



US 20140113847A1

(19) **United States**(12) **Patent Application Publication**
Givens et al.(10) **Pub. No.: US 2014/0113847 A1**(43) **Pub. Date: Apr. 24, 2014**(54) **HIGH VISCOSITY INDEX LUBRICATING OIL
BASE STOCK AND VISCOSITY MODIFIER
COMBINATIONS, AND LUBRICATING OILS
DERIVED THEREFROM***C10M 145/16* (2006.01)*C10M 145/12* (2006.01)(52) **U.S. Cl.**CPC *C10M 149/06* (2013.01); *C10M 145/12*
(2013.01); *C10M 149/04* (2013.01); *C10M*
145/16 (2013.01)USPC **508/468**; 508/472; 508/470; 508/471(71) Applicant: **ExxonMobil Research and
Engineering Company**, Annandale, NJ
(US)(72) Inventors: **Willie Allan Givens**, Williamstown, NJ
(US); **Percy Rohinton Kanga**, Cherry
Hill, NJ (US); **Jared Michael Robillard**,
Collingswood, NJ (US)(73) Assignee: **ExxonMobil Research and
Engineering Company**, Annandale, NJ
(US)(21) Appl. No.: **14/034,864**(22) Filed: **Sep. 24, 2013****Related U.S. Application Data**(60) Provisional application No. 61/717,947, filed on Oct.
24, 2012.**Publication Classification**(51) **Int. Cl.**
C10M 149/06 (2006.01)
C10M 149/04 (2006.01)(57) **ABSTRACT**

A lubricating composition including a first base stock component including: one or more metallocene catalyzed polyalphaolefins (mPAOs), each mPAO having a kinematic viscosity (K_{v100}) from 40 cSt to 155 cSt and a viscosity index (VI) from 150 to 207; a second base stock including one or more polyalphaolefins (PAOs), each PAO having a kinematic viscosity (K_{v100}) less than 10 cSt and a VI from 130 to 145; and a viscosity modifier including a copolymer having units derived from monomers of (i) an α -olefin and (ii) an ethylenically unsaturated carboxylic acid or derivatives thereof esterified with an alcohol. A lubricant including the above lubricating composition. A method for improving fuel efficiency, while maintaining or improving wear control, load carrying capacity and/or traction reduction in a driveline device, e.g., gears and transmissions, lubricated with a lubricating oil, by using as the lubricating oil the above lubricant.

Fig. 1

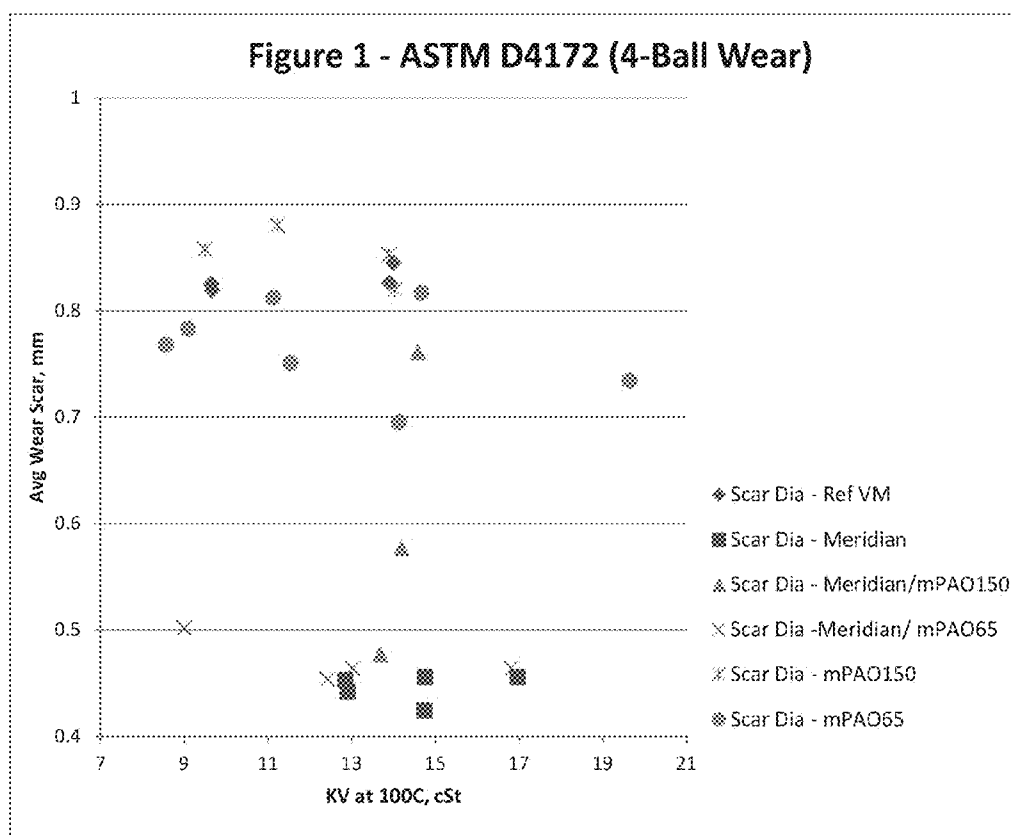


Fig. 2

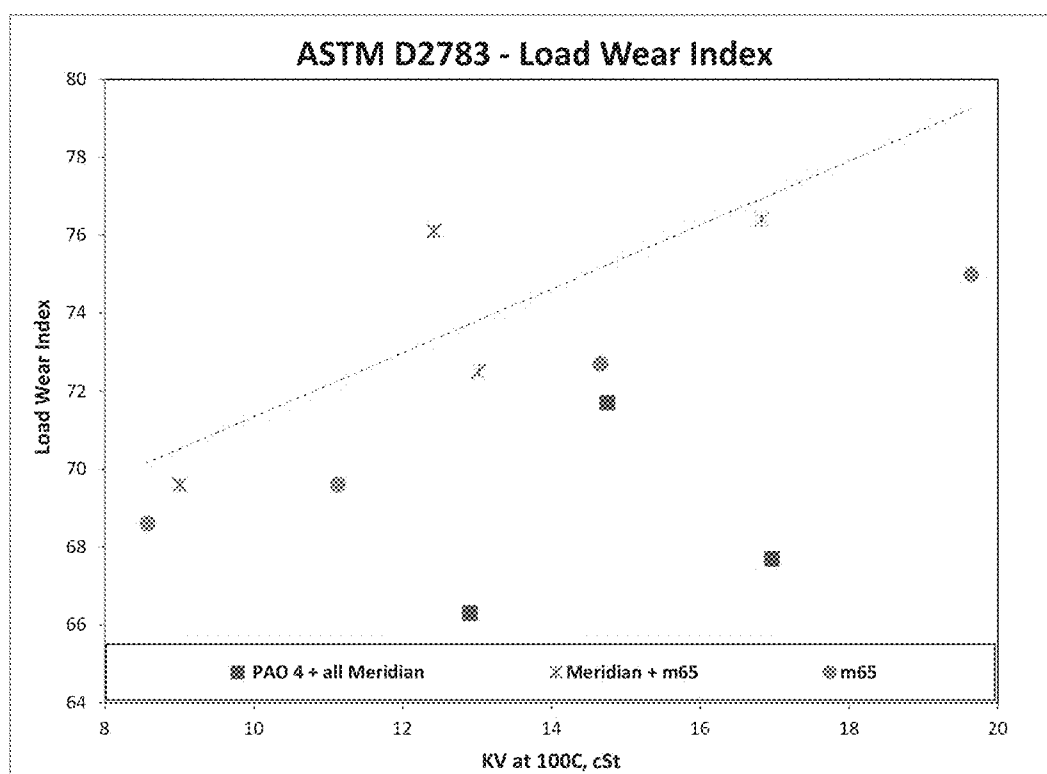


Fig. 3

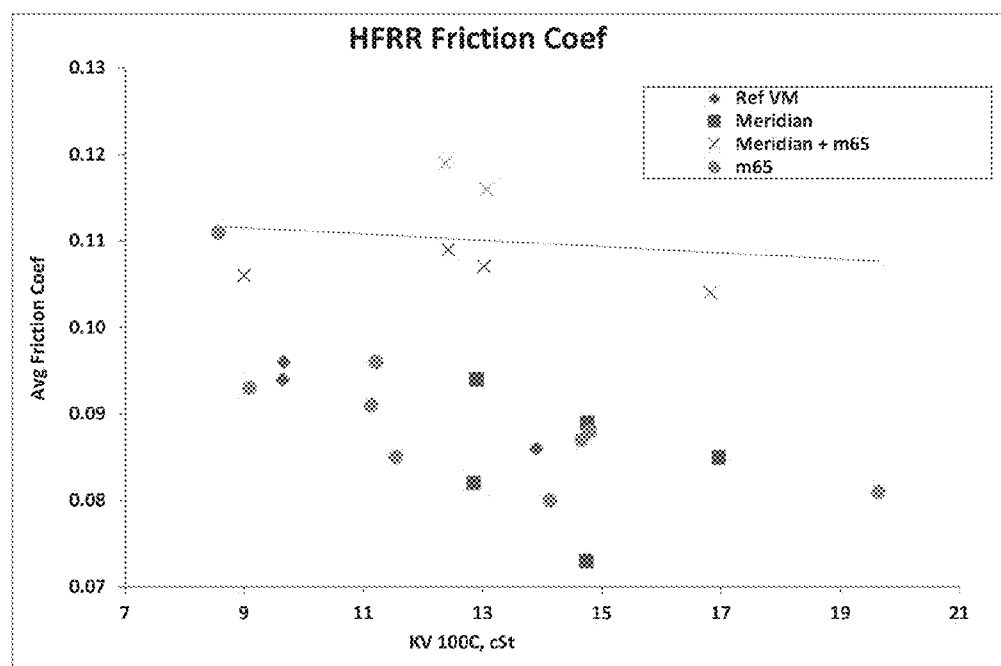


Fig. 4

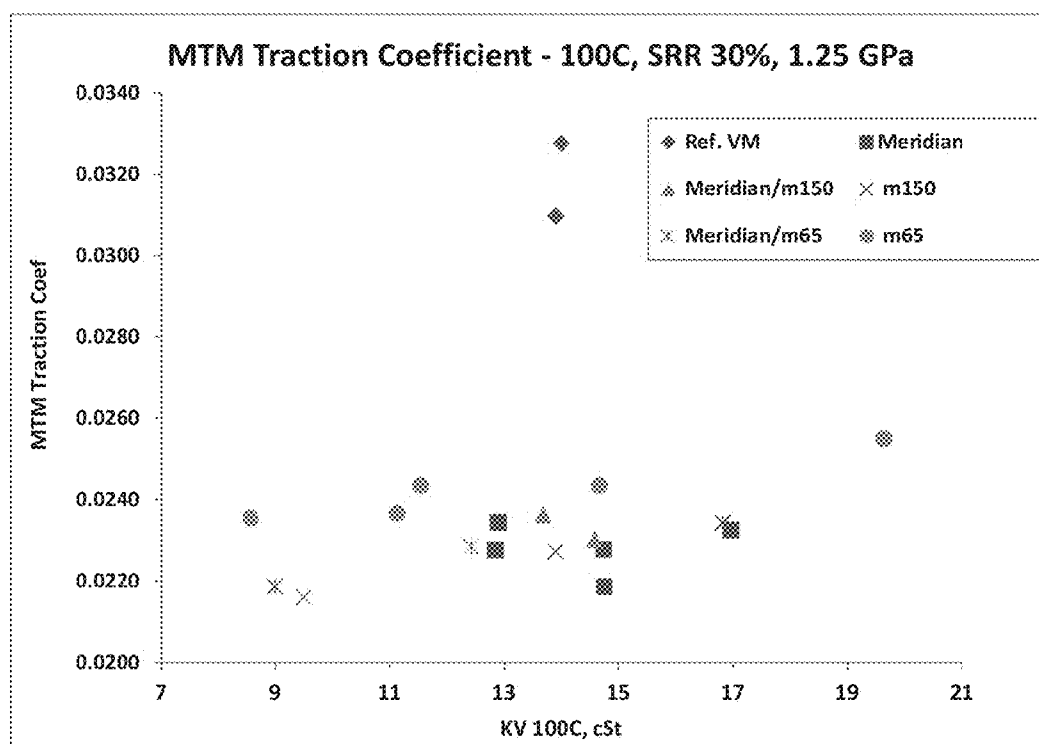


Fig. 5

	CVL-ENABLING-	CVL-ENABLING-	CVL-ENABLING-	CVL-ENABLING-	CVL-ENABLING-	CVL-ENABLING-
	A	B	C	D	E	F
Wt% mPAO 150	0	5	10	15	20	25
Wt% Meridian	25	20	15	10	5	0
Tapered Roller Bearing (CEC L-45-A-99) 40 hrs						
Unsheared	10.45	10.7	10.95	11.2	11.45	11.75
Sheared	9.67	10.47	10.81	10.81	11.25	11.18
Viscosity loss, cSt	0.58	0.23	0.14	0.39	0.21	0.58
Viscosity loss, %	5.6	2.2	1.3	3.5	1.8	4.9

Fig. 6

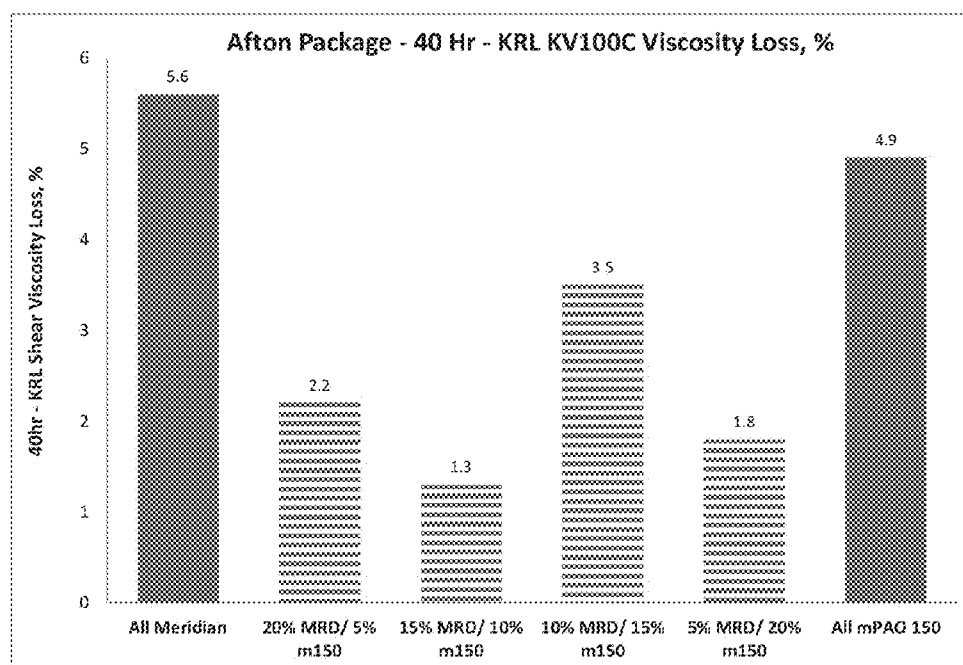


Fig. 7

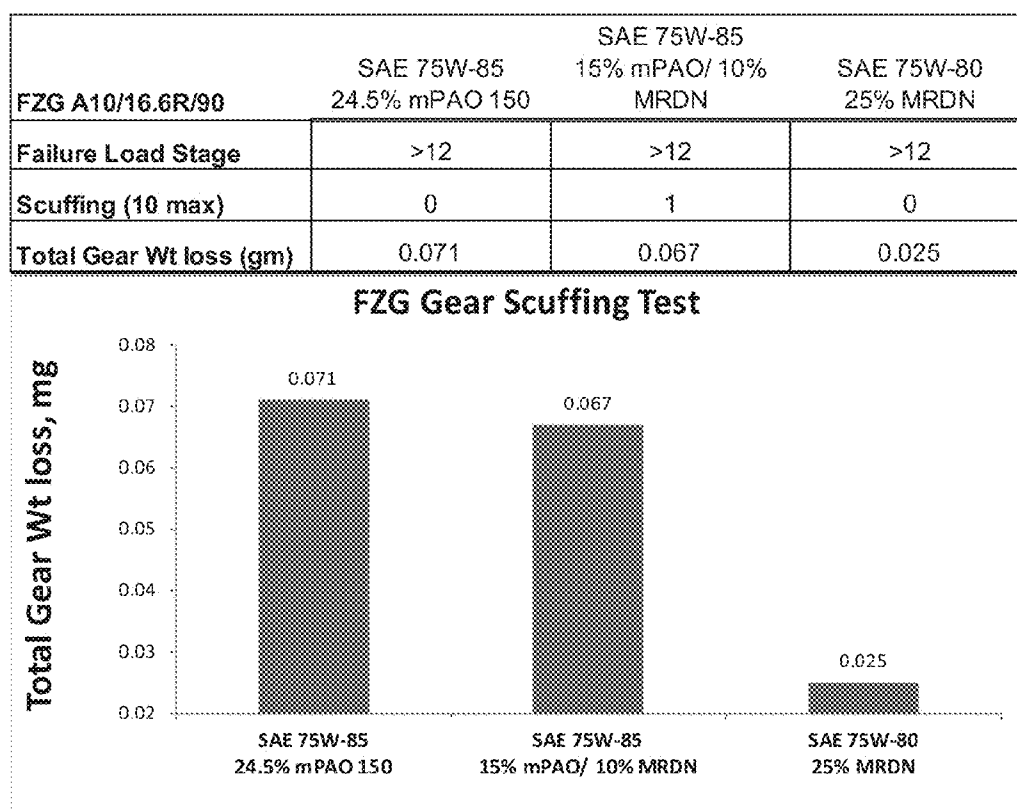


Fig. 8


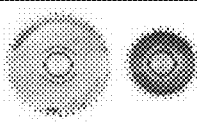


ASTM D5704 Thermal Oxidation Stability	SAE J2369 Std. limit	SAE 75W-85 24.5% mPAO 150	SAE 75W-85 15% mPAO/ 10%Meridian	SAE 75W-80 25% Meridian
NON-REFERENCE TEST LENGTH (hrs)	50	100	100	100
L-80-1 Visc Increase%	100 max	25%	23%	20%
Pentane Insolubles (% wt)	3 max	0.1	0.1	0
Toluene Insolubles (% wt)	2 max	0	0.1	0
Avg Carbon/ Varnish (merits)	7.7 min	9.3	9.8	9.6
Average Sludge (merits)	9.4 min	9.4	9.7	9.7
Large & Small Spur Gears				

Fig. 9

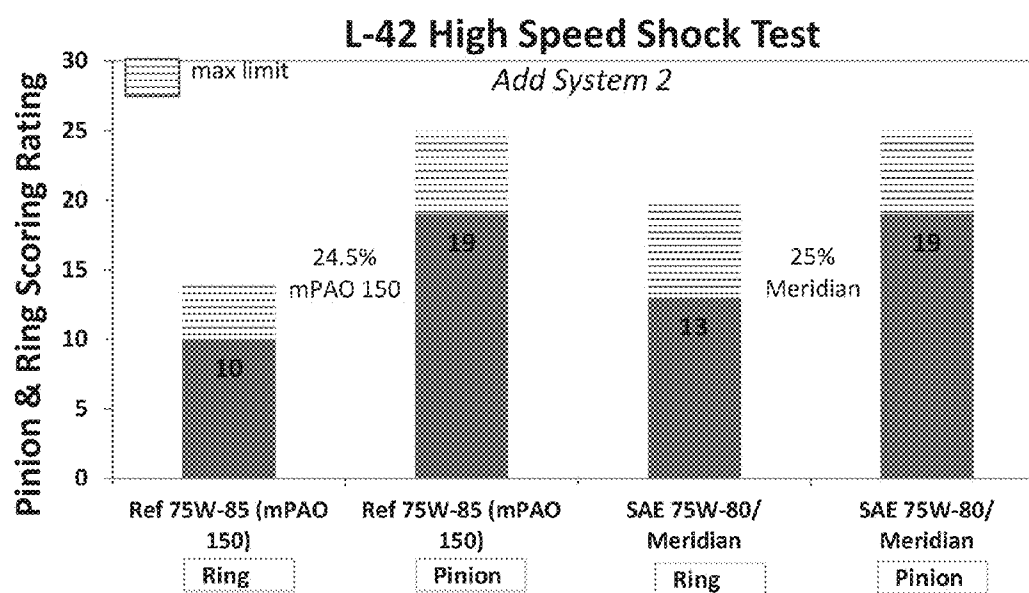


Fig. 10

Example 1	10063967	12026149	12026339	12026195	11017847	11035671	11035800	11035645	11017845	11018041	11104293	11184305	11184314
	Blend 1	Blend 2	Blend 3	Blend 4	Blend 5	Blend 6	Blend 7	Blend 8	Blend 9	Blend 10	Blend 11	Blend 12	Blend 13
Batch Number	1	1	1	1	1	1	1	1	1	1	1	1	1
Description	Ref VM/ PAO6	Ref VM/ PAO4	Ref VM/ PAO4	Ref VM/ PAO4	PAO 4 + all Meridian	PAO 4 + all Meridian	PAO 4 + all Meridian	mPAO 150 + Meridian	mPAO 150 + Meridian	mPAO 150 + Meridian	mPAO 150 only	mPAO 150 only	mPAO 150 only
ANG 6043	10	10	10	10	10	10	10	10	10	10	10	10	10
PAO 6	67.3												
PAO 4		81.9	89.8	72.9	81.8	47.8	43.8	31.78	51.76	51.78	64.9	58.8	53.76
Ref. Conventional VM	22.6	25	20	17									
Meridian VM					38	42	46	5	12	22			
mPAO 150								33.14	28.14	18.14	25	30	36.14
mPAO 65													
Kinematic Viscosity, 100C	14	13.9	9.84	9.86	12.9	14.75	18.38	14.58	14.19	13.68	9.49	11.23	13.59
Kinematic Viscosity, 40C	97.18	76.19	56.9	47.62	67.75	79.78	93.77	86.01	81.26	75.68	51.17	63.02	82.68
Viscosity Index	147	189	154	193	194	195	197	177	182	187	172	173	179
Four Ball Wear - Scar Diameter	0.845	0.626	0.825	0.819	0.442	0.456	0.456	0.761	0.577	0.477	0.858	0.86	0.853

	Blend 14	Blend 15	Blend 16	Blend 17	Blend 18	Blend 19	Blend 20	Blend 21	Blend 22	Blend 23	Blend 24
Batch Number	1	1	1	1	1	1	1	1	1	1	1
Description	mPAO 65 + Meridian	mPAO 65 + Meridian	mPAO 65 + Meridian	mPAO 65 + Meridian	mPAO 65	mPAO 65	mPAO 65	mPAO 65	mPAO 65	mPAO 65	mPAO 65
ANG 6043	10	10	10	10	10	10	10	10	10	10	10
PAO 6											
PAO 4											
Ref. Conventional VM	39.9	48.5	39.9	49.9	60	48.8	46.9	57.8	41.4	39.9	29.9
Meridian VM	10	20	25	30							
mPAO 150											
mPAO 65	20	20	25	10	30	40	41	32	45.5	30.0	60
Kinematic Viscosity, 100C	8.999	12.42	16.82	13.02	8.57	11.13	11.54	9.08	14.13	14.63	19.64
Kinematic Viscosity, 40C	47.51	68.85	96.79	70.82	48.83	64.66	67.88	48.88	87.8	92.05	133.4
Viscosity Index	173	181	184	188	164	186	166	165	166	166	169
Four Ball Wear - Scar Diameter	0.902	0.454	0.464	0.464	0.708	0.812	0.791	0.783	0.695	0.817	0.794

Fig. 11

	Blend 5	Blend 6	Blend 7	Blend 14	Blend 15	Blend 16	Blend 17	Blend 18	Blend 19	Blend 23	Blend 24
Batch Number	1	1	1	1	1	1	1	1	1	1	1
Description	PAO 4 + all Meridian	PAO 4 + all Meridian	PAO 4 + all Meridian	mPAO 65 + Meridian	mPAO 65 + Meridian	mPAO 65 + Meridian	mPAO 65 + Meridian	mPAO 65	mPAO 65	mPAO 65	mPAO 65
AKG 6043	10	10	10	10	10	10	10	10	10	10.00	10
PAO 4	51.9	47.9	43.9	58.9	49.9	39.9	49.9	50	43.9	38.90	29.9
Meridian VM	38	42	46	10	20	25	30				
mPAO 65				20	20	25	10	30	40	50.00	80
Kinematic Viscosity, 100C	12.9	14.75	16.96	8.999	12.42	16.82	13.02	8.57	11.13	14.66	19.64
Kinematic Viscosity, 40C	67.75	79.70	93.77	47.51	66.85	99.79	70.62	46.53	54.66	92.06	133.4
Viscosity Index	194	195	197	173	181	184	188	184	166	166	169
LAST NONSEIZURE LOAD	100	126	100	126	126	126	126	100	126	126	126
WELD LOAD	400	400	400	400	400	400	400	400	400	400	400
LOAD WEAR INDEX	66.3	71.7	67.7	69.6	76.1	76.4	72.5	68.8	69.6	72.7	75

Fig. 12

	Blend 2	Blend 3	Blend 4	Blend 5	Blend 5	Blend 6	Blend 6	Blend 7	Blend 15	Blend 16	Blend 16	Blend 17	Blend 18	Blend 18
Batch Number	1	1	1	1	2	1	2	1	1	1	2	1	1	2
Description	Ref VM PAO4	Ref VM PAO4	Ref VM PAO4	PAO 4 + all Meridian	PAO 4 + all Meridian	PAO 4 + all Meridian	PAO 4 + all Meridian	PAO 4 + all Meridian	mPAO 65 + Meridian	mPAO 65 + Meridian	mPAO 65 + Meridian	mPAO 65 + Meridian	mPAO 65 + Meridian	mPAO 65 + Meridian
ANG 6043	10	10	10	10	10	10	10	10	10	10	10	10	10	10
PAO 4	64.9	69.9	72.9	51.9	51.9	47.9	47.9	43.9	59.9	49.9	49.9	39.9	49.9	49.9
Ref. Conventional VM	25	20	17											
Meridian VM				38	38	42	42	46	10	20	20	25	30	30
mPAO 65									20	20	20	25	10	10
Kinematic Viscosity, 100C	13.9	9.64	9.66	12.9	12.85	14.76	14.74	16.96	6.999	12.42	12.33	16.52	13.02	13.07
Kinematic Viscosity, 40C	76.19	56.9	47.62	67.75	67.82	79.78	79.62	93.77	47.51	66.86	68.57	99.79	70.62	70.92
Viscosity Index	189	154	193	194	193	195	195	197	173	161	161	184	166	166
HFRR Avg Wear Scar	191	200	196	188	204	206	213	182	214	200	181	189	201	196
HFRR Avg Friction Coef.	0.098	0.094	0.096	0.094	0.082	0.089	0.073	0.085	0.106	0.109	0.119	0.104	0.107	0.116

	Blend 19	Blend 20	Blend 20	Blend 21	Blend 22	Blend 23	Blend 24	Blend 24	Blend 25
Batch Number	1	1	2	1	1	1	1	2	1
Description	mPAO 65	mPAO 65	mPAO 65	mPAO 65	mPAO 65	mPAO 65	mPAO 65	mPAO 65	mPAO 65
ANG 6043	10	10	10	10	10	10	10.00	10.00	10
PAO 4	90	49.9	49.9	48.9	57.9	41.4	39.90	39.90	29.9
Ref. Conventional VM									
Meridian VM									
mPAO 65	30	40	40	41	32	46.5	50.0	50.0	60
Kinematic Viscosity, 100C	8.57	11.13	11.21	11.54	9.08	14.13	14.66	14.8	19.64
Kinematic Viscosity, 40C	46.53	64.66	65.32	67.65	49.66	87.8	92.06	93.05	133.4
Viscosity Index	164	166	166	166	166	166	166	167	169
HFRR Avg Wear Scar	201	199	186	201	212	185	184	195	199
HFRR Avg Friction Coef.	0.111	0.091	0.096	0.085	0.082	0.08	0.087	0.086	0.081

HIGH VISCOSITY INDEX LUBRICATING OIL BASE STOCK AND VISCOSITY MODIFIER COMBINATIONS, AND LUBRICATING OILS DERIVED THEREFROM

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to U.S. Provisional Application Ser. No. 61/717,947 filed Oct. 24, 2012, herein incorporated by reference in its entirety.

FIELD

[0002] This disclosure relates to high viscosity index lubricating oil base stock (e.g., metallocene catalyzed polyalphaolefin and polyalphaolefin fluid) and viscosity modifier (e.g., ester-containing copolymer) combinations, lubricating oils derived therefrom, processes for preparing same, and methods of use thereof. This disclosure relates to lubricating driveline devices, e.g., gears and transmissions, using the lubricating oils to improve fuel efficiency without sacrificing driveline device durability.

BACKGROUND

[0003] Environmental regulations are driving vehicle fuel economy standards and there is increased emphasis on and market demand for higher efficiency driveline fluids, particularly axle oils that can deliver fuel economy and maintain hardware protection capability. A proven approach to enhancing lubricant derived fuel efficiency is lower fluid viscosity. Since equipment durability cannot be compromised, equal or lower viscosity lubricants must deliver improved efficiency while retaining the same level of protection against various types of hardware damage (e.g., wear, micropitting, scuffing, scoring, and the like). Improved durability and reduced component wear increases equipment operating life and reduces maintenance costs and downtime. Improved shear stability is likewise desirable to provide enduring performance (i.e., oil film stability) throughout the useful life of the lubricant. Additionally, different transmission applications have specific friction requirements, some of which benefit from higher friction.

[0004] Lubricants in commercial use today are prepared from a variety of natural and synthetic base stocks admixed with various additive packages and solvents depending upon their intended application. The base stocks typically include mineral oils, polyalphaolefins (PAO), gas-to-liquid base oils (GTL), silicone oils, phosphate esters, diesters, polyol esters, and the like.

[0005] Viscosity index improvers are known to be added to lubricating oil compositions to reduce the change in viscosity of the lubricant as a function of temperature. The most conventional types of viscosity index improvers used in axle and transmission oil applications include polyisobutylene and polymers of methacrylates. More recent viscosity index improver technologies consist of olefins (such as copolymers of alpha-olefins and maleic anhydride and esterified derivatives thereof). These viscosity index improvers tend to incorporate ester functional groups in pendant/granted/branched groups. The ester functional groups may be derived from linear alkyl alcohols with 1 to 40 carbon atoms. Recent attempts have been made to produce viscosity index improvers from copolymers of alpha-olefins. However, such viscosity index improvers remain susceptible to viscosity loss when

subjected to high shear conditions. Low temperature flow, oxidation stability, deposit control, thickening efficiency, and shear stability are performance attributes that can be controlled by design. Different core chemical structures and evolving process technologies enable design of molecules that deliver varying degrees of performance in these areas.

[0006] Lubricants capable of performing at lower viscosity (m, for instance, driveline devices) typically provide increased fuel economy (thus improving corporate average fuel efficiency (CAFE), NEDC (European Driving Cycle), or FTP-75 (Federal Test Procedure), or Japanese test cycle (JC-08)). Conversely, higher viscosity fluids contribute to elevated gear and transmission operating temperatures, which are believed to reduce fuel economy and diminish durability.

[0007] Driveline power transmitting devices such as axles and transmissions-present highly complex technological challenges for axle and manual transmission lubricants. These lubricants are required to ensure hardware durability in the form wear protection and high load-carrying capacity, while delivering enhanced fuel efficiency benefits over extended periods. Additionally, transmissions typically require specific frictional characteristics of fluids that are compatible with synchronizer material or design. One of the important parameters influencing performance is lubricant viscosity. Lubricants capable of performing at lower viscosity typically provide increased fuel economy. However viscosity that is too low to maintain sufficient and stable oil film between surface asperities results in elevated gear and transmission operating temperatures, which are believed to reduce fuel economy due to higher friction in contact zones. Therefore, increasing lubricant viscosity is conventionally believed to provide better wear protection and durability to gears and transmissions.

[0008] Consequently, it would be desirable to provide a correctly balanced lubricant composition to meet the needs of mechanical devices such as gears and transmissions, especially axle fluids and manual transmission fluids (MTFs). The discovery of new ways to control or adjust frictional properties of a lube formulation would be very beneficial.

[0009] The present disclosure provides solutions and advantages, which shall become apparent as described below.

SUMMARY

[0010] This disclosure relates in part to a lubricating composition comprising:

[0011] a first base stock component comprising one or more metallocene catalyzed polyalphaolefins (mPAOs), each mPAO having a kinematic viscosity (Kv_{100}) from 40 cSt to 155 cSt and a viscosity index (VI) from 150 to 207;

[0012] a second base stock comprising one or more polyalphaolefins (PAOs), each PAO having a kinematic viscosity (Kv_{100}) less than 10 cSt and a VI from 130 to 145; and

[0013] a viscosity modifier comprising a copolymer having units derived from monomers of (i) an α -olefin and (ii) an ethylenically unsaturated carboxylic acid or derivatives thereof esterified with an alcohol;

[0014] wherein at least one of wear control (as determined by ASTM D4172), load carrying capacity (as determined by ASTM D2783) and traction reduction (as determined by Mini-Traction Machine (MTM) Ball-on-Disc apparatus) is improved in a driveline device lubricated with said lubricating composition as compared to at least one of wear control, load carrying capacity and traction reduction achieved with a

lubricating composition containing a viscosity modifier other than said viscosity modifier copolymer, at an equal or lower kinematic viscosity ($Kv@100^{\circ}C.$).

[0015] This disclosure also relates in part to a process for producing the above lubricating composition, said process comprising:

[0016] providing a first base stock component comprising one or more metallocene catalyzed polyalphaolefins (mPAOs), each mPAO having a kinematic viscosity (Kv_{100}) from 40 cSt to 155 cSt and a viscosity index (VI) from 150 to 207;

[0017] providing a second base stock comprising one or more polyalphaolefins (PAOs), each PAO having a kinematic viscosity (Kv_{100}) less than 10 cSt and a VI from 130 to 145;

[0018] providing a viscosity modifier comprising a copolymer having units derived from monomers of (i) an α -olefin and (ii) an ethylenically unsaturated carboxylic acid or derivatives thereof esterified with an alcohol; and

[0019] blending the first base stock component, second base stock component and viscosity modifier in amounts sufficient to produce the lubricating composition.

[0020] This disclosure further relates in part to a lubricant comprising the above lubricating composition, e.g., axle fluids and manual transmission fluids (MTFs).

[0021] This disclosure yet further relates in part to a method of lubricating a mechanical device comprising supplying to the device the above lubricating composition. The mechanical device comprises a driveline device, e.g., gears or transmissions.

[0022] This disclosure further relates in part to a method for improving fuel efficiency, while maintaining or improving wear control, load carrying capacity and/or traction reduction in a driveline device, e.g., gears or transmissions, lubricated with a lubricating composition, by using a lubricating composition comprising: a first base stock component comprising one or more metallocene catalyzed polyalphaolefins (mPAOs), each mPAO having a kinematic viscosity (Kv_{100}) from 40 cSt to 155 cSt and a viscosity index (VI) from 150 to 207; a second base stock comprising one or more polyalphaolefins (PAOs), each PAO having a kinematic viscosity (Kv_{100}) less than 10 cSt and a VI from 130 to 145; and a viscosity modifier comprising a copolymer having units derived from monomers of (i) an α -olefin and (ii) an ethylenically unsaturated carboxylic acid or derivatives thereof esterified with an alcohol. In driveline devices such as axles, higher viscosity fluids can result in lower fuel efficiency due to churning losses. The internal friction of the fluid measured by its traction properties is an indicator of its efficiency benefits in high pressure contact areas within axles. The method of blending of this disclosure delivers lower traction and lower viscosity fluids.

[0023] It has been surprisingly found that the lubricating compositions of this disclosure exhibit improved wear control (as determined by ASTM D4172), load carrying capacity (as determined by ASTM D2783) and/or traction reduction (as determined by Mini-Traction Machine (MTM) Ball-on-Disc apparatus) with said lubricating composition as compared to wear control, load carrying capacity and traction reduction achieved, at an equal or lower kinematic viscosity ($Kv@100^{\circ}C.$), with a lubricating composition containing a viscosity modifier other than a viscosity modifier comprising a copolymer having units derived from monomers of (i) an α -olefin and (ii) an ethylenically unsaturated carboxylic acid or derivatives thereof esterified with an alcohol.

[0024] Further objects, features and advantages of the present disclosure will be understood by reference to the following drawings and detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025] FIG. 1 depicts Four-Ball Wear Scar (ASTM D4172) results for lubricating compositions in Example 1. Consistently lower wear is achieved by incorporating a viscosity modifier comprising a copolymer having units derived from monomers of (i) an α -olefin and (ii) an ethylenically unsaturated carboxylic acid or derivatives thereof esterified with an alcohol.

[0026] FIG. 2 depicts LWI results which are a measure of the relative ability of a lubricant to prevent wear under applied loads. LWI is calculated from data obtained from the Four Ball EP Method (ASTM D2783) in Example 2. Across a broad range of finished lubricant kinematic viscosity at $100^{\circ}C.$ (Kv_{100}), the combination of viscosity modifier and mPAO 65 showed surprisingly higher LWI than either the Meridian VM or the mPAO 65 alone.

[0027] FIG. 3 depicts average friction coefficient measurements for lubricating compositions in Example 2. The combination of mPAO 65 and Meridian show surprisingly higher friction than other base oil and/or VM combinations indicating the possibility to control friction of lubricants designed for automotive transmission applications such as continuously variable transmissions (CVT) or infinitely variable transmissions (IVT).

[0028] FIG. 4 depicts average traction coefficient for lubricating compositions in Example 1. Improved traction coefficients are observed over a range of finished lubricant kinematic viscosity at $100^{\circ}C.$ for these compositions compared to conventional PIB-based viscosity modifier.

[0029] FIG. 5 is a tabular listing of tapered roller bearing 40-hr shear stability test results for lubricating compositions in Example 3.

[0030] FIG. 6 depicts 40-hr shear kinematic viscosity (Kv_{100}) loss (%) for lubricating compositions in Example 3. The reduction in viscosity loss observed with the combination of Meridian and mPAO 150 compared to either high viscosity component by itself is unexpected.

[0031] FIG. 7 depicts FZG scuffing testing results for lubricating compositions in Example 4. Results indicate unexpected directional improvement in wear protection with higher concentration of Meridian viscosity modifier even at lower finished fluid viscosity.

[0032] FIG. 8 depicts thermal oxidation results for lubricating compositions in Example 4. Oxidation and deposit control in severe L60-1 test improves with incorporation of Meridian viscosity modifier.

[0033] FIG. 9 depicts L-42 high speed shock testing results for lubricating compositions in Example 4.

[0034] FIG. 10 shows the results of 4-Ball Wear Scar (ASTM D4172) for the designated lubricant compositions (i.e., blends) of Example 1.

[0035] FIG. 11 shows the results of 4-Ball EP (ASTM D2783) load wear index for the designated lubricant compositions (i.e., blends) of Example 2.

[0036] FIG. 12 shows the results of High Frequency Reciprocating Rig (HFRR) friction coefficient for the designated lubricant compositions (i.e., blends) of Example 2.

DETAILED DESCRIPTION

[0037] All numerical values within the detailed description and the claims herein are modified by “about” or “approximately” the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

[0038] For purposes of this disclosure and the claims thereto, a polymer is referred to as comprising homopolymers and copolymers, where copolymers include any polymer having two or more chemically distinct monomers.

[0039] For the purposes of this disclosure and the claims thereto the term “polyalphaolefin” or “PAO” includes homopolymers and copolymers of C_3 or greater alphaolefin monomers.

[0040] The lubricating compositions of this disclosure exhibit improved wear control (as determined by ASTM D4172), improved load carrying capacity (as determined by ASTM D2783) and/or improved traction reduction (as determined by Mini-Traction Machine (MTM) Ball-on-Disc apparatus) as compared to wear control, load carrying capacity and traction reduction achieved, at an equal or lower kinematic viscosity ($Kv@100^\circ C.$), with a lubricating composition containing a viscosity modifier other than a viscosity modifier comprising a copolymer having units derived from monomers of (i) an α -olefin and (ii) an ethylenically unsaturated carboxylic acid or derivatives thereof esterified with an alcohol.

[0041] The lubricating compositions of this disclosure are also capable of providing at least one of improved oxidative stability, reduced mechanical device operating temperatures, increased mechanical device durability, improved shear stability, improved viscosity index, improved low temperature viscometrics and improved high temperature viscometrics.

[0042] In an embodiment, this disclosure relates to a combination of a high viscosity synthetic base stock and an ester-containing viscosity modifier that enables improvement in wear control, load carrying capacity and traction and provides improved efficiency at equal or lower kinematic viscosity ($Kv@100^\circ C.$). Current high performance commercial axle fluids are blended with low viscosity synthetic base stocks (such as <10 cSt PAO) in combination with conventional viscosity modifiers. In axles, higher viscosity fluids can result in lower fuel efficiency due to churning losses. The internal friction of the fluid measured by its traction properties provides an indicator of its efficiency benefits in high pressure contact areas within axles. The method of blending a high viscosity synthetic base stock and an ester-containing viscosity modifier in accordance with this disclosure provides lower traction and lower viscosity fluids.

[0043] This disclosure relates to lubricating driveline devices, e.g., gears and transmissions, using the lubricating oils to improve fuel efficiency without sacrificing driveline device durability.

Lubricating Oil Base Stocks:

[0044] A wide range of lubricating oils is known in the art. Lubricating oils that are useful in the present disclosure are both natural oils and synthetic oils. Natural and synthetic oils (or mixtures thereof) can be used unrefined, refined, or rerefined (the latter is also known as reclaimed or reprocessed oil). Unrefined oils are those obtained directly from a natural or synthetic source and used without added purification. These include shale oil obtained directly from retorting

operations, petroleum oil obtained directly from primary distillation, and ester oil obtained directly from an esterification process. Refined oils are similar to the oils discussed for unrefined oils except refined oils are subjected to one or more purification steps to improve the at least one lubricating oil property. One skilled in the art is familiar with many purification processes. These processes include solvent extraction, secondary distillation, acid extraction, base extraction, filtration, and percolation. Rerefined oils are obtained by processes analogous to refined oils but using an oil that has been previously used as a feed stock.

[0045] Groups I, II, III, IV, V and VI are broad categories of base oil stocks developed and defined by the American Petroleum Institute (API Publication 1509; www.API.org) to create guidelines for lubricant base oils. Group I base stocks generally have a viscosity index of between 80 to 120 and contain greater than 0.03% sulfur and less than 90% saturates. Group II base stocks generally have a viscosity index of between 80 to 120, and contain less than or equal to 0.03% sulfur and greater than or equal to 90% saturates. Group III stock generally has a viscosity index greater than 120 and contains less than or equal to 0.03% sulfur and greater than 90% saturates. Group IV includes polyalphaolefins (PAO). Group V base stocks include base stocks not included in Groups I-IV. The table below summarizes properties of each of these six groups.

[0046] Group VI are polyinternal olefins (“PIO”). Polyinternal olefins are long-chain hydrocarbons, typically a linear backbone with some branching randomly attached; they are obtained by oligomerization of internal n -olefins. The catalyst is usually a BF_3 complex with a proton source that leads to a cationic polymerization, or promoted BF_3 or $AlCl_3$ catalyst system. The process to produce polyinternal olefins (PIO) consists of four steps: reaction, neutralization/washing, hydrogenation and distillation. These steps are somewhat similar to PAO process. PIO are typically available in low viscosity grades, 4 cSt, 6 cSt and 8 cSt. If necessary, low viscosity, 1.5 to 3.9 cSt can also be made conveniently by the BF_3 process or other cationic processes. Typically, the n -olefins used as starting material are $n-C_{12}$ - C_{18} internal olefins, more preferably, $n-C_{14}$ - C_{16} olefins are used. PIO can be made with VI and pour points very similar to PAO, only slightly inferior. They can be used in engine and industrial lubricant formulations. For more detailed discussion, see Chapter 2, Polyinternalolefins in the book, “Synthetics, Mineral Oils, and Bio-Based Lubricants-Chemistry and Technology” Edited by Leslie R. Rudnick, p. 37-46, published by CRC Press, Taylor & Francis Group, 2006; or “Polyinternal Olefins” by Corsico, G.; Mattei, L.; Roselli, A.; Gommellini, Carlo. EURON, Milan. Italy. Chemical Industries (Dekker) (1999), 77 (Synthetic Lubricants and High-Performance Functional Fluids, (2nd Edition)), 53-62. Publisher: Marcel Dekker, Inc. PIO was classified by itself as Group VI fluid in API base stock classification

	Base Stock Properties		
	Saturates	Sulfur	Viscosity Index
Group I	<90 and/or	>0.03% and	≥ 80 and <120
Group II	≥ 90 and	$\leq 0.03\%$ and	≥ 80 and <120
Group III	≥ 90 and	$\leq 0.03\%$ and	≥ 120

-continued

Base Stock Properties		
Saturates	Sulfur	Viscosity Index
Group IV	Includes polyalphaolefins (PAO)	
Group V	All other base oil stocks not included in Groups I, II, III or IV	
Group VI	Polyinternal olefins (PIO)	

[0047] Natural oils include animal oils, vegetable oils (castor oil and lard oil, for example), and mineral oils. Animal and vegetable oils possessing favorable thermal oxidative stability can be used. Of the natural oils, mineral oils are preferred. Mineral oils vary widely as to their crude source, for example, as to whether they are paraffinic, naphthenic, or mixed paraffinic-naphthenic. Oils derived from coal or shale are also useful in the present disclosure. Natural oils vary also as to the method used for their production and purification, for example, their distillation range and whether they are straight run or cracked, hydrorefined, or solvent extracted.

[0048] Group II and/or Group III hydroprocessed or hydrocracked base stocks, as well as synthetic oils such as polyalphaolefins, alkyl aromatics and synthetic esters, i.e., Group IV and Group V oils are also well known base stock oils.

[0049] Synthetic oils include hydrocarbon oil such as polymerized and interpolymerized olefins (polybutylenes, polypropylenes, propylene isobutylene copolymers, ethylene-olefin copolymers, and ethylene-alphaolefin copolymers, for example). Polyalphaolefin (PAO) oil base stocks, the Group IV API base stocks, are a commonly used synthetic hydrocarbon oil. By way of example, PAOs derived from C₈, C₁₀, C₁₂, C₁₄ olefins or mixtures thereof may be utilized. See U.S. Pat. Nos. 4,956,122; 4,827,064; and 4,827,073, which are incorporated herein by reference in their entirety. Group IV oils, that is, the PAO base stocks have viscosity indices preferably greater than 130, more preferably greater than 135, still more preferably greater than 140.

[0050] Esters in a minor amount may be useful in the lubricating oils of this disclosure. Additive solvency and seal compatibility characteristics may be secured by the use of esters such as the esters of dibasic acids with monoalkanols and the polyol esters of monocarboxylic acids. Esters of the former type include, for example, the esters of dicarboxylic acids such as phthalic acid, succinic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acid, alkenyl malonic acid, etc., with a variety of alcohols such as butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, etc. Specific examples of these types of esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, etc.

[0051] Particularly useful synthetic esters are those which are obtained by reacting one or more polyhydric alcohols, preferably the hindered polyols such as the neopentyl polyols; e.g., neopentyl glycol, trimethylol ethane, 2-methyl-2-propyl-1,3-propanediol, trimethylol propane, pentaerythritol and dipentaerythritol with alkanolic acids containing at least 4 carbon atoms, preferably C₅ to C₃₀ acids such as saturated straight chain fatty acids including caprylic acid, capric acids, lauric acid, myristic acid, palmitic acid, stearic acid, arachic acid, and behenic acid, or the corresponding branched chain

fatty acids or unsaturated fatty acids such as oleic acid, or mixtures of any of these materials.

[0052] Esters should be used in an amount such that the improved wear and corrosion resistance provided by the lubricating oils of this disclosure are not adversely affected. The esters preferably have a D5293 viscosity of less than 10,000 cP at -35° C.

[0053] Non-conventional or unconventional base stocks and/or base oils include one or a mixture of base stock(s) and/or base oil(s) derived from: (1) one or more Gas-to-Liquids (GTL) materials, as well as (2) hydrodewaxed, or hydroisomerized/cat (and/or solvent) dewaxed base stock(s) and/or base oils derived from synthetic wax, natural wax or waxy feeds, mineral and/or non-mineral oil waxy feed stocks such as gas oils, slack waxes (derived from the solvent dewaxing of natural oils, mineral oils or synthetic oils; e.g., Fischer-Tropsch feed stocks), natural waxes, and waxy stocks such as gas oils, waxy fuels hydrocracker bottoms, waxy raffinate, hydrocrackate, thermal crackates, foots oil or other mineral, mineral oil, or even non-petroleum oil derived waxy materials such as waxy materials recovered from coal liquefaction or shale oil, linear or branched hydrocarbyl compounds with carbon number of 20 or greater, preferably 30 or greater and mixtures of such base stocks and/or base oils.

[0054] GTL materials are materials that are derived via one or more synthesis, combination, transformation, rearrangement, and/or degradation/deconstructive processes from gaseous carbon-containing compounds, hydrogen-containing compounds and/or elements as feed stocks such as hydrogen, carbon dioxide, carbon monoxide, water, methane, ethane, ethylene, acetylene, propane, propylene, propyne, butane, butylenes, and butynes. GTL base stocks and/or base oils are GTL materials of lubricating viscosity that are generally derived from hydrocarbons; for example, waxy synthesized hydrocarbons, that are themselves derived from simpler gaseous carbon-containing compounds, hydrogen-containing compounds and/or elements as feed stocks. GTL base stock(s) and/or base oil(s) include oils boiling in the lube oil boiling range (1) separated/fractionated from synthesized GTL materials such as, for example, by distillation and subsequently subjected to a final wax processing step which involves either or both of a catalytic dewaxing process, or a solvent dewaxing process, to produce lube oils of reduced/low pour point; (2) synthesized wax isomerates, comprising, for example, hydrodewaxed or hydroisomerized cat and/or solvent dewaxed synthesized wax or waxy hydrocarbons; (3) hydrodewaxed or hydroisomerized cat and/or solvent dewaxed Fischer-Tropsch (F-T) material (i.e., hydrocarbons, waxy hydrocarbons, waxes and possible analogous oxygenates); preferably hydrodewaxed or hydroisomerized/ followed by cat and/or solvent dewaxing dewaxed F-T waxy hydrocarbons, or hydrodewaxed or hydroisomerized/ followed by cat (or solvent) dewaxing dewaxed, F-T waxes, or mixtures thereof.

[0055] GTL base stock(s) and/or base oil(s) derived from GTL materials, especially, hydrodewaxed or hydroisomerized/ followed by cat and/or solvent dewaxed wax or waxy feed, preferably F-T material derived base stock(s) and/or base oil(s), are characterized typically as having kinematic viscosities at 100° C. of from 2 mm²/s to 50 mm²/s (ASTM D445). They are further characterized typically as having pour points of -5° C. to -40° C. or lower (ASTM D97). They are also characterized typically as having viscosity indices of 80 to 140 or greater (ASTM D2270).

[0056] In addition, the GTL base stock(s) and/or base oil(s) are typically highly paraffinic (>90% saturates), and may contain mixtures of monocycloparaffins and multicycloparaffins in combination with non-cyclic isoparaffins. The ratio of the naphthenic (i.e., cycloparaffin) content in such combinations varies with the catalyst and temperature used. Further, GTL base stock(s) and/or base oil(s) typically have very low sulfur and nitrogen content, generally containing less than 10 ppm, and more typically less than 5 ppm of each of these elements. The sulfur and nitrogen content of GTL base stock(s) and/or base oil(s) obtained from F-T material, especially F-T wax, is essentially nil. In addition, the absence of phosphorous and aromatics make this materially especially suitable for the formulation of low SAP products.

[0057] The term GTL base stock and/or base oil and/or wax isomerate base stock and/or base oil is to be understood as embracing individual fractions of such materials of wide viscosity range as recovered in the production process, mixtures of two or more of such fractions, as well as mixtures of one or two or more low viscosity fractions with one, two or more higher viscosity fractions to produce a blend wherein the blend exhibits a target kinematic viscosity.

[0058] The GTL material, from which the GTL base stock(s) and/or base oil(s) is/are derived is preferably an F-T material (i.e., hydrocarbons, waxy hydrocarbons, wax).

[0059] Base oils for use in the formulated lubricating oils useful in the present disclosure are any of the variety of oils corresponding to API Group I, Group II, Group III, Group IV, Group V and Group VI oils and mixtures thereof, preferably API Group II, Group III, Group IV, Group V and Group VI oils and mixtures thereof, more preferably the Group III to Group VI base oils due to their exceptional volatility, stability, viscometric and cleanliness features. Minor quantities of Group I stock, such as the amount used to dilute additives for blending into formulated lube oil products, can be tolerated but should be kept to a minimum, i.e. amounts only associated with their use as diluent/carrier oil for additives used on an "as-received" basis. Even in regard to the Group II stocks, it is preferred that the Group II stock be in the higher quality range associated with that stock, i.e. a Group II stock having a viscosity index in the range $100 < VI < 120$.

[0060] In addition, the GTL base stock(s) and/or base oil(s) are typically highly paraffinic (>90% saturates), and may contain mixtures of monocycloparaffins and multicycloparaffins in combination with non-cyclic isoparaffins. The ratio of the naphthenic (i.e., cycloparaffin) content in such combinations varies with the catalyst and temperature used. Further, GTL base stock(s) and/or base oil(s) and hydrodewaxed, or hydroisomerized/cat (and/or solvent) dewaxed base stock(s) and/or base oil(s) typically have very low sulfur and nitrogen content, generally containing less than 10 ppm, and more typically less than 5 ppm of each of these elements. The sulfur and nitrogen content of GTL base stock(s) and/or base oil(s) obtained from F-T material, especially F-T wax, is essentially nil. In addition, the absence of phosphorous and aromatics make this material especially suitable for the formulation of low sulfur, sulfated ash, and phosphorus (low SAP) products.

[0061] Polyalphaolefins (PAOs) are preferred lubricating oil basestocks of this disclosure. The PAOs can preferably comprise one or more C_8 to C_{12} monomers. The PAOs have a viscosity (Kv_{100}) from 2 to 700 cSt at 100° C., preferably from 3 to 155 cSt at 100° C., and more preferably from 4 to 150 cSt at 100° C.; and a viscosity index (VI) from 130 to 207, preferably from 140 to 200, and more preferably from 150 to

197. As used herein, viscosity (Kv_{100}) is determined by ASTM D 445-01, and viscosity index (VI) is determined by ASTM D 2270-93 (1998).

[0062] The PAOs useful in this disclosure can have a pour point (PP) less than -25° C.; a molecular weight distribution (Mw/Mn) less than 2.0; and a glass transition temperature T_g less than -60° C.

[0063] In another embodiment according to the present disclosure, any PAO described herein may have a kinematic viscosity (Kv) at 100° C. in any of the following ranges: from 65 to 1,000 cSt, from 100 to 950 cSt, from 250 cSt to 900 cSt, from 400 cSt to 800 cSt, wherein all values are measured by ASTM D445-01.

[0064] The PAOs useful in this disclosure have a high viscosity index and a Kv_{100} of 2 cSt or more, alternatively 3 cSt or more, alternatively 4 cSt or more, up to 700 cSt, with a VI of 130 or more, alternatively 140 or more, alternatively 150 or more. Usually base stock VI is a function of fluid viscosity. Usually, the higher the VI, the better it is for lube application. Base stock VI also depends on feed composition. Fluids made from single 1-octene, 1-nonene, 1-decene, or 1-dodecene have excellent VI and good low pour point. Fluids made from two or more olefins selected from C_8 to C_{12} alphaolefins generally have excellent high VI and superior low pour points if the average carbon chain length of feed LAOs is kept within 8 to 12 carbons. A relatively much lower average chain length in the feed (much below 6 carbons) of the mixed LAO would result in lower VI. Too high of a average chain length in the feed (much above 12 carbons) of the mixed LAO would result in very high pour point, around room temperature.

[0065] The viscosity-temperature relationship of lubricating oil is one of the critical criteria which must be considered when selecting a lubricant for a particular application. Viscosity Index (VI) is an empirical, unitless number which indicates the rate of change in the viscosity of an oil within a given temperature range and is related to kinematic viscosities measured at 40° C. and 100° C. (typically using ASTM Method D 445). Fluids exhibiting a relatively large change in viscosity with temperature are said to have a low viscosity index. The low VI oil, for example, will thin out at elevated temperatures faster than the high VI oil. Usually, the high VI oil is more desirable because it has higher viscosity at higher temperature, which translates into better or thicker lubrication film and better protection of the contacting machine elements. As the oil operating temperature decreases, the viscosity of the high VI oil will not increase as much as the viscosity of low VI oil. This is advantageous because the excessive high viscosity of the low VI oil will decrease the efficiency of the operating machine. Thus high VI oil has performance advantages in both high and low temperature operation.

[0066] The PAOs useful in this disclosure have low pour points (PP) less than -25° C. preferably less than -30° C., and more preferably less than -35° C. As used herein, pour point is determined by ASTM D97.

[0067] In an embodiment of this disclosure, any PAO described herein may have a pour point of less than -25° C. (as measured by ASTM D97), preferably less than -35° C., preferably less than -45° C., preferably less than -55° C., preferably less than -65° C., and preferably between -25° C. and -75° C.

[0068] The PAOs useful in this disclosure have a narrow molecular weight distribution (Mw/Mn) less than 2.0, preferably less than 1.95, and more preferably less than 1.9 as

synthesized. As used herein, molecular weight distribution (Mw/Mn) is determined by GPC using a column for medium to low molecular weight polymers, tetrahydrofuran as solvent and polystyrene as calibration standard.

[0069] The PAOs useful in this disclosure have a Mw of 100,000 g/mol or less, or between 2000 and 80,000 g/mol, or between 2500 and 60,000 g/mol, or between 2800 and 50,000 g/mol, or between 3360 and 40,000 g/mol. Preferred Mw's include those from 840 to 55,100 g/mol, or from 900 to 45,000 g/mol, or 1000 to 40,000 g/mol, or 2,000 to 37,500 g/mol. Alternatively preferred Mw's include 2240 to 67900 g/mol and 2240 to 37200 g/mol.

[0070] The PAOs useful in this disclosure preferably have an Mn of 50,000 g/mol or less, or 40,000 g/mol or less, or between 2000 and 40,000 g/mol, or between 2500 and 30,000 g/mol, preferably between 5000 and 20,000 g/mol. Preferred Mn ranges include those from 2800 to 10,000 g/mol or from 2800 to 8,000 g/mol. Alternatively preferred Mn ranges are from 2000 to 20,900 g/mol, or 2800 to 20,000 g/mol, or 2000 to 17000 g/mol, or 2000 to 12000 g/mol, or 2800 to 29000 g/mol, or 2800 to 17000 g/mol, or 2000 to 5000 g/mol.

[0071] The Mw and Mn are measured by GPC using a column for medium to low molecular weight polymers, tetrahydrofuran as solvent and polystyrene as calibration standard, correlated with the fluid viscosity according to a power equation.

[0072] In another embodiment, the PAOs described herein have a narrow molecular weight distribution of greater than 1 and less than 2, alternatively less than 1.95, alternatively less than 1.90, alternatively less than 1.85. The Mn and Mw are measured by gel permeation chromatography (GPC) using a column for medium to low molecular weight polymers, tetrahydrofuran as solvent and narrow molecular weight distribution polystyrene as calibration standard, correlated with the fluid viscosity according to a power equation. The MWD of PAO is a function of fluid viscosity. Alternatively any of the polyalphaolefins described herein preferably have an Mw/Mn of between 1 and 2.0, alternatively between 1 and 1.95, depending on fluid viscosity.

[0073] The PAOs useful in this disclosure have low glass transition temperature T_g , less than -60°C ., preferably less than -70°C ., and more preferably less than -80°C . As used herein, glass transition temperature T_g is determined by differential scanning calorimetry (DSC). The polyolefin products produced in accordance with the process of this disclosure have no crystallization peak as measured by differential scanning calorimetry and high thermal stability.

[0074] The PAOs useful in this disclosure can comprise a single alphaolefin monomer type, or may comprise two or more different alphaolefin monomers. In one embodiment, this disclosure relates to PAOs comprising a molar amount of C_8 to C_{12} alphaolefin monomers selected from the group consisting of 55 mol % or more, 60 mol % or more, 65 mol % or more, 70 mol % or more, 75 mol % or more, 80 mol % or more, 85 mol % or more, 90 mol % or more, 95 mol % or more, 100 mol %, all based on the total moles of monomers present in the polyalphaolefin, as measured by ^{13}C NMR. When two or more alphaolefin monomers are present, it is sometimes desirable to add propylene, or butene (typically 1-butene) olefins into the feed. Use of these smaller olefins in the feed offers the advantage of lower feed cost and/or more abundant feed source. When adding C_3 or 1- C_4 olefins as one of the feed components, it is important to maintain the total

average carbon chain length of the feed LAO (linear alphaolefin) between 8 to 12 carbons.

[0075] In one or more embodiments, the PAOs comprise polymers of one or more alphaolefins (also known as 1-olefins) with carbon numbers of C_8 to C_{12} . Preferably, at least one of the alphaolefins is a linear alphaolefin (LAO); more preferably, all the alphaolefins are LAOs. Suitable LAOs include 1-octene, 1-nonene, 1-decene, 1-undecene, and 1-dodecene, and blends thereof.

[0076] In one or more embodiments, the PAO comprises polymers of two or more C_8 to C_{12} LAOs to make 'copolymer' or 'terpolymer' or higher-order copolymer combinations. Other embodiments involve polymerization of a mixture of LAOs selected from C_8 to C_{12} LAOs with even carbon numbers, preferably a mixture of two or three LAOs selected from 1-octene, 1-decene, and 1-dodecene.

[0077] In one or more embodiments, the PAO comprises polymers of a single alphaolefin species having a total carbon count of 8 to 12. In other embodiments, the PAO comprises polymers of mixed (i.e., two or more) alphaolefin species, wherein each alphaolefin species has a carbon number of 8 to 12. In other embodiments, the PAO comprises polymers of mixed alphaolefin species wherein the molar-average carbon number (" C_{LAO} ") is 8 to 12 or 9 to 11.

[0078] In another embodiment according to the present disclosure, any PAO described herein may have a density of 0.75 to 0.96 g/cm³, preferably 0.80 to 0.94 g/cm³, alternatively from 0.76 to 0.855 g/cm³.

[0079] The high viscosity PAOs useful in this disclosure are desirable for use as lubricating oil base stocks and also blend stocks with API Groups I to V or gas-to-liquid (GTL) derived lube base stocks for use in industrial and automotive engine or gear oil, especially certain high Kv₁₀₀ grades of 65 to 155 cSt which are especially desirable for use as lubricating oil base stocks or blend stocks with Groups I to V or GTL-derived lube base stocks for use in industrial and automotive engine or gear oil.

[0080] These higher viscosity PAOs can be used as lubricating oil base stocks and also superior blend stocks. They can be blend stocks with any of the API Group I to V and GTL fluids to give the optimum viscometrics, solvency, high and low temperature lubricity, etc. The PAOs can be further blended with proper additives, including antioxidants, anti-wear additives, friction modifiers, dispersants, detergents, corrosion inhibitors, defoamants, extreme pressure additives, seal swell additives, and optionally viscosity modifiers, etc. Description of typical additives can be found in the book "Lubricant Additives: Chemistry and Applications," L. R. Rudnick, ed. Marcel Dekker Inc., New York, 2001.

[0081] The PAOs can be produced by conventional methods known in the art. The preferred high viscosity PAOs used in this disclosure can be prepared from different feed olefins using metallocene catalysts. The metallocene catalyst system, products, process and feeds are described, for example, in U.S. Application Publication No. 2011/0136714.

[0082] The basestock component of the present lubricating oils will typically be from 80 to 99 weight percent of the total composition (all proportions and percentages set out in this specification are by weight unless the contrary is stated) and more usually in the range of 90 to 99 weight percent.

Viscosity Modifiers:

[0083] The viscosity modifiers useful in the lubricating compositions of the disclosure include substantially linear

polymers with a weight average molecular weight of 45,000 or less, or 35,000 or less, or 25,000 or less, or 8000 to 25,000, or 12,000 to 20,000.

[0084] The substantially linear polymers may be copolymers comprising units derived from monomers (i) an α -olefin and (ii) an ethylenically unsaturated carboxylic acid or derivatives thereof esterified with an alcohol. In one embodiment, the substantially linear polymer may be a copolymer comprising units derived from monomers (i) one or more α -olefins and (ii) one or more alkyl (meth)acrylate esters. The ethylenically unsaturated carboxylic acid may be esterified with alcohol before or after polymerization with the α -olefin. In one embodiment the ethylenically unsaturated carboxylic acid may be esterified with alcohol before polymerization with the α -olefin. In one embodiment the ethylenically unsaturated carboxylic acid may be esterified with alcohol after polymerization with the α -olefin.

[0085] A commercially available copolymer prepared by esterification before polymerization is available from Akzo Nobel sold under the tradename Ketjenlube®3700. The alcohol may have 1 to 40, or 1 to 30, or 4 to 20, or 6 to 16 carbon atoms. Examples of a suitable alcohol include 2-ethylhexanol, 2-butyloctanol, 2-hexyldecanol, 2-octyldodecanol, 2-decyltetradecanol, butanol, pentanol, hexanol, heptanol, octanol, nonanol, decanol, undecanol, dodecanol, tridecanol, tetradecanol, pentadecanol, hexadecanol, heptadecanol, octadecanol, eicosanol, or mixtures thereof. A copolymer of this type is described in more detail in U.S. Pat. Nos. 4,526, 950, 6,419,714, 6,573,224, or 6,174,843.

[0086] The ethylenically unsaturated carboxylic acid may be esterified with alcohol after polymerization with the α -olefin. A copolymer of this type may be a substantially linear polymer that may in one embodiment be (a) a copolymer comprising units derived from monomers (i) an α -olefin and (ii) an ethylenically unsaturated carboxylic acid or derivatives thereof esterified with a primary alcohol branched at the β - or higher position, wherein the copolymer typically has a reduced specific viscosity of up to 0.2, (b) a poly(meth)acrylate, or mixtures thereof.

[0087] The substantially linear polymer may be present in the lubricating compositions described herein at 0.1 wt % to 50 wt %, or 2 wt % to 40 wt %, or 5 wt % to 30 wt %, or 8 wt % to 20 wt % of the lubricating composition. In certain embodiments the lubricating composition contains 65 to 99 wt % of synthetic base stock and 1 to 35 wt % of substantially linear polymer. In other embodiments, the lubricating composition contains 75 to 98 wt % of synthetic base stock and 2 to 25 wt % of substantially linear polymer.

[0088] In one embodiment, the substantially linear polymer may be a copolymer comprising units derived from monomers (i) one or more α -olefins and (ii) one or more alkyl (meth)acrylate esters. In another embodiment the substantially linear polymer includes a mixtures of (a) a copolymer comprising units derived from monomers of (i) an α -olefin and (ii) an ethylenically unsaturated carboxylic acid or derivatives thereof esterified with a primary alcohol, and (b) a poly(meth)acrylate.

[0089] The poly(meth)acrylate (typically a polymethacrylate) can have units derived from a mixture of alkyl (meth)acrylate ester monomers containing (a) 8 to 24, or 12 to 18, or to 15 carbon atoms in the alcohol-derived portion of the ester group and (b) 6 to 11, or 8 to 11, or 8 carbon atoms in the alcohol-derived portion of the ester group, and which have 2-(C₁₋₄ alkyl)-substituents, and optionally, at least one mono-

mer selected from the group consisting of (meth)acrylic acid esters containing 1 to 7 carbon atoms in the alcohol-derived portion of the ester group and which are different from (meth)acrylic acid esters (a) and (b), vinyl aromatic compounds (or vinyl aromatic monomers); and nitrogen-containing vinyl monomers; provided that no more than 60% by weight, or no more than 50% by weight, or no more than 35% by weight of the esters contain not more than 10 carbon atoms in the alcohol-derived portion of the ester group. The linear polymer of this type is described in more detail in U.S. Pat. No. 6,124,249 or EP 0 937 769 A1. The "alcohol-derived portion" refers to the "—OR" portion of an ester, when written as R'C(=O)-OR, whether or not it is actually prepared by reaction with an alcohol. Optionally, the linear polymer may further contain a third monomer. The third monomer may be styrene, or mixtures thereof. The third monomer may be present in an amount 0% to 25% of the polymer composition, or from 1% to 15% of the composition, 2% to 10% of the composition, or even from 1% to 3% of the composition.

[0090] Typically, the mole ratio of esters (a) to esters (b) in the copolymer ranges from 95:5 to 35:65, or 90:10 to 60:40, or 80:20 to 50:50.

[0091] The esters are usually aliphatic esters, typically alkyl esters. In one embodiment the ester of (a) may be a C₁₂₋₁₅ alkyl methacrylate and the ester of (b) may be 2-ethylhexyl methacrylate.

[0092] In one embodiment, the ester groups in ester (a) contain branched alkyl groups. The ester groups may contain 2 to 65%, or 5 to 60% or greater of the ester groups having branched alkyl groups.

[0093] The C₁₋₄ alkyl substituents may be methyl, ethyl, and any isomers of propyl and butyl.

[0094] The weight average molecular weight of the poly(meth)acrylate may be 45,000 or less, or 35,000 or less, or 25,000 or less, or 8000 to 25,000, or 12,000 to 20,000.

[0095] In one embodiment the substantially linear polymer includes a copolymer comprising units derived from monomers (i) an α -olefin and (ii) an ethylenically unsaturated carboxylic acid or derivatives thereof esterified with a primary alcohol branched at the β - or higher position, wherein the copolymer typically has a reduced specific viscosity of up to 0.2, or up to 0.15, or up to 0.10, or up to 0.08. In one embodiment the reduced specific viscosity may be up to 0.08 (or 0.02 to 0.08 (or 0.02 to 0.07, 0.03 to 0.07 or 0.04 to 0.06)).

[0096] A measurement correlating with molecular weight of the copolymer (or interpolymer such as an alternating copolymer) may be expressed in terms of the "reduced specific viscosity" of the copolymer which is a recognized means of expressing the molecular size of a polymeric substance. As used herein, the reduced specific viscosity (abbreviated as RSV) is the value typically obtained in accordance with the formula $RSV = (\text{Relative Viscosity} - 1) / \text{Concentration}$, wherein the relative viscosity is determined by measuring, by means of a dilution viscometer, the viscosity of a solution of 1.6 g of the polymer in 100 cm³ of acetone and the viscosity of acetone at 30° C. For purpose of computation by the above formula, the concentration is adjusted to 1.6 g of the copolymer per 100 cm³ of acetone. A more detailed discussion of the reduced specific viscosity, also known as the specific viscosity, as well as its relationship to the average molecular weight of a copolymer, appears in Paul J. Flory, Principles of Polymer Chemistry, (1953 Edition) pages 308 et seq.

[0097] In one embodiment the copolymer may be derived from monomers (i) an α -olefin and (ii) an ethylenically unsaturated carboxylic acid or derivatives thereof,

[0098] wherein 0.1 to 99.89% of the carboxylic acid units are esterified with a primary alcohol branched at the β - or higher position,

[0099] wherein 0.1 to 99.89% of the carboxylic acid units are esterified with a linear alcohol or an alpha-branched alcohol (e.g., a secondary alcohol),

[0100] wherein 0.01 to 10% of the carboxylic acid units has at least one of an amino-, amido- and/or imido-group, and

[0101] wherein the copolymer has a reduced specific viscosity (prior to esterification) of up to 0.08.

[0102] In one embodiment the copolymer may be derived from monomers (i) an α -olefin and (ii) an ethylenically unsaturated carboxylic acid or derivatives thereof,

[0103] wherein 0.1 to 99.89% of the carboxylic acid units are esterified with a primary alcohol branched at the β - or higher position,

[0104] wherein 0.1 to 99.9% of the carboxylic acid units are esterified with a linear alcohol or an alpha-branched alcohol,

[0105] wherein 0 to 10% of the carboxylic acid units has at least one of an amino-, amido- and/or imido-group, and

[0106] wherein the copolymer has a reduced specific viscosity of up to 0.08.

[0107] A linear alcohol may include methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, nonanol, decanol, undecanol, dodecanol, tridecanol, tetradecanol, pentadecanol, hexadecanol, heptadecanol, octadecanol, nonadecanol, eicosanol, or mixtures thereof. In one embodiment the linear alcohol contains 6 to 30, or 8 to 20, or 8 to 15 carbon atoms (typically 8 to 15 carbon atoms).

[0108] The linear alcohol may include commercially available materials such as Oxo Alcohol® 7911, Oxo Alcohol® 7900 and Oxo Alcohol® 1 100 of Monsanto; Alphanol® 79 of ICI; Nafol® 1620, Alfol® 610 and Alfol® 810 of Condea (now Sasol); Epal® 610 and Epal® 810 of Ethyl Corporation (now Afton); Linevol® 79, Linevol® 91 1 and Dobanol® 25 L of Shell AG; Lial® 125 of Condea Augusta, Milan; Dehydad® and Lorol® of Henkel KGaA (now Cognis) as well as Linopol® 7-1 1 and Acropol® 91 of Uguine Kuhlmann.

[0109] In one embodiment the copolymer may be derived from monomers of (i) an α -olefin and (ii) an ethylenically unsaturated carboxylic acid or derivatives thereof,

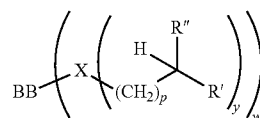
[0110] wherein 5 to 15% of the carboxylic acid units are esterified with a primary alcohol branched at the β - or higher position,

[0111] wherein 0.1 to 95% of the carboxylic acid units are esterified with a linear alcohol or an alpha-branched alcohol,

[0112] wherein 0 to less than 2% of the carboxylic acid units has at least one of an amino-, amido- and/or imido-group, and

[0113] wherein the copolymer has a reduced specific viscosity of up to 0.08.

[0114] In one embodiment the copolymer comprises units derived from monomers (i) an α -olefin and (ii) an ethylenically unsaturated carboxylic acid or derivatives thereof esterified with a primary alcohol branched at the β - or higher position. In certain embodiments the copolymer may be represented by the formula below. Ester or other groups with the primary alcohol-derived moiety branched at the β - or higher position may be represented within the $()_w$ shown in the formula:



Formula (I)

wherein

[0115] Formula (I) may comprise a copolymer backbone (BB), and one or more pendant groups as shown, wherein BB may be derived from a copolymer of (i) an α -olefin and (ii) an ethylenically unsaturated carboxylic acid or derivatives thereof (typically fumaric acid, maleic anhydride, maleic acid, (meth)acrylic acid, itaconic anhydride or itaconic acid);

[0116] X may be a functional group which either (i) contains a carbon and at least one oxygen or nitrogen atom (such as an ester or amide, or imide linkage), or (ii) is an alkylene group with 1 to 5 carbon atoms (typically $-\text{CH}_2-$), connecting the copolymer backbone and a branched hydrocarbyl group contained within $()_y$, (typically X may be a functional group which either (i) contains a carbon and at least one oxygen or nitrogen atom);

[0117] w may be the number of pendant groups attached to the copolymer backbone, which may be in the range of 2 to 2000, or 2 to 500, or 5 to 250;

[0118] y may be 0, 1, 2 or 3, provided that in at least 1 mol % of the pendant groups, y is not zero; and with the proviso that when y is 0, X is bonded to a terminal group in a manner sufficient to satisfy the valence of X, wherein the terminal group is selected from hydrogen, alkyl, aryl, a metal (typically introduced during neutralization of ester reactions; suitable metals include calcium, magnesium, barium, zinc, sodium, potassium or lithium) or ammonium cation, and mixtures thereof;

[0119] p may be an integer in the range of 1 to 15 (or 1 to 8, or 1 to 4); and

[0120] R' and R'' may independently be linear or branched hydrocarbyl groups, and the combined total number of carbon atoms present in R' and R'' may be at least 12 (or at least 16, or at least 18 or at least 20).

[0121] In different embodiments the copolymer with pendant groups may contain 0.10% to 100%, or 0.5% to 20%, or 0.75% to 10%, branched hydrocarbyl groups represented by a group within $()_y$ of the formula (I) above, expressed as a percentage of the total number of pendant groups. The pendant groups of formula (I) may also be used to define the ester groups as defined above by the phrase "esterified with a primary alcohol branched at the β - or higher position".

[0122] In different embodiments the functional groups defined by X on the formula above, may comprise at least one of $-\text{CO}_2-$, $-\text{C}(\text{O})\text{N}-$ or $-(\text{CH}_2)_v-$, wherein v is an integer in the range of 1 to 20, or 1 to 10, or 1 to 2.

[0123] In one embodiment X may be derived from an ethylenically unsaturated carboxylic acid or derivatives thereof. Examples of a suitable carboxylic acid or derivatives thereof typically include maleic anhydride, maleic acid, (meth) acrylic acid, itaconic anhydride or itaconic acid. In one embodiment the ethylenically unsaturated carboxylic acid or derivatives thereof may be at least one of maleic anhydride or maleic acid.

[0124] In one embodiment X is other than an alkylene group, connecting the copolymer backbone and the branched hydrocarbyl groups.

[0125] In different embodiments the pendant groups may be esterified, amidated or imidated functional groups.

[0126] In one embodiment the pendant groups may be derived from esterified and/or amidated functional groups.

[0127] In one embodiment the copolymer includes esterified pendant groups. The pendant groups may be derived from Guerbet alcohols. The Guerbet alcohols may contain 10 to 60, or 12 to 60, or 16 to 40 carbon atoms. In one embodiment the primary alcohol branched at the β - or higher position described herein may be a Guerbet alcohol. Methods to prepare Guerbet alcohols are disclosed in U.S. Pat. No. 4,767, 815.

[0128] Examples of suitable groups for R' and R'' on the formula defined above include the following:

[0129] 1) alkyl groups containing C_{15-16} polymethylene groups, such as 2- C_{1-15} alkyl-hexadecyl groups (e.g., 2-octyl-hexadecyl) and 2-alkyl-octadecyl groups (e.g., 2-ethyl-octadecyl, 2-tetradecyl-octadecyl and 2-hexadecyl-octadecyl);

[0130] 2) alkyl groups containing C_{13-14} polymethylene groups, such as 1- C_{1-15} alkyl-tetradecyl groups (e.g., 2-hexyl-tetradecyl, 2-decyl-tetradecyl and 2-undecyl-tridecyl) and 2- C_{1-15} alkyl-hexadecyl groups (e.g., 2-ethyl-hexadecyl and 2-dodecyl-hexadecyl);

[0131] 3) alkyl groups containing C_{10-12} polymethylene groups, such as 2- C_{1-15} alkyl-dodecyl groups (e.g., 2-octyl-dodecyl) and 2- C_{1-15} alkyl-dodecyl groups (2-hexyl-dodecyl and 2-octyl-dodecyl), 2- C_{1-15} alkyl-tetradecyl groups (e.g., 2-hexyl-tetradecyl and 2-decyl-tetradecyl);

[0132] 4) alkyl groups containing C_{6-9} polymethylene groups, such as 2- C_{1-15} alkyl-decyl groups (e.g., 2-octyl-decyl) and 2,4-di- C_{1-15} alkyl-decyl groups (e.g., 2-ethyl-4-butyl-decyl group);

[0133] 5) alkyl groups containing C_{1-5} polymethylene groups, such as 2-(3-methylhexyl)-7-methyl-decyl and 2-(1,4-dimethylbutyl)-5,7,7-trimethyl-octyl groups; and

[0134] 6) and mixtures of two or more branched alkyl groups, such as alkyl residues of oxoalcohols corresponding to propylene oligomers (from hexamer to undecamer), ethylene/propylene (molar ratio 16:1-1:11) oligomers, iso-butene oligomers (from pentamer to octamer), C_{5-17} α -olefin oligomers (from dimer to hexamer).

[0135] The pendant groups may contain a total combined number of carbon atoms on R' and R'' in the range of 12 to 60, or 14 to 50, or 16 to 40, or 18 to 40, or 20 to 36.

[0136] Each of R' and R'' may individually contain 5 to 25, or 8 to 32, or 10 to 18 methylene carbon atoms. In one embodiment the number of carbon atoms on each R' and R'' group may be 10 to 24.

[0137] Examples of suitable primary alcohol branched at the 3- or higher position include 2-ethylhexanol, 2-propyl heptanol, 2-butyloctanol, 2-hexyldecanol, 2-octyldodecanol, 2-decyltetradecanol, or mixtures thereof.

[0138] The ethylenically unsaturated carboxylic acid or derivatives thereof may be an acid or anhydride or derivatives thereof that may be wholly esterified, partially esterified or mixtures thereof. When partially esterified, other functional groups include acids, salts or mixtures thereof. Suitable salts include alkali metals, alkaline earth metals or mixtures thereof. The salts include lithium, sodium, potassium, magnesium, calcium or mixtures thereof. The unsaturated carboxylic acid or derivatives thereof includes acrylic acid, methyl acrylate, methacrylic acid, maleic acid or anhydride, fumaric acid, itaconic acid or anhydride or mixtures thereof, or substituted equivalents thereof.

[0139] Suitable examples of the ethylenically unsaturated carboxylic acid or derivatives thereof include itaconic anhydride, maleic anhydride, methyl maleic anhydride, ethyl maleic anhydride, dimethyl maleic anhydride or mixtures thereof.

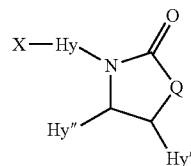
[0140] In one embodiment the ethylenically unsaturated carboxylic acid or derivatives thereof includes maleic anhydride or derivatives thereof.

[0141] Examples of an α -olefin include 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-hepta-decene 1-octadecene, or mixtures thereof. An example of a useful α -olefin is 1-dodecene. The α -olefin may be a branched α -olefin, or mixtures thereof. If the α -olefin is branched, the number of carbon atoms of the α -olefin may range from 4 to 32, or 6 to 20, or 8 to 16.

[0142] In one embodiment the copolymer of the disclosure further includes a nitrogen containing group such as those disclosed above. The nitrogen containing group may be derived from a nitrogen containing compound capable of being incorporated during copolymerization. In one embodiment the copolymer of the disclosure further includes a nitrogen containing group that may be capable of reacting with the functionalized copolymer backbone, typically for capping the copolymer backbone. The capping may result in the copolymer having ester, amide, imide or amine groups. The nitrogen group is described in more detail in PCT Patent Application No. PCT/US09/052,028.

[0143] In one embodiment the copolymer comprises units derived from monomers (i) an α -olefin and (ii) an ethylenically unsaturated carboxylic acid or derivatives thereof may be further reacted with an amine to additionally provide oxidation control. Typically, the copolymer with oxidation control contains an incorporated residue of an amine-containing compound such as morpholines, pyrrolidinones, imidazolidinones, acetamides, β -alanine alkyl esters, or mixtures thereof. Examples of suitable nitrogen-containing compounds include 3-morpholin-4-yl-propylamine, 3-morpholin-4-yl-ethylamine, [beta]-alanine alkyl esters (typically alkyl esters have 1 to 30, or 6 to 20 carbon atoms), or mixtures thereof.

[0144] In one embodiment the compounds based on imidazolidinones, cyclic carbamates or pyrrolidinones may be derived from a compound of general structure:



wherein:

X=OH or NH₂;

[0145] Hy'' may be hydrogen, or a hydrocarbyl group (typically alkyl, or C_{1-4} , or C_{2-} alkyl);

Hy may be a hydrocarbylene group (typically alkylene, or C_{1-4} , or C_{2-} alkylene); Q=>NH, >NR, >CH₂, >CHR, >CR₂, or —O— (typically >NH, or >NR) and R may be C_{1-4} alkyl.

[0146] In one embodiment the imidazolidinone includes 1-(2-amino-ethyl)-imidazolidin-2-one (may also be called

aminoethylethyleneurea), 1-(3-amino-propyl)-imidazolidin-2-one, 1-(2-hydroxy-ethyl)-imidazolidin-2-one, 1-(3-amino-propyl)-pyrrolidin-2-one, 1-(3-amino-ethyl)-pyrrolidin-2-one, or mixtures thereof.

[0147] In one embodiment the copolymer may be reacted with an amine-containing compound selected from morpholines, imidazolidinones, and mixtures thereof.

[0148] Other illustrative copolymers and interpolymers useful as viscosity modifiers of this disclosure are described, for example, in U.S. Patent Application Publication Nos. 2010/0144566 and 2011/0190182, and also WO 2011/066242, the disclosures of which are incorporated herein in their entirety.

Other Additives:

[0149] The formulated lubricating oil useful in the present disclosure may additionally contain one or more of the other commonly used lubricating oil performance additives including but not limited to dispersants, other detergents, corrosion inhibitors, rust inhibitors, metal deactivators, other antiwear agents and/or extreme pressure additives, anti-seizure agents, wax modifiers, viscosity index improvers, fluid-loss additives, seal compatibility agents, other friction modifiers, lubricity agents, anti-staining agents, chromophoric agents, defoamants, demulsifiers, emulsifiers, densifiers, wetting agents, gelling agents, tackiness agents, colorants, and others. For a review of many commonly used additives, see Klamann in *Lubricants and Related Products*, Verlag Chemie, Deerfield Beach, Fla.; ISBN 0-89573-177-0. Reference is also made to "Lubricant Additives" by M. W. Ranney, published by Noyes Data Corporation of Parkridge, N.J. (1973).

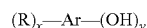
[0150] The types and quantities of performance additives used in combination with the instant disclosure in lubricant compositions are not limited by the examples shown herein as illustrations.

Antioxidants

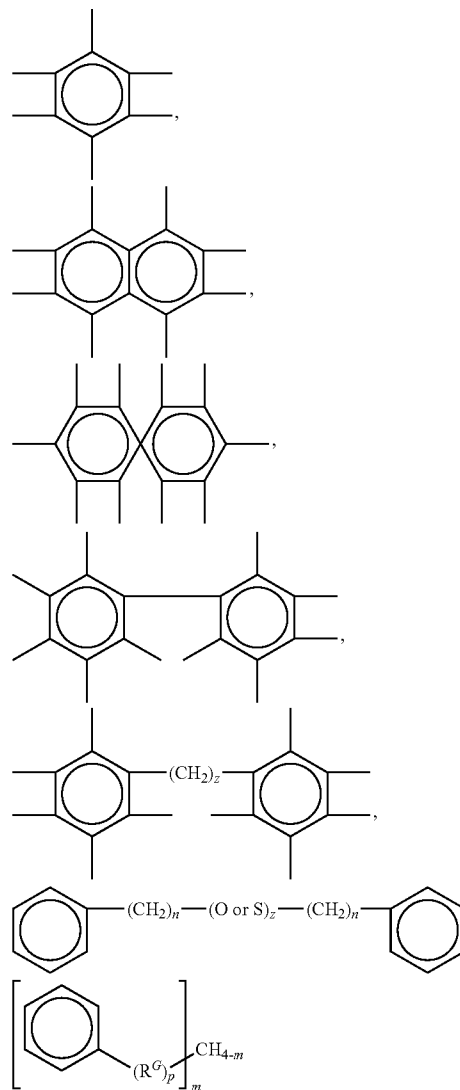
[0151] Typical antioxidant include phenolic antioxidants, aminic antioxidants and oil-soluble copper complexes.

[0152] The phenolic antioxidants include sulfurized and non-sulfurized phenolic antioxidants. The terms "phenolic type" or "phenolic antioxidant" used herein includes compounds having one or more than one hydroxyl group bound to an aromatic ring which may itself be mononuclear, e.g., benzyl, or poly-nuclear, e.g., naphthyl and spiro aromatic compounds. Thus "phenol type" includes phenol per se, catechol, resorcinol, hydroquinone, naphthol, etc., as well as alkyl or alkenyl and sulfurized alkyl or alkenyl derivatives thereof, and bisphenol type compounds including such bi-phenol compounds linked by alkylene bridges sulfuric bridges or oxygen bridges. Alkyl phenols include mono- and poly-alkyl or alkenyl phenols, the alkyl or alkenyl group containing from 3-100 carbons, preferably 4 to 50 carbons and sulfurized derivatives thereof, the number of alkyl or alkenyl groups present in the aromatic ring ranging from 1 to up to the available unsatisfied valences of the aromatic ring remaining after counting the number of hydroxyl groups bound to the aromatic ring.

[0153] Generally, therefore, the phenolic anti-oxidant may be represented by the general formula:



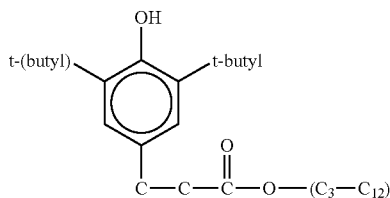
where Ar is selected from the group consisting of:



wherein R is a C₃-C₁₀₀ alkyl or alkenyl group, a sulfur substituted alkyl or alkenyl group, preferably a C₄-C₅₀ alkyl or alkenyl group or sulfur substituted alkyl or alkenyl group, more preferably C₃-C₁₀₀ too alkyl or sulfur substituted alkyl group, most preferably a C₄-C₅₀ alkyl group, R^g is a C₁-C₁₀₀ alkylene or sulfur substituted alkylene group, preferably a C₂-C₅₀ alkylene or sulfur substituted alkylene group, more preferably a C₂-C₂ alkylene sulfur substituted alkylene group, y is at least 1 to up to the available valences of Ar, x ranges from 0 to up to the available valences of Ar-y, z ranges from 1 to 10, n ranges from 0 to 20, and m is 0 to 4 and p is 0 or 1, preferably y ranges from 1 to 3, x ranges from 0 to 3, z ranges from 1 to 4 and n ranges from 0 to 5, and p is 0.

[0154] Preferred phenolic antioxidant compounds are the hindered phenolics and phenolic esters which contain a sterically hindered hydroxyl group, and these include those derivatives of dihydroxy aryl compounds in which the hydroxyl groups are in the o- or p-position to each other. Typical phenolic anti-oxidants include the hindered phenols

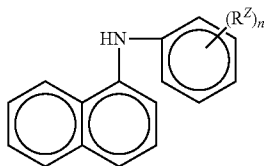
substituted with C_1 + alkyl groups and the alkylene coupled derivatives of these hindered phenols. Examples of phenolic materials of this type 2-t-butyl-4-heptyl phenol; 2-t-butyl-4-octyl phenol; 2-t-butyl-4-dodecyl phenol; 2,6-di-t-butyl-4-heptyl phenol; 2,6-di-t-butyl-4-dodecyl phenol; 2-methyl-6-t-butyl-4-heptyl phenol; 2-methyl-6-t-butyl-4-dodecyl phenol; 2,6-di-t-butyl-4 methyl phenol; 2,6-di-t-butyl-4-ethyl phenol; and 2,6-di-t-butyl 4 alkoxy phenol; and



[0155] Phenolic type antioxidants are well known in the lubricating industry and commercial examples such as Ethanox® 4710, Irganox® 1076, Irganox® L1035, Irganox® 1010, Irganox® L109, Irganox® L118, Irganox® L135 and the like are familiar to those skilled in the art. The above is presented only by way of exemplification, not limitation on the type of phenolic anti-oxidants which can be used.

[0156] The phenolic antioxidant can be employed in an amount in the range of 0.1 to 3 wt %, preferably 0.25 to 2.5 wt %, more preferably 0.5 to 2 wt % on an active ingredient basis.

[0157] Aromatic amine antioxidants include phenyl- α -naphthyl amine which is described by the following molecular structure:



wherein R^Z is hydrogen or a C_1 to C_{14} linear or C_3 to C_{14} branched alkyl group, preferably C_1 to C_{10} linear or C_3 to C_{10} branched alkyl group, more preferably linear or branched C_6 to C_8 and n is an integer ranging from 1 to 5 preferably 1. A particular example is Irganox L06.

[0158] Other aromatic amine antioxidants include other alkylated and non-alkylated aromatic amines such as aromatic monoamines of the formula $R^8R^9R^{10}N$ where R^8 is an aliphatic, aromatic or substituted aromatic group, R^9 is an aromatic or a substituted aromatic group, and R^{10} is H, alkyl, aryl or $R^{11}S(O)_xR^{12}$ where R^{11} is an alkylene, alkenylene, or aralkylene group, R^{12} is a higher alkyl group, or an alkenyl, aryl, or alkaryl group, and x is 0, 1 or 2. The aliphatic group R^8 may contain from 1 to 20 carbon atoms, and preferably contains from 6 to 12 carbon atoms. The aliphatic group is a saturated aliphatic group. Preferably, both R^8 and R^9 are aromatic or substituted aromatic groups, and the aromatic group may be a fused ring aromatic group such as naphthyl. Aromatic groups R^8 and R^9 may be joined together with other groups such as S.

[0159] Typical aromatic amines anti-oxidants have alkyl substituent groups of at least 6 carbon atoms. Examples of aliphatic groups include hexyl, heptyl, octyl, nonyl, and

decyl. Generally, the aliphatic groups will not contain more than 14 carbon atoms. The general types of such other additional amine antioxidants which may be present include diphenylamines, phenothiazines, imidodibenzyls and diphenyl phenylene diamines. Mixtures of two or more of such other additional aromatic amines may also be present. Polymeric amine antioxidants can also be used.

[0160] Another class of antioxidant used in lubricating oil compositions and which may also be present are oil-soluble copper compounds. Any oil-soluble suitable copper compound may be blended into the lubricating oil. Examples of suitable copper antioxidants include copper dihydrocarbyl thio- or dithio-phosphates and copper salts of carboxylic acid (naturally occurring or synthetic). Other suitable copper salts include copper dithiacarbamates, sulphonates, phenates, and acetylacetonates. Basic, neutral, or acidic copper Cu(I) and or Cu(II) salts derived from alkenyl succinic acids or anhydrides are known to be particularly useful.

[0161] Such antioxidants may be used individually or as mixtures of one or more types of antioxidants, the total amount employed being an amount of 0.50 to 5 wt %, preferably 0.75 to 3 wt % (on an as-received basis).

Detergents

[0162] In addition to the alkali or alkaline earth metal salicylate detergent which is an optional component in the present disclosure, other detergents may also be present. While such other detergents can be present, it is preferred that the amount employed be such as to not interfere with the synergistic effect attributable to the presence of the salicylate. Therefore, most preferably such other detergents are not employed.

[0163] If such additional detergents are present, they can include alkali and alkaline earth metal phenates, sulfonates, carboxylates, phosphonates and mixtures thereof. These supplemental detergents can have total base number (TBN) ranging from neutral to highly overbased, i.e. TBN of 0 to over 500, preferably 2 to 400, more preferably 5 to 300, and they can be present either individually or in combination with each other in an amount in the range of from 0 to 10 wt %, preferably 0.5 to 5 wt % (active ingredient) based on the total weight of the formulated lubricating oil. As previously stated, however, it is preferred that such other detergent not be present in the formulation.

[0164] Such additional other detergents include by way of example and not limitation calcium phenates, calcium sulfonates, magnesium phenates, magnesium sulfonates and other related components (including borated detergents).

Dispersants

[0165] During engine operation, oil-insoluble oxidation byproducts are produced. Dispersants help keep these byproducts in solution, thus diminishing their deposition on metal surfaces. Dispersants may be ashless or ash-forming in nature. Preferably, the dispersant is ashless. So called ashless dispersants are organic materials that form substantially no ash upon combustion. For example, non-metal-containing or borated metal-free dispersants are considered ashless. In contrast, metal-containing detergents discussed above form ash upon combustion.

[0166] Suitable dispersants typically contain a polar group attached to a relatively high molecular weight hydrocarbon chain. The polar group typically contains at least one element

of nitrogen, oxygen, or phosphorus. Typical hydrocarbon chains contain 50 to 400 carbon atoms.

[0167] A particularly useful class of dispersants are the alkenylsuccinic derivatives, typically produced by the reaction of a long chain substituted alkenyl succinic compound, usually a substituted succinic anhydride, with a polyhydroxy or polyamino compound. The long chain group constituting the oleophilic portion of the molecule which confers solubility in the oil, is normally a polyisobutylene group. Many examples of this type of dispersant are well known commercially and in the literature. Exemplary U.S. patents describing such dispersants are U.S. Pat. Nos. 3,172,892; 3,215,707; 3,219,666; 3,316,177; 3,341,542; 3,444,170; 3,454,607; 3,541,012; 3,630,904; 3,632,511; 3,787,374 and 4,234,435. Other types of dispersant are described in U.S. Pat. Nos. 3,036,003; 3,200,107; 3,254,025; 3,275,554; 3,438,757; 3,454,555; 3,565,804; 3,413,347; 3,697,574; 3,725,277; 3,725,480; 3,726,882; 4,454,059; 3,329,658; 3,449,250; 3,519,565; 3,666,730; 3,687,849; 3,702,300; 4,100,082; 5,705,458. A further description of dispersants may be found, for example, in European Patent Application No. 471 071, to which reference is made for this purpose.

[0168] Hydrocarbyl-substituted succinic acid compounds are popular dispersants. In particular, succinimide, succinate esters, or succinate ester amides prepared by the reaction of a hydrocarbon-substituted succinic acid compound preferably having at least 50 carbon atoms in the hydrocarbon substituent, with at least one equivalent of an alkylene amine are particularly useful.

[0169] Succinimides are formed by the condensation reaction between alkenyl succinic anhydrides and amines. Molar ratios can vary depending on the amine or polyamine. For example, the molar ratio of alkenyl succinic anhydride to TEPA can vary from 1:1 to 5:1.

[0170] Succinate esters are formed by the condensation reaction between alkenyl succinic anhydrides and alcohols or polyols. Molar ratios can vary depending on the alcohol or polyol used. For example, the condensation product of an alkenyl succinic anhydride and pentaerythritol is a useful dispersant.

[0171] Succinate ester amides are formed by condensation reaction between alkenyl succinic anhydrides and alkanol amines. For example, suitable alkanol amines include ethoxylated polyalkylpolyamines, propoxylated polyalkylpolyamines and polyalkenylpolyamines such as polyethylene polyamines. One example is propoxylated hexamethylenediamine.

[0172] The molecular weight of the alkenyl succinic anhydrides will typically range between 800 and 2,500. The above products can be post-reacted with various reagents such as sulfur, oxygen, formaldehyde, carboxylic acids such as oleic acid, and boron compounds such as borate esters or highly borated dispersants. The dispersants can be borated with from 0.1 to 5 moles of boron per mole of dispersant reaction product.

[0173] Mannich base dispersants are made from the reaction of alkylphenols, formaldehyde, and amines. Process aids and catalysts, such as oleic acid and sulfonic acids, can also be part of the reaction mixture. Molecular weights of the alkylphenols range from 800 to 2,500 or more.

[0174] Typical high molecular weight aliphatic acid modified Mannich condensation products can be prepared from high molecular weight alkyl-substituted hydroxyaromatics or HN(R)₂ group-containing reactants.

[0175] Examples of high molecular weight alkyl-substituted hydroxyaromatic compounds are polypropylphenol, polybutylphenol, and other polyalkylphenols. These polyalkylphenols can be obtained by the alkylation, in the presence of an alkylating catalyst, such as BF₃, of phenol with high molecular weight polypropylene, polybutylene, and other polyalkylene compounds to give alkyl substituents on the benzene ring of phenol having an average 600-100,000 molecular weight.

[0176] Examples of HN(R)₂ group-containing reactants are alkylene polyamines, principally polyethylene polyamines. Other representative organic compounds containing at least one HN(R)₂ group suitable for use in the preparation of Mannich condensation products are well known and include the mono- and di-amino alkanes and their substituted analogs, e.g., ethylamine and diethanol amine; aromatic diamines, e.g., phenylene diamine, diamino naphthalenes; heterocyclic amines, e.g., morpholine, pyrrole, pyrrolidine, imidazole, imidazolidine, and piperidine; melamine and their substituted analogs.

[0177] Examples of alkylene polyamine reactants include ethylenediamine, diethylene triamine, triethylene tetraamine, tetraethylene pentaamine, pentaethylene hexamine, hexaethylene heptaamine, heptaethylene octaamine, octaethylene nonaamine, nonaethylene decamine, and decaethylene undecamine and mixture of such amines having nitrogen contents corresponding to the alkylene polyamines, in the formula H₂N—(Z—NH—)_nH, mentioned before, Z is a divalent ethylene and n is 1 to 10 of the foregoing formula. Corresponding propylene polyamines such as propylene diamine and di-, tri-, tetra-, pentapropylene tri-, tetra-, penta- and hexamines are also suitable reactants. The alkylene polyamines are usually obtained by the reaction of ammonia and dihalo alkanes, such as dichloro alkanes. Thus the alkylene polyamines obtained from the reaction of 2 to 11 moles of ammonia with 1 to 10 moles of dichloroalkanes having 2 to 6 carbon atoms and the chlorines on different carbons are suitable alkylene polyamine reactants.

[0178] Aldehyde reactants useful in the preparation of the high molecular products useful in this disclosure include the aliphatic aldehydes such as formaldehyde (also as paraformaldehyde and formalin), acetaldehyde and aldol (β-hydroxybutyraldehyde). Formaldehyde or a formaldehyde-yielding reactant is preferred.

[0179] Preferred dispersants include borated and non-borated succinimides, including those derivatives from mono-succinimides, bis-succinimides, and/or mixtures of mono- and bis-succinimides, wherein the hydrocarbyl succinimide is derived from a hydrocarbylene group such as polyisobutylene having a Mn of from 500 to 5000 or more or a mixture of such hydrocarbylene groups. Other preferred dispersants include succinic acid-esters and amides, alkylphenol-polyamine-coupled Mannich adducts, their capped derivatives, and other related components. Such additives may be used in an amount of 0.1 to 20 wt %, preferably 0.1 to 8 wt %, more preferably 1 to 6 wt % (on an as-received basis) based on the weight of the total lubricant.

Pour Point Depressants

[0180] Conventional pour point depressants (also known as lube oil flow improvers) may also be present. Pour point depressant may be added to lower the minimum temperature at which the fluid will flow or can be poured. Examples of suitable pour point depressants include alkylated naphtha-

lenes polymethacrylates, polyacrylates, polyarylamides, condensation products of haloparaffin waxes and aromatic compounds, vinyl carboxylate polymers, and terpolymers of dialkylfumarates, vinyl esters of fatty acids and allyl vinyl ethers. Such additives may be used in amount of 0.0 to 0.5 wt %, preferably 0 to 0.3 wt %, more preferably 0.001 to 0.1 wt % on an as-received basis.

Corrosion Inhibitors/Metal Deactivators

[0181] Corrosion inhibitors are used to reduce the degradation of metallic parts that are in contact with the lubricating oil composition. Suitable corrosion inhibitors include aryl thiazines, alkyl substituted dimercapto thiodiazoles thiadiazoles and mixtures thereof. Such additives may be used in an amount of 0.01 to 5 wt %, preferably 0.01 to 1.5 wt %, more preferably 0.01 to 0.2 wt %, still more preferably 0.01 to 0.1 wt % (on an as-received basis) based on the total weight of the lubricating oil composition.

Seal Compatibility Additives

[0182] Seal compatibility agents help to swell elastomeric seals by causing a chemical reaction in the fluid or physical change in the elastomer. Suitable seal compatibility agents for lubricating oils include organic phosphates, aromatic esters, aromatic hydrocarbons, esters (butylbenzyl phthalate, for example), and polybutenyl succinic anhydride and sulfolane-type seal swell agents such as Lubrizol 730-type seal swell additives. Such additives may be used in an amount of 0.01 to 3 wt %, preferably 0.01 to 2 wt % on an as-received basis.

Anti-Foam Agents

[0183] Anti-foam agents may advantageously be added to lubricant compositions. These agents retard the formation of stable foams. Silicones and organic polymers are typical anti-foam agents. For example, polysiloxanes, such as silicon oil or polydimethyl siloxane, provide antifoam properties. Anti-foam agents are commercially available and may be used in conventional minor amounts along with other additives such as demulsifiers; usually the amount of these additives combined is less than 1 percent, preferably 0.001 to 0.5 wt %, more preferably 0.001 to 0.2 wt %, still more preferably 0.0001 to 0.15 wt % (on an as-received basis) based on the total weight of the lubricating oil composition.

Inhibitors and Antirust Additives

[0184] Antirust additives (or corrosion inhibitors) are additives that protect lubricated metal surfaces against chemical attack by water or other contaminants. One type of antirust additive is a polar compound that wets the metal surface preferentially, protecting it with a film of oil. Another type of antirust additive absorbs water by incorporating it in a water-in-oil emulsion so that only the oil touches the surface. Yet another type of antirust additive chemically adheres to the metal to produce a non-reactive surface. Examples of suitable additives include zinc dithiophosphates, metal phenolates, basic metal sulfonates, fatty acids and amines. Such additives may be used in an amount of 0.01 to 5 wt %, preferably 0.01 to 1.5 wt % on an as-received basis.

[0185] The term "organo molybdenum-nitrogen complexes" embraces the organo molybdenum-nitrogen complexes described in U.S. Pat. No. 4,889,647. The complexes are reaction products of a fatty oil, dithanolamine and a molybdenum source. Specific chemical structures have not

been assigned to the complexes. U.S. Pat. No. 4,889,647 reports an infrared spectrum for a typical reaction product of that disclosure; the spectrum identifies an ester carbonyl band at 1740 cm^{-1} and an amide carbonyl band at 1620 cm^{-1} . The fatty oils are glyceryl esters of higher fatty acids containing at least 12 carbon atoms up to 22 carbon atoms or more. The molybdenum source is an oxygen-containing compound such as ammonium molybdates, molybdenum oxides and mixtures.

[0186] Other organo molybdenum complexes which can be used in the present disclosure are tri-nuclear molybdenum-sulfur compounds described in EP 1 040 115 and WO 99/31113 and the molybdenum complexes described in U.S. Pat. No. 4,978,464.

Viscosity Modifiers

[0187] In addition to the copolymers described herein as part of the disclosure the lubricating composition may optionally further contain other known viscosity modifiers. The viscosity modifiers may be hydrogenated styrene-butadiene rubbers, ethylene-propylene copolymers, hydrogenated styrene-isoprene polymers, hydrogenated diene polymers, poly-alkyl styrenes, polyolefins, esters of maleic anhydride-styrene copolymers, or mixtures thereof.

Antiwear Agents

[0188] The lubricating compositions can include at least one antiwear agent. Examples of suitable antiwear agents include oil soluble amine salts of phosphorus compounds, sulphurised olefins, metal dihydrocarbyldithio-phosphates (such as zinc dialkyldithiophosphates), thiocarbamate-containing compounds, such as thiocarbamate esters, thiocarbamate amides, thiocarbamic ethers, alkylene-coupled thiocarbamates, and bis(S-alkyldithiocarbamyl) disulphides.

[0189] In one embodiment the oil soluble phosphorus amine salt antiwear agent includes an amine salt of a phosphorus acid ester or mixtures thereof. The amine salt of a phosphorus acid ester includes phosphoric acid esters and amine salts thereof; dialkyldithiophosphoric acid esters and amine salts thereof; amine salts of phosphites; and amine salts of phosphorus-containing carboxylic esters, ethers, and amides; and mixtures thereof. The amine salt of a phosphorus acid ester may be used alone or in combination.

[0190] In one embodiment the oil soluble phosphorus amine salt includes partial amine salt-partial metal salt compounds or mixtures thereof. In one embodiment the phosphorus compound further includes a sulphur atom in the molecule. In one embodiment the amine salt of the phosphorus compound may be ashless, i.e., metal-free (prior to being mixed with other components).

[0191] The amines which may be suitable for use as the amine salt include primary amines, secondary amines, tertiary amines, and mixtures thereof. The amines include those with at least one hydrocarbyl group, or, in certain embodiments, two or three hydrocarbyl groups. The hydrocarbyl groups may contain 2 to 30 carbon atoms, or in other embodiments 8 to 26, or 10 to 20, or 13 to 19 carbon atoms.

[0192] Primary amines include ethylamine, propylamine, butylamine, 2-ethylhexylamine, octylamine, and dodecylamine, as well as such fatty amines as n-octylamine, n-decylamine, n-dodecylamine, n-tetradecylamine, n-hexadecylamine, n-octadecylamine and oleyamine. Other useful fatty amines include commercially available fatty amines such as

“Armeen®” amines (products available from Akzo Chemicals, Chicago, Ill.), such as Armeen C, Armeen O, Armeen OL, Armeen T, Armeen HT, Armeen S and Armeen SD, wherein the letter designation relates to the fatty group, such as coco, oleyl, tallow, or stearyl groups.

[0193] Examples of suitable secondary amines include dimethylamine, diethylamine, dipropylamine, dibutylamine, diamylamine, dihexylamine, diheptylamine, methylethylamine, ethylbutylamine and ethylamylamine. The secondary amines may be cyclic amines such as piperidine, piperazine and morpholine.

[0194] The amine may also be a tertiary-aliphatic primary amine. The aliphatic group in this case may be an alkyl group containing 2 to 30, or 6 to 26, or 8 to 24 carbon atoms. Tertiary alkyl amines include monoamines such as tert-butylamine, tert-hexylamine, 1-methyl-1-amino-cyclohexane, tert-octylamine, tert-decylamine, tert-dodecylamine, tert-tetradecylamine, tert-hexadecylamine, tert-octadecylamine, tert-tetracosanylamine, and tert-octacosanylamine.

[0195] In one embodiment the phosphorus acid amine salt includes an amine with C₁₁ to C₁₄ tertiary alkyl primary groups or mixtures thereof. In one embodiment the phosphorus acid amine salt includes an amine with C₁₄ to C₁₈ tertiary alkyl primary amines or mixtures thereof. In one embodiment the phosphorus acid amine salt includes an amine with C₁₈ to C₂₂ tertiary alkyl primary amines or mixtures thereof.

[0196] Mixtures of amines may also be used in the disclosure. In one embodiment a useful mixture of amines is “Primene® 81R” and “Primene® JMT.” Primene® 81R and Primene® JMT (both produced and sold by Rohm & Haas) are mixtures of C₁₁ to C₁₄ tertiary alkyl primary amines and C₁₈ to C₂₂ tertiary alkyl primary amines, respectively.

[0197] In one embodiment oil soluble amine salts of phosphorus compounds include a sulphur-free amine salt of a phosphorus-containing compound may be obtained/obtainable by a process comprising: reacting an amine with either (i) a hydroxy-substituted di-ester of phosphoric acid, or (ii) a phosphorylated hydroxy-substituted di- or tri-ester of phosphoric acid. A more detailed description of compounds of this type is disclosed in International Application PCT/US08/051, 126.

[0198] In one embodiment the hydrocarbyl amine salt of an alkylphosphoric acid ester is the reaction product of a C₁₄ to C₁₈ alkylated phosphoric acid with Primene 81R™ (produced and sold by Rohm & Haas) which is a mixture of C₁₁ to C₁₄ tertiary alkyl primary amines.

[0199] Examples of hydrocarbyl amine salts of dialkylidithiophosphoric acid esters include the reaction product(s) of isopropyl, methyl-amyl (4-methyl-2-pentyl or mixtures thereof), 2-ethylhexyl, heptyl, octyl or nonyl dithiophosphoric acids with ethylene diamine, morpholine, or Primene 81R™, and mixtures thereof.

[0200] In one embodiment the dithiophosphoric acid may be reacted with an epoxide or a glycol. This reaction product is further reacted with a phosphorus acid, anhydride, or lower ester. The epoxide includes an aliphatic epoxide or a styrene oxide. Examples of useful epoxides include ethylene oxide, propylene oxide, butene oxide, octene oxide, dodecene oxide, and styrene oxide. In one embodiment the epoxide may be propylene oxide. The glycols may be aliphatic glycols having from 1 to 12, or from 2 to 6, or 2 to 3 carbon atoms. The dithiophosphoric acids, glycols, epoxides, inorganic phosphorus reagents and methods of reacting the same are described in U.S. Pat. Nos. 3,197,405 and 3,544,465. The

resulting acids may then be salted with amines. An example of suitable dithiophosphoric acid is prepared by adding phosphorus pentoxide (64 grams) at 58° C. over a period of 45 minutes to 514 grams of hydroxypropyl 0,0-di(4-methyl-2-pentyl)phosphorodithioate (prepared by reacting di(4-methyl-2-pentyl)-phosphorodithioic acid with 1.3 moles of propylene oxide at 25° C.). The mixture may be heated at 75° C. for 2.5 hours, mixed with a diatomaceous earth and filtered at 70° C. The filtrate contains 11.8% by weight phosphorus, 15.2% by weight sulphur, and an acid number of 87 (bromophenol blue).

[0201] The dithiocarbamate-containing compounds may be prepared by reacting a dithiocarbamate acid or salt with an unsaturated compound. The dithiocarbamate containing compounds may also be prepared by simultaneously reacting an amine, carbon disulphide and an unsaturated compound. Generally, the reaction occurs at a temperature from 25° C. to 125° C.

[0202] Examples of suitable olefins that may be sulphurised to form an the sulphurised olefin include propylene, butylene, isobutylene, pentene, hexane, heptene, octane, nonene, decene, undecene, dodecene, undecyl, tridecene, tetradecene, pentadecene, hexadecene, heptadecene, octadecene, octadecenene, nonadecene, eicosene or mixtures thereof. In one embodiment, hexadecene, heptadecene, octadecene, octadecenene, nonadecene, eicosene or mixtures thereof and their dimers, trimers and tetramers are especially useful olefins. Alternatively, the olefin may be a Diels-Alder adduct of a diene such as 1,3-butadiene and an unsaturated ester, such as, butylacrylate.

[0203] Another class of sulphurised olefin includes fatty acids and their esters. The fatty acids are often obtained from vegetable oil or animal oil; and typically contain 4 to 22 carbon atoms. Examples of suitable fatty acids and their esters include triglycerides, oleic acid, linoleic acid, palmitoleic acid or mixtures thereof. Often, the fatty acids are obtained from lard oil, tall oil, peanut oil, soybean oil, cottonseed oil, sunflower seed oil or mixtures thereof. In one embodiment fatty acids and/or ester are mixed with olefins.

[0204] In an alternative embodiment, the ashless antiwear agent may be a monoester of a polyol and an aliphatic carboxylic acid, often an acid containing 12 to 24 carbon atoms. Often the monoester of a polyol and an aliphatic carboxylic acid is in the form of a mixture with a sunflower oil or the like, which may be present in the friction modifier mixture from 5 to 95, in several embodiments from 10 to 90, or from 20 to 85, or 20 to 80 weight percent of said mixture. The aliphatic carboxylic acids (especially a monocarboxylic acid) which form the esters are those acids typically containing 12 to 24, or from 14 to 20 carbon atoms. Examples of carboxylic acids include dodecanoic acid, stearic acid, lauric acid, behenic acid, and oleic acid.

[0205] Polyols include diols, triols, and alcohols with higher numbers of alcoholic OH groups. Polyhydric alcohols include ethylene glycols, including di-, tri- and tetraethylene glycols; propylene glycols, including di-, tri- and tetrapropylene glycols; glycerol; butane diol; hexane diol; sorbitol; arabitol; mannitol; sucrose; fructose; glucose; cyclohexane diol; erythritol; and pentaerythritols, including di- and tri-pentaerythritol. Often the polyol is diethylene glycol, triethylene glycol, glycerol, sorbitol, penta erythritol or dipentaerythritol.

[0206] The commercially available monoester known as “glycerol monooleate” is believed to include 60±5 percent by

weight of the chemical species glycerol monooleate, along with 35+5 percent glycerol dioleate, and less than 5 percent trioleate and oleic acid. The amounts of the monoesters, described above, are calculated based on the actual, corrected, amount of polyol monoester present in any such mixture.

Extreme Pressure Agents

[0207] Extreme Pressure (EP) agents that are soluble in the oil include sulphur- and chlorosulphur-containing EP agents, chlorinated hydrocarbon EP agents and phosphorus EP agents. Examples of such EP agents include chlorinated wax; sulphurised olefins (such as sulphurised isobutylene), organic sulphides and polysulphides such as dibenzyl disulphide, bis-(chlorobenzyl) disulphide, dibutyl tetrasulphide, sulphurised methyl ester of oleic acid, sulphurised alkylphenol, sulphurised dipentene, sulphurised terpene, and sulphurised Diels-Alder adducts; phosphosulphurised hydrocarbons such as the reaction product of phosphorus sulphide with turpentine or methyl oleate; phosphorus esters such as the dihydrocarbon and trihydrocarbon phosphites, e.g., dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentylphenyl phosphite; dipentylphenyl phosphite, tridecyl phosphite, distearyl phosphite and polypropylene substituted phenol phosphite; metal thiocarbamates such as zinc dioctyldithiocarbamate and barium heptylphenol diacid; amine salts of alkyl and dialkylphosphoric acids or derivatives; and mixtures thereof (as described in U.S. Pat. No. 3,197,405).

[0208] The method and lubricating compositions of this disclosure may be suitable for greases, gear oils, axle oils, drive shaft oils, traction oils, manual transmission oils, automatic transmission oils, metal working fluids, hydraulic oils, or internal combustion engine oils.

[0209] In one embodiment the method and lubricating composition of the disclosure may be suitable for at least one of gear oils, axle oils, drive shaft oils, traction oils, manual transmission oils or automatic transmission oils. In one embodiment the disclosure provides a method of lubricating a manual transmission.

[0210] An automatic transmission includes continuously variable transmissions (CVT), infinitely variable transmissions (IVT), toroidal transmissions, continuously slipping torque converter clutches (CSTCC), stepped automatic transmissions or dual clutch transmissions (DCT).

[0211] The internal combustion engines may be 2-stroke or 4-stroke engines. Suitable internal combustion engines include marine diesel engines, aviation piston engines, low-load diesel engines, and automobile and truck engines.

[0212] As used herein, the term “(meth) acrylic” and related terms includes both acrylic and methacrylic groups.

[0213] As used herein, the term “a primary alcohol branched at the β - or higher position” relates to an alcohol with branching at the 2-position or a higher position (e.g., 3-, or 4-, or 5-, or 6-, or 7-position, etc.).

[0214] As used herein the number of carbon atoms present in the ester groups of the polymers of the disclosure is counted to include only those carbon atoms of the alcohol-derived portion of the ester group. Specifically, the number of carbon atoms excludes the carbonyl carbon of the ester.

[0215] As used herein, the term “hydrocarbyl substituent” or “hydrocarbyl group” is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon

character. Examples of hydrocarbyl groups include: hydrocarbon substituents, including aliphatic, alicyclic, and aromatic substituents; substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this disclosure, do not alter the predominantly hydrocarbon nature of the substituent; and hetero substituents, that is, substituents which similarly have a predominantly hydrocarbon character but contain other than carbon in a ring or chain.

[0216] In the above detailed description, the specific embodiments of this disclosure have been described in connection with its preferred embodiments. However, to the extent that the above description is specific to a particular embodiment or a particular use of this disclosure, this is intended to be illustrative only and merely provides a concise description of the exemplary embodiments. Accordingly, the disclosure is not limited to the specific embodiments described above, but rather, the disclosure includes all alternatives, modifications, and equivalents falling within the true scope of the appended claims. Various modifications and variations of this disclosure will be obvious to a worker skilled in the art and it is to be understood that such modifications and variations are to be included within the purview of this application and the spirit and scope of the claims.

[0217] The following examples are for purposes of illustration only and are non-limiting examples.

EXAMPLES

[0218] Lubricant compositions (i.e., axle oil blends) were prepared by blending a polyalphaolefin base stock (e.g., mPAO 700, mPAO 450, mPAO 300, mPAO 150, mPAO 65, mPAO 14, PAO 70, PAO 4, and PAO 6), a hybrid olefin ester polymer (HOEP) viscosity modifier (Meridian™), and an axle oil additive package. The Meridian™ viscosity modifier is available from Lubrizol Corporation. The axle oil additive package used in Examples 1 and 2 is available from Lubrizol Corporation as Anglamol™ 6043M. The axle oil additive package used in Examples 3 and 4 is available from Afton Chemicals.

Example 1

[0219] Wear control and load carrying capacity were determined for lubricant compositions prepared as described hereinabove. The results in FIG. 1 show 4-Ball Wear Scar (ASTM D4172) is reduced when using the Meridian™ viscosity modifier alone or in combination with mPAO 150 or mPAO 65. A surprising aspect of this disclosure is that base oil and viscosity modifiers are not expected to have significant impact on wear or load-carrying properties of the fluid. FIG. 10 shows the results of 4-Ball Wear Scar (ASTM D4172) for the designated lubricant compositions (i.e., blends).

Example 2

[0220] Over a broad viscosity range, a synergy was observed where mixtures of mPAO 65 and Meridian™ gave higher Load Wear Index (LWI) than either high viscosity component alone (FIG. 2). The average friction coefficient measurements for multiple blends over a broad viscosity range (FIG. 3) show lower friction as the relative concentration of high viscosity components increase. Surprisingly, however, the combination of mPAO 65 and Meridian™ showed higher friction than either component alone. This synergy implies the possibility of adjusting friction in appli-

cations such as transmissions, which require a specific balance of frictional characteristics, i.e., higher friction in some cases. FIG. 4 shows on average 25-30% lower traction coefficients for lubricating compositions containing mPAO 150, mPAO 65, and/or Meridian™ compared to a conventional viscosity modifier. Lower traction indicates potential axle efficiency enhancement and therefore improved fuel economy. FIG. 11 shows the results of 4-Ball EP (ASTM D2783) load wear index for the designated lubricant compositions (i.e., blends). FIG. 12 shows the results of High Frequency Reciprocating Rig (HFRR) friction coefficient for the designated lubricant compositions (i.e., blends).

Example 3

[0221] Similar to Example 1 using a lubricating composition containing mPAO 150 and Meridian™ (except for a different axle oil additive package), an unexpected synergy was observed as shown in FIGS. 5 and 6. Keeping to total concentration of high viscosity material constant at 25 wt %, less viscosity loss was observed for combinations of mPAO and Meridian™ than for either component alone. This synergy was obvious in terms of absolute viscosity loss and percent loss and shown in FIG. 5. Results are illustrated graphically in FIG. 6. Durability of oil film due to enhanced shear stability results in consistent performance and protection of hardware over an extended period time compared to less shear stable fluids. For high dispersant treated systems such as the lubricating composition of this Example 3, this disclosure provides a method for improving shear stability of axle fluids.

Example 4

[0222] Similar to Examples 1 and 3 using a lubricating compositions containing mPAO 150 and Meridian™ (except for different axle oil additive packages), FIG. 7 indicates a potential antiwear/antiscuffing advantage for a Meridian™ viscosity modifier in the FZG scuffing test even in a lower SAE 75W-80 viscosity formulation containing all Meridian™ as the viscosity modifier. A trend reflecting lower Total Gear weight loss with increased concentration of Meridian™ was observed in the FZG test. All formulations showed excellent performance by delivering ">Stage 12" passing results, a requirement for premium high performance gear oils.

[0223] Additional performance testing of these lower viscosity axle fluid formulations were conducted to assess the impact of the high VI synthetic components in areas such as oxidation stability and deposit control. FIG. 8 shows surprisingly excellent sludge and varnish results for fluids evaluated in 100-hr L60-1 Thermal and Oxidative Stability test, which is double the standard duration (i.e., 50 hours) required for SAE J2360 high performance gear oil specification. The results clearly demonstrate that incorporation of the Meridian™ viscosity modifier in the lubricating compositions of this disclosure provides improved stability and cleanliness even for already high performing technology. This further substantiates the potential to formulation even higher performing lower viscosity finished products by incorporating new synthetic base fluids and viscosity modifiers.

[0224] Referring to FIG. 9, additional durability testing in a high speed shock test for axle/gear oils used to assess anti-scoring performance of fluids showed that even at lower kinematic viscosity @100° C., these oils still retained passing performance under severe operating conditions. In the L-42

test procedure, which is part of the SAE J2360 gear oil specification, the ring and pinion gears are evaluated for scoring after a series of high speed accelerations and rapid decelerations at temperatures up to 280° F. In order to pass, the candidate lubricant must show less scoring than the established passing reference oil.

[0225] All patents and patent applications, test procedures (such as ASTM methods, UL methods, and the like), and other documents cited herein are fully incorporated by reference to the extent such disclosure is not inconsistent with this disclosure and for all jurisdictions in which such incorporation is permitted.

[0226] When numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated. While the illustrative embodiments of the disclosure have been described with particularity, it will be understood that various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the spirit and scope of the disclosure. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the examples and descriptions set forth herein but rather that the claims be construed as encompassing all the features of patentable novelty which reside in the present disclosure, including all features which would be treated as equivalents thereof by those skilled in the art to which the disclosure pertains.

[0227] The present disclosure has been described above with reference to numerous embodiments and specific examples. Many variations will suggest themselves to those skilled in this art in light of the above detailed description. All such obvious variations are within the full intended scope of the appended claims.

What is claimed is:

1. A lubricating composition comprising:

- a first base stock component comprising one or more metallocene catalyzed polyalphaolefins (mPAOs), each mPAO having a kinematic viscosity (Kv_{100}) from 40 cSt to 155 cSt and a viscosity index (VI) from 150 to 207;
- a second base stock comprising one or more polyalphaolefins (PAOs), each PAO having a kinematic viscosity (Kv_{100}) less than 10 cSt and a VI from 130 to 145; and
- a viscosity modifier comprising a copolymer having units derived from monomers of (i) an α -olefin and (ii) an ethylenically unsaturated carboxylic acid or derivatives thereof esterified with an alcohol;

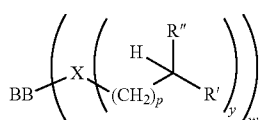
wherein at least one of wear control (as determined by ASTM D4172), load carrying capacity (as determined by ASTM D2783) and traction reduction (as determined by Mini-Traction Machine (MTM) Ball-on-Disc apparatus) is improved in a driveline device lubricated with said lubricating composition as compared to at least one of wear control, load carrying capacity and traction reduction achieved with a lubricating composition containing a viscosity modifier other than said viscosity modifier copolymer, at an equal or lower kinematic viscosity ($Kv@100^\circ C.$).

2. The lubricating composition of claim 1 wherein the lubricating oil base stock comprises a Group I, II, III, IV, V or VI base oil stock, or mixtures thereof.

3. The lubricating composition of claim 1 wherein the lubricating oil base stock comprises a synthetic polyalphaolefin (PAO) fluid, said PAO comprising a polymer of one or more C_8 to C_{12} alphaolefin monomers.

4. The lubricating composition of claim 1 wherein the lubricating oil base stock has a kinematic viscosity (KV_{100}) from 4 to 65 cSt at 100° C., and a VI from 140 to 200.

5. The lubricating composition of claim 1 wherein the viscosity modifier is represented by the formula:



Formula (I)

wherein

Formula (I) comprises a copolymer backbone (BB), and one or more pendant groups, wherein BB is derived from a copolymer of (i) an α -olefin and (ii) an ethylenically unsaturated carboxylic acid or derivatives thereof;

X is a functional group which either (i) contains a carbon and at least one oxygen or nitrogen atom, or (ii) is an alkylene group with 1 to 5 carbon atoms, connecting the copolymer backbone and a branched hydrocarbyl group contained within ()_y;

w is the number of pendant groups attached to the copolymer backbone, which is in the range of 2 to 2000;

y is 0, 1, 2 or 3, provided that in at least 1 mol % of the pendant groups, y is not zero; and with the proviso that when y is 0, X is bonded to a terminal group in a manner sufficient to satisfy the valence of X, wherein the terminal group is selected from hydrogen, alkyl, aryl, a metal or ammonium cation, and mixtures thereof;

p may be an integer in the range of 1 to 15; and

R' and R'' are independently linear or branched hydrocarbyl groups, and the combined total number of carbon atoms present in R' and R'' is at least 12.

6. The lubricating composition of claim 1 wherein the α -olefin is selected from the group consisting of 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-hepta-decene 1-octadecene, and mixtures thereof.

7. The lubricating composition of claim 1 wherein the ethylenically unsaturated carboxylic acid or derivative thereof is selected from the group consisting of acrylic acid, methyl acrylate, methacrylic acid, maleic acid or anhydride, fumaric acid, itaconic acid or anhydride or mixtures thereof, and substituted equivalents thereof.

8. The lubricating composition of claim 1 wherein the alcohol is selected from the group consisting of 2-ethylhexanol, 2-butyloctanol, 2-hexyldecanol, 2-octyldodecanol, 2-decyltetradecanol, butanol, pentanol, hexanol, heptanol, octanol, nonanol, decanol, undecanol, dodecanol, tridecanol, tetradecanol, pentadecanol, hexadecanol, heptadecanol, octadecanol, eicosanol, and mixtures thereof.

9. The lubricating composition of claim 1 wherein the viscosity modifier is a copolymer derived from monomers of (i) an α -olefin and (ii) an ethylenically unsaturated carboxylic acid or derivatives thereof,

wherein 0.1 to 99.89 percent of the carboxylic acid units are esterified with a primary alcohol branched at the β - or higher position,

wherein 0.1 to 99.89 percent of the carboxylic acid units are esterified with a linear alcohol or an α -branched alcohol, and

wherein 0.01 to 10 percent of the carboxylic acid units has at least one of an amino-, amido- and/or imido-group.

10. The lubricating composition of claim 1 wherein the viscosity modifier copolymer has a weight average molecular weight of 45,000 or less.

11. The lubricating composition of claim 1 wherein the first base stock component is present in the amount from 10 weight percent to 60 weight percent, the second base stock component is present in an amount from 30 weight percent to 60 weight percent, and the viscosity modifier is present in an amount from 2 weight percent to 46 weight percent, based on the total weight of the lubricating composition.

12. A process for producing the lubricating composition of claim 1, said process comprising:

providing a first base stock component comprising one or more metallocene catalyzed polyalphaolefins (mPAOs), each mPAO having a kinematic viscosity (KV_{100}) from 40 cSt to 155 cSt and a viscosity index (VI) from 150 to 207;

providing a second base stock comprising one or more polyalphaolefins (PAOs), each PAO having a kinematic viscosity (KV_{100}) less than 10 cSt and a VI from 130 to 145;

providing a viscosity modifier comprising a copolymer having units derived from monomers of (i) an α -olefin and (ii) an ethylenically unsaturated carboxylic acid or derivatives thereof esterified with an alcohol; and

blending the first base stock component, second base stock component and viscosity modifier in amounts sufficient to produce the lubricating composition.

13. A lubricant comprising the lubricating composition of claim 1.

14. The lubricant of claim 13 further comprising one or more of an antioxidant, detergent, dispersant, pour point depressant, corrosion inhibitor, metal deactivator, seal compatibility additive, anti-foam agent, inhibitor, antiwear, extreme pressure agent, friction modifier, and antirust additive.

15. A method of lubricating a mechanical device comprising supplying to the device a lubricating composition of claim 1, wherein the mechanical device comprises a driveline device.

16. The method of claim 15 wherein the driveline device comprises gears or transmissions.

17. The lubricant of claim 13 which comprises an axle fluid or manual transmission fluid (MTF).

18. A method for improving fuel efficiency or shear stability, while maintaining or improving wear control, load carrying capacity and/or traction reduction in a driveline device lubricated with a lubricating oil, by using as the lubricating oil a lubricant of claim 13.

19. The method of claim 18 wherein the driveline device comprises gears or transmissions.

20. The method of claim 18 wherein the lubricant comprises an axle fluid or manual transmission fluid (MTF).

* * * * *