822
CCS @ -25° C., cP	ASTM D 5293	1400	2660	5600	N/A	1350
CCS @ -30° C., cP	ASTM D 5293	2650	5070	N/A	N/A	2450
Pour Point, ° C.	ASTM D 5950/1C	-15	-15	-13	-17	-15
Flash Point, COC, ° C.	ASTM D 92	206	227	230	270	216
Volatility, wt. % distilled at 700° F./371° C.	ASTM D 2887	13	N/A	N/A	N/A	N/A
Evaporative Loss, NOACK, wt %	ASTM D5800 (B)	26	14	10	2	16
Water, ppm	ASTM D 6304-98	<50	<50	<50	<50	<50
Sulfur, ppm	ICP/XRF	<10	<10	<10	<10	<6
Saturates, HPLC wt. %	Chevron	>99	>99	>99	>99	>99
Aromatics, HPLC wt. %	Chevron	<1	<1	<1	<1	<1

[0089] The prefix “bio,” as used herein, refers to an association with a renewable resource of biological origin, such as resource generally being exclusive of fossil fuels.

[0090] The term “internal olefin,” as used herein, refers to an olefin (i.e., an alkene) having a non-terminal carbon-carbon double bond (C=C). This is in contrast to “a-olefins” which do bear a terminal carbon-carbon double bond.

[0091] The phrase an “upgraded base oil blend” refers to a base oil or base oil blend that has had a portion replaced with a diester herein to afford the upgraded base oil blend having improved cold flow properties and lower Noack compared to the starting base oil or base oil blend.

[0092] The terms Yubase 4 and Yubase 6 are base oils defined as presented in Table 1 shown below.

[0094] Unless otherwise indicated herein, scientific and technical terms used in connection with the present invention shall have the meanings that are commonly understood by those of ordinary skill in the art. Further, unless otherwise required by context, singular terms shall include pluralities and plural terms shall include the singular. More specifically, as used in this specification and the appended claims, the singular forms “a”, “an” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a fatty acid” includes a plurality of fatty acids, and the like. In addition, ranges provided in the specification and appended claims include both end points and all points between the end points. Therefore, a range of 2.0 to 3.0 includes 2.0, 3.0 and all points between 2.0 and 3.0. Furthermore, all numbers expressing quantities, percentages

or proportions, and other numerical values used in the specification and claims, are to be understood as being modified in all instances by the term “about”. As used herein, the term “include” and its grammatical variants are intended to be non-limiting, such that recitation of items in a list is not to the exclusion of other like items that can be substituted or added to the listed items. As used herein, the term “comprising” means including elements or steps that are identified following that term, but any such elements or steps are not exhaustive, and an embodiment can include other elements or steps.

EXAMPLES

[0095] The following examples are provided to demonstrate particular embodiments of the present invention. It should be appreciated by those of skill in the art that the methods disclosed in the examples which follow merely represent exemplary embodiments of the present invention. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments described and still obtain a like or similar result without departing from the spirit and scope of the present invention.

Example 1

[0096] This example serves to illustrate the base oil blends with and without the diesters of the present invention with the analytics presented in Table 3 below.

[0097] The diester-free base oil blend was prepared by mixing 82.67 wt % Yubase 4 and 17.33 wt % Yubase 6. The base oil component with diester was prepared by mixing 69.7 wt % Yubase 4, 13.8 wt % Yubase 6, and 16.5 wt % diester of Formula I wherein R_1 and R_2 are combined to have a carbon number of C_{12} and R_3 and R_4 are both C_{12} . Both samples were

submitted for standard base oil testing, including API gravity, viscosity at 40° C. and 100° C., Viscosity Index, pour point, cloud point, Noack volatility, cold cranking viscosity, and Bromine number.

TABLE 3

Base Oil Blend	Example 1	
Diester A, wt %	0	16.5
Yubase 4, wt %	82.67	69.7
Yubase 6, wt %	17.33	13.8
Properties		
API	42.5	36.2
Vis @ 100° C., cSt	4.515	4.523
VI	130	132
Pour point, ° C.	-14	-17
Cloud point, ° C.	-10	-12
Noack, wt %	12.65	12.46
CCS @ -35° C., cP	3225	2928
Bromine number	0.1	0.08

Example 2

[0098] This example serves to illustrate the base oil blends with the diesters of the present invention, a single comparative without diester and a second comparative with a commercially available ester (i.e., Esterex A51) with the analytics presented in Table 4 below. Diester A is a diester of Formula I, wherein R_1 and R_2 are combined to have a carbon number of C_{12} and R_3 and R_4 are both C_{12} . Diester B2 is a diester of Formula I, wherein R_1 and R_2 are combined to have a carbon number of C_{12} and R_3 and R_4 are both independently C_6 - C_{10} . The examples in Table 3 were prepared in a similar manner as those of Example 1 herein.

TABLE 4

Composition, wt %	BOB02958	BOB02959	BOB02960	BOB02961
110RLV	52.43	59.31	59.25	59.16
100R	13.01			
220R	34.56	35.55	35.51	35.46
Diester A		5.14		
Diester B2			5.24	
Esterex A51				5.37
BOB Properties, Calculated				
KV100, centistokes	4.988	5.07	5.044	5.103
KV40, centistokes	26.76	27.06	27.03	27.46
VI	112	115	114	115
CCS, cP @ -25° C.	2137	2103	2120	2164
CCS, cP @ -30° C.	3929	3840	3880	3961
Noack volatility, % wt loss	14.8			
BOB Properties, Observed				
KV100, centistokes	4.971	5.002	4.975	5.047
KV40, centistokes	26.51	26.35	26.27	26.73
VI	113	117	115	117
CCS, cP @ -25° C.	2165	1952	1972	2084
CCS, cP @ -30° C.	3912	3513	3529	3751
Noack, wt %	14.2	13.4	13.9	13.1

Example 3

[0099] This example serves to illustrate the diesters prepared and their respective properties as presented in Table 5.

TABLE 5

Starting Materials			Properties						
			Cloud	Pour	Viscosity	Viscosity	Viscosity	Oxidator	NOACK,
No.	Olefins	Fatty Acids	Point	Point	(40° C.)	(100° C.)	Index	BN	wt % loss
A	C14	C12	-28	-27	19.5 cSt	4.76 cSt	176	26 hrs	8.9
B	B1 C14	C6(high)-C10	-69	-66	16.41 cSt	3.68 cSt	109	19.3 hrs	—
	B2 C14	C6(low)-C10	-60	-60	19.47 cSt	4.191 cSt	120	26.25 hrs	9.1
C	C16	C12	-18	-19	24.44 cSt	5.218 cSt	152	38 hrs	—
E	C18	C6-C10	-24	-26	20.4 cSt	4.5 cSt	137	25.5	—
D	D1 C16	C6(high)-C10	-51	-51	17.90 cSt	4.015 cSt	124	—	—
	D2 C16	C6(low)-C10	-51	-53	21.54 cSt	4.545 cSt	128	26 hrs	6.3

Example 4

[0100] This example serves to illustrate the Noack and CCS Viscosity of the diesters of the present invention as compared to the current commercial esters and other Group II and III bases oils as presented in Table 6 and FIG. 1.

TABLE 6

Sample	CCS (-25)	CCS (-30)	Noack	KV100
Diester A	542	812	8.9	4.76
Diester B2	1002	1717	9.1	4.19
Diester D2	1104	1875	6.3	4.545
Esterex A51	1468	2487	7.4	5.4
Esterex A32	212	319	30.3	2.8

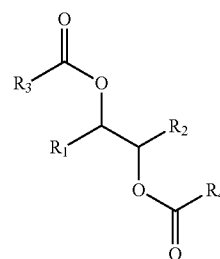
[0101] All patents, patent applications and publications are herein incorporated by reference to the same extent as if each individual patent, patent application or publication was specifically and individually indicated to be incorporated by reference.

[0102] The present invention is not to be limited in scope by the specific embodiments described herein, which are intended as single illustrations of individual aspects of the invention, and functionally equivalent methods and components are within the scope of the invention. Indeed, various modifications of the invention, in addition to those shown and described herein will become apparent to those skilled in the art from the foregoing description and accompanying drawings. Such modifications are intended to fall within the scope of the appended claims.

What is claimed is:

1. A process for improving cold flow properties and lowering Noack in a starting base oil or starting base oil blend, comprising: replacing between about 5 to 60 wt % of a starting base oil or starting base oil blend with an equal quantity of a base oil comprising:

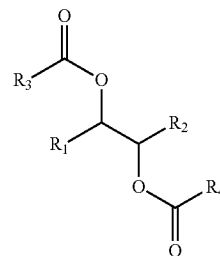
a) a diester component, comprising a quantity of at least one diester species of Formula I:



wherein R_1 , R_2 , R_3 and R_4 are the same or independently selected from C_2 to C_{17} hydrocarbon groups, and wherein the process affords an upgraded base oil blend.

2. The process of claim 1, further comprising a process for lowering CCS Viscosity and lowering Noack in a starting base oil or starting base oil blend, comprising: replacing between about 5 to 60 wt % of a starting base oil or starting base oil blend with an equal quantity of a base oil comprising:

a) a diester component, comprising a quantity of at least one diester species of Formula I:



wherein R_1 , R_2 , R_3 and R_4 are the same or independently selected from C_2 to C_{17} hydrocarbon groups, and wherein the process affords an upgraded base oil blend.

3. The process of claim 1, further comprising a diester component that comprises a mixture of isomers where R_1 and R_2 are independently different for each isomer.

4. The process of claim 1, wherein the starting base oil or starting base oil blend comprises a Group I base oil, Group II base oil or Group III base oil.

5. The process of claim 1, wherein the upgraded base oil blend comprises at least one of light neutral base oil, medium neutral base oil, Yubase 4, Yubase 6, 150R, 600R, 110RLV, 100R and 220R.

6. The process of claim 1, wherein the diester component has a Noack Volatility between about 6 and 10 wt %, a pour point less than about -10°C ., a CCS Viscosity at -30°C . between about 700 and 2000 cP, a cloud point less than about -10°C ., a kinematic viscosity at 100°C . between about 2.5 to 6.5 centistokes, a VI greater than about 110 and a BN Oxidator greater than about 20 hours.

7. The process of claim 1, wherein the upgraded base oil blend has:

- a) a viscosity index between about 110 to 140;
- b) a Noack volatility of less than about 16 wt %;
- c) a Pour Point less than about -12°C .; and
- d) a Cloud Point less than about -12°C .

8. The process of claim 1, wherein the kinematic viscosity of the upgraded base oil blend at a temperature of 100°C . is between about 3 to 5.5 centistokes.

9. The process of claim 7, wherein the Pour Point and Cloud Point that are independently about -20°C . or lower.

10. The process of claim 1, wherein the upgraded base oil blend has a CCS Viscosity at -30°C . less than about 4,200 cP.

11. The process of claim 1, wherein the upgraded base oil blend has a CCS Viscosity at -35°C . less than about 3,400 cP.

12. The process of claim 1, wherein the upgraded base oil blend has a CCS Viscosity at -25°C . less than about 2,400 cP.

13. The process of claim 1, wherein R_1 and R_2 of Formula I are selected to have a combined carbon number of from 6 to 16 and R_3 and R_4 are selected to have a combined carbon number of from 10 to 34.

14. The process of claim 1, wherein R_1 and R_2 of Formula I are selected to have a combined carbon number of C_{16} , C_{14} or C_{12} and R_3 and R_4 are independently selected from the group consisting of C_{12} and a mixture of C_6 - C_{10} .

15. The process of claim 1, wherein the diester component is derived from a C_8 to C_{18} olefin and a C_6 to C_{14} carboxylic acid.

16. The process of claim 3, wherein the upgraded base oil blend comprises quantities of at least two different diester isomers.

17. The process of claim 1, further comprising an upgraded base oil blend with about a 2 to 35% lower Noack Volatility as compared to the starting base oil or starting base oil blend.

18. The process of claim 1, further comprising an upgraded base oil blend with about a 2 to 35% lower CCS Viscosity at -35° or CCS Viscosity at -30° as compared to the starting base oil or starting base oil blend.

19. The process of claim 1, wherein the diester component has a molecular mass that is from at least about 340 a.m.u. to at most about 780 a.m.u.

20. The process of claim 1, wherein the diester component is selected from the group consisting of decanoic acid 2-decanoyloxy-1-hexyl-octyl ester and its isomers, tetradecanoic acid-1-hexyl-2-tetradecanoyloxy-octyl esters and its isomers, dodecanoic acid 2-dodecanoyloxy-1-hexyl-octyl ester and its isomers, hexanoic acid 2-hexanoyloxy-1-hexy-octyl ester and its isomers, octanoic acid 2-octanoyloxy-1-hexyl-octyl ester and its isomers, hexanoic acid 2-hexanoyloxy-1-pentyl-heptyl ester and isomers, octanoic acid 2-octanoyloxy-1-pentyl-heptyl ester and isomers, decanoic acid 2-decanoyloxy-1-pentyl-heptyl ester and isomers, decanoic acid-2-ecanoyloxy-1-pentyl-heptyl ester and its isomers, dodecanoic acid-2-dodecanoyloxy-1-pentyl-heptyl ester and isomers, tetradecanoic acid 1-penty-2-tetradecanoyloxy-heptyl ester and isomers, tetradecanoic acid 1-butyl-2-tetradecanoyloxy-hexyl ester and isomers, dodecanoic acid-1-butyl-2-dodecanoyloxy-hexyl ester and isomers, decanoic acid 1-butyl-2-decanoyloxy-hexyl ester and isomers, octanoic acid 1-butyl-2-octanoyloxy-hexyl ester and isomers, hexanoic acid 1-butyl-2-hexanoyloxy-hexyl ester and isomers, tetradecanoic acid 1-propyl-2-tetradecanoyloxy-pentyl ester and isomers, dodecanoic acid 2-dodecanoyloxy-1-propyl-pentyl ester and isomers, decanoic acid 2-decanoyloxy-1-propyl-pentyl ester and isomers, octanoic acid 1-2-octanoyloxy-1-propyl-pentyl ester and isomers, hexanoic acid 2-hexanoyloxy-1-propyl-pentyl ester and isomers, and mixtures thereof.

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