



(51) International Patent Classification:

C10M 137/10 (2006.01) C10M 171/00 (2006.01)

C10M 169/04 (2006.01) C10N 40/25 (2006.01)

(21) International Application Number:

PCT/US2022/078491

(22) International Filing Date:

21 October 2022 (21.10.2022)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

17/558,168 21 December 2021 (21.12.2021) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH,

(54) Title: LUBRICATING OIL COMPOSITION HAVING RESISTANCE TO ENGINE DEPOSITS

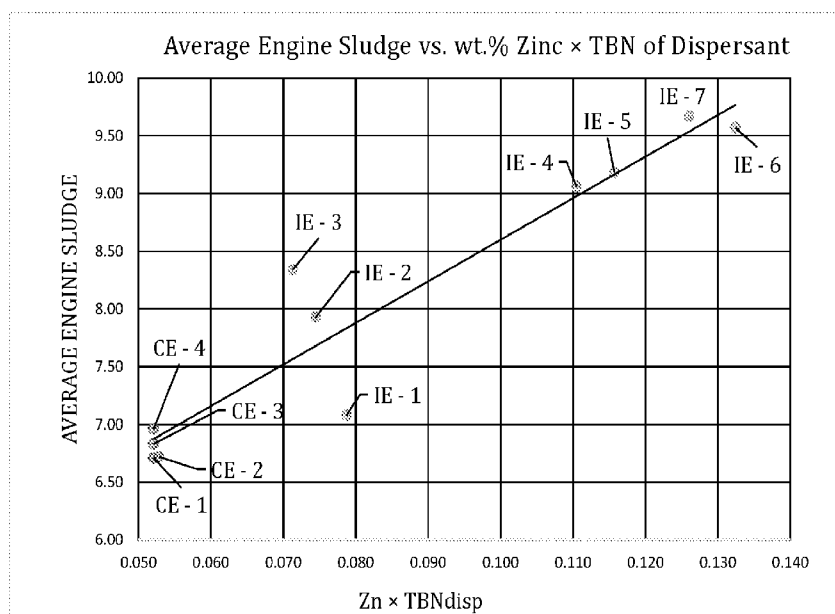


Figure 1

(57) Abstract: A lubricating oil composition comprising greater than 50 wt.% of a base oil of lubricating viscosity, and either: a) an additive comprising: one or more zinc dialkyl dithiophosphates (ZDDP compounds) and one or more dispersants, wherein the weight percent of zinc (Zn) provided to the oil composition by the ZDDP compounds multiplied by the contribution of the total base number (TBN) of the dispersants to the TBN of the oil composition is a multiplication factor $Zn \times TBN_{disp}$ of at least about 0.06; or b) an additive comprising one or more ZDDP compounds and one or more dispersants, wherein the weight percent of phosphorus (P) provided to the oil composition by the ZDDP compounds multiplied by the contribution of the total base number (TBN) of the dispersants to the TBN of the oil composition is a multiplication factor $P \times TBN_{disp}$ of at least about 0.051.



TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS,
ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- with amended claims (Art. 19(1))

TITLE**LUBRICATING OIL COMPOSITION HAVING RESISTANCE TO ENGINE
DEPOSITS****TECHNICAL FIELD**

[0001] This disclosure relates to engine lubricating oils with good oxidation resistance and dispersancy to reduce engine deposits. In particular, this disclosure relates to lubricating oils, and methods for improving resistance to deposits of a lubricating oil in an engine or other mechanical components lubricated with the lubricating oil. The lubricating oils of this disclosure are useful as internal combustion engine oils or other applications where lubricating oils are subjected to heat and oxidative conditions.

BACKGROUND

[0002] It is desirable for lubricant compositions to exhibit good oxidation resistance and dispersancy properties and tolerance to soot and sludge, to which a lubricant composition employed in an internal combustion engine is inevitably exposed during its lifetime. Good dispersancy properties can extend the useful lifetime of a lubricant composition, for instance, by reducing soot-induced lubricant composition thickening, or by reducing sludge build-up in the lubricant composition, which can otherwise rapidly lead to a loss of fuel economy. Typically, dispersancy properties of a lubricant composition are improved by the addition of dispersants. A significant proportion of the composition of the lubricant may be made up of dispersants and therefore these represent a significant cost component of the lubricant composition.

[0003] Also, the oxidation of molecules in lubricating oils can cause oligomerization and eventually result in a dramatic, irreversible increase in the viscosity of the oil. Such increase in oil viscosity can both hamper the operation of the engine and reduce efficiency.

[0004] Accordingly, there is a need in the art for a lubricant composition having a desirable viscosity profile, including good low-temperature viscosity characteristics. There is also a need for a lubricant composition which exhibits good dispersancy properties without requiring a high dispersant treat rate, as is typically associated with a high performance engine oil.

SUMMARY AND TERMS

[0005] The present disclosure meets the above-described need in the art for a lubricant composition having a desirable viscosity profile, including good low-temperature viscosity characteristics. The present disclosure also meets the need for a lubricant composition which exhibits good dispersancy properties without requiring a high dispersant treat rate, as is typically associated with a high performance engine oil.

[0006] The present disclosure may be described by the following sentences.

1. In a first aspect, the present disclosure relates to a lubricating oil composition comprising greater than 50 wt.% of a base oil of lubricating viscosity, and an additive composition comprising:

one or more zinc dialkyl dithiophosphates (ZDDP compounds) and one or more dispersants, wherein the amount of zinc (Zn) in weight percent provided to the lubricating oil composition by the one or more ZDDP compounds multiplied by the contribution of the total base number (TBN) of the one or more dispersants to the TBN of the lubricating oil composition is a multiplication factor $Zn*TBNDisp$ of at least about 0.06.

2. The lubricating oil composition of sentence 1, wherein the $Zn*TBNDisp$ multiplication factor may be more than about 0.07; or about 0.07 to 0.4; or about 0.075 to about 0.2.

3. The lubricating oil composition of any one of the previous sentences, wherein the $Zn*TBNDisp$ multiplication factor may be at least about 0.06 and the one or more ZDDP compounds is present in a sufficient amount to provide greater than about 0.071 wt.% of zinc based on the total weight of the lubricating oil composition; or the $Zn*TBNDisp$ multiplication factor is more than about 0.07 and the one or more ZDDP compounds is present in a sufficient amount to provide greater than about 0.080 wt.% of zinc based on the total weight of the lubricating oil composition.

4. The lubricating oil composition of any one of the previous sentences, wherein the $Zn*TBNDisp$ multiplication factor may be at least about 0.06 and the contribution of TBN of the one or more dispersants to the TBN of the lubricating oil composition is at least 0.79 mg KOH/g; or the $Zn*TBNDisp$ multiplication factor is more than about 0.07 and the

contribution of TBN of the one or more dispersants to the TBN of the lubricating oil composition is at least 0.85 mg KOH/g.

5. In a second aspect, the present disclosure relates to a lubricating oil composition comprising greater than 50 wt.% of a base oil of lubricating viscosity, and an additive composition comprising:

one or more zinc dialkyl dithiophosphates (ZDDP compounds) and one or more dispersants, wherein the amount of phosphorus (P) in weight percent provided to the lubricating oil composition by the one or more ZDDP compounds multiplied by the contribution of the total base number (TBN) of the one or more dispersants to the TBN of the lubricating oil composition is a multiplication factor $P*TBNDisp$ of at least about 0.051.

6. The lubricating oil composition of sentence 5, wherein the $P*TBNDisp$ multiplication factor may be more than about 0.06 to 0.5; or about 0.07 to about 0.25.

7. The lubricating oil composition of any one of sentences 5-6, wherein the $P*TBNDisp$ multiplication factor may be at least about 0.051 and the one or more ZDDP compounds is present in a sufficient amount to provide greater than about 0.065 wt.% of P based on the total weight of the lubricating oil composition; or the $P*TBNDisp$ multiplication factor is more than about 0.06 to 0.5 and the one or more ZDDP compounds is present in a sufficient amount to provide greater than about 0.07 wt.% of P based on the total weight of the lubricating oil composition.

8. The lubricating oil composition of any one of sentences 5-7, wherein the $P*TBNDisp$ multiplication factor may be at least about 0.051 and the contribution of TBN of the one or more dispersants to the TBN of the lubricating oil composition is at least 0.79 mg KOH/g; or the $P*TBNDisp$ multiplication factor is more than about 0.06 to 0.5 and the contribution of TBN of the one or more dispersants to the TBN of the lubricating oil composition is at least 0.85 mg KOH/g.

9. The lubricating oil composition of any one of sentences 1-4, wherein the one or more ZDDP compounds may be present in the lubricating oil composition in amounts of from about 0.01 wt.% to about 15 wt.%, or about 0.1 wt.% to about 10 wt.%, or about 0.5 wt.% to

about 5 wt.%, or about 0.75 wt.% to about 3 wt.% based on the total weight of the lubricating oil composition.

10. The lubricating oil composition of any one of sentences 5-8, wherein the one or more ZDDP compounds may be present in the lubricating oil composition in amounts of from about 0.01 wt.% to about 15 wt.%, or about 0.1 wt.% to about 10 wt.%, or about 0.5 wt.% to about 5 wt.%, or about 0.75 wt.% to about 3 wt.% based on the total weight of the lubricating oil composition.

11. The lubricating oil composition of any one of sentences 1-4 and 9, wherein the amount of the one or more dispersants may be greater than about 0.5 wt.%; or about 0.5 wt.% to about 30 wt.%; or about 0.9 wt.% to about 25 wt.%; or about 1.0 wt.% to about 15 wt.%; or about 1.0 wt.% to about 10 wt.%, wherein the amount is based on the total weight of the lubricating oil composition.

12. The lubricating oil composition of any one of sentences 5-8 and 10, wherein the amount of the one or more dispersants may be greater than about 0.5 wt.%; or about 0.5 wt.% to about 30 wt.%; or about 0.9 wt.% to about 25 wt.%; or about 1.0 wt.% to about 15 wt.%; or about 1.0 wt.% to about 10 wt.%, wherein the amount is based on the total weight of the lubricating oil composition.

13. The lubricating oil composition of any one of sentences 1-4, 9 and 11, wherein the one or more ZDDP compounds may be derived from one or more secondary alkyl alcohol(s) having an alkyl group with 3 to 8 carbon atoms.

14. The lubricating oil composition of any one of sentences 5-8, 10 and 12, wherein the one or more ZDDP compounds may be derived from one or more secondary alkyl alcohol(s) having an alkyl group with 3 to 8 carbon atoms.

15. The lubricating oil composition of any one of sentences 1-4, 9, 11 and 13, wherein the one or more ZDDP compounds may be derived from a secondary alkyl alcohol selected from the group consisting of isopropyl alcohol, amyl alcohol, and methyl isobutyl carbinol.

16. The lubricating oil composition of any one of sentences 5-8, 10, 12 and 14, wherein the one or more ZDDP compounds may be derived from a secondary alkyl alcohol selected from the group consisting of isopropyl alcohol, amyl alcohol, and methyl isobutyl carbinol.
17. The lubricating oil composition of any one of sentences 1-4, 9, 11, 13 and 15, wherein the one or more ZDDP compounds may be derived from two or more secondary alkyl alcohols.
18. The lubricating oil composition of any one of sentences 5-8, 10, 12, 14 and 16, wherein the one or more ZDDP compounds may be derived from two or more secondary alkyl alcohols.
19. The lubricating oil composition of any one of sentences 1-4, 9, 11, 13, 15 and 17, wherein the one or more ZDDP compounds may be a mixture of all primary alcohol ZDDP compounds and all secondary alcohol ZDDP compounds.
20. The lubricating oil composition of any one of sentences 5-8, 10, 12, 14, 16 and 18, wherein the one or more ZDDP compounds may be a mixture of all primary alcohol ZDDP compounds and all secondary alcohol ZDDP compounds.
21. The lubricating oil composition of sentence 19, wherein the mixture may comprise all primary alcohol ZDDP compounds contributing 15 to 500 ppmw zinc and all secondary alcohol ZDDP compounds contributing 100 to 1000 ppmw zinc to the lubricating oil composition based on the weight of the lubricating oil composition; or the mixture comprises all primary alcohol ZDDP compounds contributing 100 to 400 ppmw zinc and all secondary alcohol ZDDP compounds contributing 300 to 700 ppmw zinc to the lubricating oil composition based on the weight of the lubricating oil composition.
22. The lubricating oil composition of sentence 20, wherein the mixture may comprise all primary alcohol ZDDP compounds contributing 15 to 500 ppmw zinc and all secondary alcohol ZDDP compounds contributing 100 to 1000 ppmw zinc to the lubricating oil composition based on the weight of the lubricating oil composition; or the mixture comprises all primary alcohol ZDDP compounds contributing 100 to 400 ppmw zinc and all secondary

alcohol ZDDP compounds contributing 300 to 700 ppmw zinc to the lubricating oil composition based on the weight of the lubricating oil composition.

23. The lubricating oil composition of any one of sentences 1-4, 9, 11, 13, 15, 17, 19 and 21, wherein the one or more ZDDP compounds may be derived from one or more primary alkyl alcohol(s) each having an alkyl group with 3 to 8 carbon atoms.

24. The lubricating oil composition of any one of sentences 5-8, 10, 12, 14, 16, 18, 20 and 22, wherein the one or more ZDDP compounds may be derived from one or more primary alkyl alcohol(s) each having an alkyl group with 3 to 8 carbon atoms.

25. The lubricating oil composition of any one of sentences 1-4, 9, 11, 13, 15, 17, 19, 21 and 23, wherein the alkyl group of the one or more primary alkyl alcohol(s) may have branching at the beta carbon relative to the hydroxyl group.

26. The lubricating oil composition of any one of sentences 5-8, 10, 12, 14, 16, 18, 20, 22 and 24 wherein the alkyl group of the one or more primary alkyl alcohol(s) may have branching at the beta carbon relative to the hydroxyl group.

27. The lubricating oil composition of any one of sentences 1-4, 9, 11, 13, 15, 17, 19, 21, 23 and 25, wherein the one or more ZDDP compounds may be derived from one or more primary alkyl alcohol selected from the group consisting of n-propyl alcohol, isopropyl alcohol, isobutyl alcohol, n-butyl alcohol, 2-butanol, n-pentyl alcohol, hexanol, methyl isobutyl carbinol, isohexanol, n-heptanol, isoheptanol, octanol, amyl alcohol, and 2-ethylhexanol.

28. The lubricating oil composition of any one of sentences 5-8, 10, 12, 14, 16, 18, 20, 22, 24 and 26, wherein the one or more ZDDP compounds may be derived from one or more primary alkyl alcohol selected from the group consisting of n-propyl alcohol, isopropyl alcohol, isobutyl alcohol, n-butyl alcohol, 2-butanol, n-pentyl alcohol, hexanol, methyl isobutyl carbinol, isohexanol, n-heptanol, isoheptanol, octanol, amyl alcohol, and 2-ethylhexanol.

29. The lubricating oil composition of any one of sentences 1-4, 9, 11, 13, 15, 17, 19, 21, 23, 25 and 27, wherein the one or more ZDDP compounds may be derived from two or more primary alkyl alcohols.

30. The lubricating oil composition of any one of sentences 5-8, 10, 12, 14, 16, 18, 20, 22, 24, 26 and 28, wherein the one or more ZDDP compounds may be derived from two or more primary alkyl alcohols.

31. The lubricating oil composition of any one of sentences 1-4, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27 and 29, wherein the one or more ZDDP compounds may be derived from a molar ratio of the one or more primary alkyl alcohol(s) to the one or more secondary alkyl alcohol(s) of from 100:20 to 50:50.

32. The lubricating oil composition of any one of sentences 5-8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28 and 30, wherein the one or more ZDDP compounds may be derived from a molar ratio of the one or more primary alkyl alcohol(s) to the one or more secondary alkyl alcohol(s) of from 100:20 to 50:50.

33. The lubricating oil composition of any one of sentences 1-4, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29 and 31, wherein the one or more ZDDP compounds may have a zinc to phosphorus molar ratio of from 1.08 to 1.2.

34. The lubricating oil composition of any one of sentences 5-8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30 and 32, wherein the one or more ZDDP compounds may have a zinc to phosphorus molar ratio of from 1.08 to 1.2.

35. The lubricating oil composition of any one of sentences 1-4, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29, 31 and 33, wherein the one or more dispersants may be ashless-type dispersants.

36. The lubricating oil composition of any one of sentences 5-8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32 and 34, wherein the one or more dispersants may be ashless-type dispersants.

37. The lubricating oil composition of any one of sentences 1-4, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29, 31, 33 and 35, wherein the one or more dispersants may comprise at least one N-substituted polyisobutylene succinimide dispersant derived from polyisobutylene with a number average molecular weight in the range about 350 to about 50,000 g/mol, or to about 5000 g/mol, or about 500 g/mol to about 3000 g/mol, as determined by GPC.

38. The lubricating oil composition of any one of sentences 5-8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34 and 36, wherein the one or more dispersants may comprise at least one N-substituted polyisobutylene succinimide dispersant derived from polyisobutylene with a number average molecular weight in the range about 350 to about 50,000 g/mol, or to about 5000 g/mol, or about 500 g/mol to about 3000 g/mol, as determined by GPC.

39. The lubricating oil composition of any one of sentences 1-4, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29, 31, 33, 35 and 37, wherein the one or more dispersants may comprise at least one N-substituted polyisobutylene succinimide dispersant derived from a polyamine or hydroxylamine.

40. The lubricating oil composition of any one of sentences 5-8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36 and 38, wherein the one or more dispersants may comprise at least one N-substituted polyisobutylene succinimide dispersant derived from a polyamine or hydroxylamine.

41. The lubricating oil composition of any one of sentences 1-4, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29, 31, 33, 35, 37 and 39, wherein the one or more dispersants may comprise at least one N-substituted polyisobutylene succinimide dispersant derived from diethylene triamine (DETA), triethylene tetramine (TETA), tetraethylene pentamine (TEPA), higher polyethylene amine (PEA) homolog and mixtures thereof; or the one or more dispersants comprises at least one N-substituted polyisobutylene succinimide dispersant derived from pentaethylamine hexamine (PEHA); or the one or more dispersants comprises at least one N-substituted polyisobutylene succinimide dispersant derived from PEA taken alone or in combination with TEPA.

42. The lubricating oil composition of any one of sentences 5-8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38 and 40, wherein the one or more dispersants may comprise at least one N-substituted polyisobutylene succinimide dispersant derived from diethylene triamine (DETA), triethylene tetramine (TETA), tetraethylene pentamine (TEPA), higher polyethylene amine (PEA) homolog and mixtures thereof; or the one or more dispersants comprises at least one N-substituted polyisobutylene succinimide dispersant derived from pentaethylamine hexamine (PEHA); or the one or more dispersants comprises at least one N-substituted polyisobutylene succinimide dispersant derived from PEA taken alone or in combination with TEPA.

43. The lubricating oil composition of any one of sentences 1-4, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29, 31, 33, 35, 37, 39 and 41, wherein the one or more dispersants may have 0.1 to 5 wt.% nitrogen; or 0.25 to 3 wt.% nitrogen; or 0.5 to 2 wt.% nitrogen based on the total weight of the one or more dispersants.

44. The lubricating oil composition of any one of sentences 5-8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40 and 42, wherein the one or more dispersants may have 0.1 to 5 wt.% nitrogen; or 0.25 to 3 wt.% nitrogen; or 0.5 to 2 wt.% nitrogen based on the total weight of the one or more dispersants.

45. The lubricating oil composition of any one of sentences 1-4, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29, 31, 33, 35, 37, 39, 41 and 43, wherein the one or more dispersants may comprise at least one dispersant derived from polyisobutylene succinic anhydride ("PIBSA"), and the PIBSA has an average of about 1.0 and about 2.0 succinic acid moieties per polyisobutylene (PIB) polymer; or about 1.1 and about 1.8 succinic acid moieties per PIB polymer.

46. The lubricating oil composition of any one of sentences 5-8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 42 and 44, wherein the one or more dispersants may comprise at least one dispersant derived from polyisobutylene succinic anhydride ("PIBSA"), and the PIBSA has an average of about 1.0 and about 2.0 succinic acid moieties per polyisobutylene (PIB) polymer; or about 1.1 and about 1.8 succinic acid moieties per PIB polymer.

47. The lubricating oil composition of any one of sentences 1-4, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29, 31, 33, 35, 37, 39, 41, 43 and 45, wherein each of the one or more dispersants may have a TBN of from about 10 mg KOH/g to about 65 mg KOH/g on an oil-free basis, measured by the method of ASTM D2896.

48. The lubricating oil composition of any one of sentences 5-8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 42, 44 and 46, wherein each of the one or more dispersants may have a TBN of from about 10 mg KOH/g to about 65 mg KOH/g on an oil-free basis, measured by the method of ASTM D2896.

49. The lubricating oil composition of any one of sentences 1-4, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29, 31, 33, 35, 37, 39, 41, 43, 45 and 47, wherein the contribution of TBN of the total dispersant to the TBN of the lubricating oil composition may be at least 0.79 mg KOH/g; or is at least 0.85 mg KOH/g; or is 0.85 mg KOH/g to 5 mg KOH/g; or is 0.9 mg KOH/g to 2.5 mg KOH/g.

50. The lubricating oil composition of any one of sentences 5-8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 42, 44, 46 and 48, wherein the contribution of TBN of the total dispersant to the TBN of the lubricating oil composition may be at least 0.79 mg KOH/g; or is at least 0.85 mg KOH/g; or is 0.85 mg KOH/g to 5 mg KOH/g; or is 0.9 mg KOH/g to 2.5 mg KOH/g.

51. The lubricating oil composition of any one of sentences 1-4, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29, 31, 33, 35, 37, 39, 41, 43, 45, 47 and 49, wherein the one or more dispersants may comprise at least one dispersant which is post-treated by a reaction with boron, urea, thiourea, dimercaptothiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, carbonates, cyclic carbonates, hindered phenolic esters, phosphorus compounds and mixtures thereof; or the one or more dispersants comprises at least one dispersant which is post-treated by a reaction with boron and maleic anhydride.

52. The lubricating oil composition of any one of sentences 5-8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 42, 44, 46, 48 and 50, wherein the one or more dispersants

may comprise at least one dispersant which is post-treated by a reaction with boron, urea, thiourea, dimercaptothiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, carbonates, cyclic carbonates, hindered phenolic esters, phosphorus compounds and mixtures thereof; or the one or more dispersants comprises at least one dispersant which is post-treated by a reaction with boron and maleic anhydride.

53. The lubricating oil composition of any one of sentences 1-4, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29, 31, 33, 35, 37, 39, 41, 43, 45, 47, 49 and 51, wherein the one or more dispersants may be a mixture of at least one dispersant that is post-treated and at least one dispersant that is not post-treated.

54. The lubricating oil composition of any one of sentences 5-8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 42, 44, 46, 48, 50 and 52, wherein the one or more dispersants may be a mixture of at least one dispersant that is post-treated and at least one dispersant that is not post-treated.

55. The lubricating oil composition of any one of sentences 1-4, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29, 31, 33, 35, 37, 39, 41, 43, 45, 47, 49, 51 and 53, wherein the amount of the one or more dispersants may be about 0.1 wt.% to about 15 wt.%, or about 0.1 wt.% to about 10 wt.%, or about 0.1 to about 8 wt.%, or about 1 wt.% to about 10 wt.%, or about 1 wt.% to about 8 wt.%, or about 1 wt.% to about 7 wt.%, based upon the total weight of the lubricating oil composition.

56. The lubricating oil composition of any one of sentences 5-8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 42, 44, 46, 48, 50, 52 and 54, wherein the amount of the one or more dispersants may be about 0.1 wt.% to about 15 wt.%, or about 0.1 wt.% to about 10 wt.%, or about 0.1 to about 8 wt.%, or about 1 wt.% to about 10 wt.%, or about 1 wt.% to about 8 wt.%, or about 1 wt.% to about 7 wt.%, based upon the total weight of the lubricating oil composition.

57. The lubricating oil composition of any one of sentences 1-4, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29, 31, 33, 35, 37, 39, 41, 43, 45, 47, 49, 51, 53 and 55, may further comprise at

least one additive selected from the group consisting of dispersants, antioxidants, anti-wear agents, antifoam agents, molybdenum-containing compounds, titanium-containing compounds, phosphorus-containing compounds, pour point depressants, and diluent oils.

58. The lubricating oil composition of any one of sentences 5-8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 42, 44, 46, 48, 50, 52, 54 and 56, may further comprise at least one additive selected from the group consisting of dispersants, antioxidants, anti-wear agents, antifoam agents, molybdenum-containing compounds, titanium-containing compounds, phosphorus-containing compounds, pour point depressants, and diluent oils.

59. The lubricating oil composition of any one of sentences 1-4, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29, 31, 33, 35, 37, 39, 41, 43, 45, 47, 49, 51, 53, 55 and 57, wherein the lubricating oil composition may provide results of an Average Engine Sludge test (ASTM D8256) of 7.01 minutes or higher, or 7.05 minutes or higher, or 7.05 minutes to about 15 minutes.

60. The lubricating oil composition of any one of sentences 5-8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 42, 44, 46, 48, 50, 52, 54, 56, and 58 wherein the lubricating oil composition may provide results of an Average Engine Sludge test (ASTM D8256) of 7.01 minutes or higher, or 7.05 minutes or higher, or 7.05 minutes to about 15 minutes.

61. A method of reducing engine sludge of an internal combustion engine, the method comprising adding to the engine the lubricating oil composition of any one of sentences 1-4, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29, 31, 33, 35, 37, 39, 41, 43, 45, 47, 49, 51, 53, 55, 57, and 59 and operating said engine.

62. A method of reducing engine sludge of an internal combustion engine, the method comprising adding to the engine the lubricating oil composition of any one of sentences 5-8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 42, 44, 46, 48, 50, 52, 54, 56, 58 and 60 and operating said engine.

63. A method of improving the fuel economy performance and/or piston cleanliness performance of an engine and/or a vehicle, comprising the step of providing the engine and/or the vehicle with a lubricant composition according to any one of sentences 1-4, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29, 31, 33, 35, 37, 39, 41, 43, 45, 47, 49, 51, 53, 55, 57 and 59.

64. A method of improving the fuel economy performance and/or piston cleanliness performance of an engine and/or a vehicle, comprising the step of providing the engine and/or the vehicle with a lubricant composition according to any one of sentences 5-8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 42, 44, 46, 48, 50, 52, 54, 56, 58 and 60.

[0007] The following definitions of terms are provided in order to clarify the meanings of certain terms as used herein.

[0008] The terms “oil composition,” “lubrication composition,” “lubricating oil composition,” “lubricating oil,” “lubricant composition,” “lubricating composition,” “fully formulated lubricant composition,” “lubricant,” “crankcase oil,” “crankcase lubricant,” “engine oil,” “engine lubricant,” “motor oil,” and “motor lubricant” are considered synonymous, fully interchangeable terminology referring to the finished lubrication product comprising a major amount of a base oil plus a minor amount of an additive composition.

[0009] As used herein, the terms “additive package,” “additive concentrate,” “additive composition,” “engine oil additive package,” “engine oil additive concentrate,” “crankcase additive package,” “crankcase additive concentrate,” “motor oil additive package,” “motor oil concentrate,” are considered synonymous, fully interchangeable terminology referring the portion of the lubricating oil composition excluding the major amount of base oil stock mixture. The additive package may or may not include the viscosity index improver or pour point depressant.

[0010] The term “overbased” relates to metal salts, such as metal salts of sulfonates, carboxylates, salicylates, and/or phenates, wherein the amount of metal present exceeds the stoichiometric amount. Such salts may have a conversion level in excess of 100% (i.e., they may comprise more than 100% of the theoretical amount of metal needed to convert the acid to its “normal,” “neutral” salt). The expression “metal ratio,” often abbreviated as MR, is used to designate the ratio of total chemical equivalents of metal in the overbased salt to chemical equivalents of the metal in a neutral salt according to known chemical reactivity and stoichiometry. In a normal or neutral salt, the metal ratio is one and in an overbased salt, MR,

is greater than one. They are commonly referred to as overbased, hyperbased, or superbased salts and may be salts of organic sulfur acids, carboxylic acids, salicylates, and/or phenols.

[0011] 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 a predominantly hydrocarbon character. Each hydrocarbyl group is independently selected from hydrocarbon substituents, and substituted hydrocarbon substituents containing one or more of halo groups, hydroxyl groups, alkoxy groups, mercapto groups, nitro groups, nitroso groups, amino groups, pyridyl groups, furyl groups, imidazolyl groups, oxygen and nitrogen, and wherein no more than two non-hydrocarbon substituents are present for every ten carbon atoms in the hydrocarbyl group.

[0012] As used herein, the term "hydrocarbylene substituent" or "hydrocarbylene group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group that is directly attached at two locations of the molecule to the remainder of the molecule by a carbon atom and having predominantly hydrocarbon character. Each hydrocarbylene group is independently selected from divalent hydrocarbon substituents, and substituted divalent hydrocarbon substituents containing halo groups, alkyl groups, aryl groups, alkylaryl groups, arylalkyl groups, hydroxyl groups, alkoxy groups, mercapto groups, nitro groups, nitroso groups, amino groups, pyridyl groups, furyl groups, imidazolyl groups, oxygen and nitrogen, and wherein no more than two non-hydrocarbon substituents is present for every ten carbon atoms in the hydrocarbylene group.

[0013] As used herein, the term "percent by weight", unless expressly stated otherwise, means the percentage the recited component represents to the weight of the entire composition.

[0014] The terms "soluble," "oil-soluble," or "dispersible" used herein may, but does not necessarily, indicate that the compounds or additives are soluble, dissolvable, miscible, or capable of being suspended in the oil in all proportions. The foregoing terms do mean, however, that they are, for instance, soluble, suspendable, dissolvable, or stably dispersible in oil to an extent sufficient to exert their intended effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular additive, if desired.

[0015] The term "TBN" as employed herein is used to denote the Total Base Number in mg KOH/g as measured by the method of ASTM D2896 or ASTM D4739 or DIN 51639-1.

[0016] The term "alkyl" as employed herein refers to straight, branched, cyclic, and/or substituted saturated chain moieties of from about 1 to about 100 carbon atoms.

[0017] The term "alkenyl" as employed herein refers to straight, branched, cyclic, and/or substituted unsaturated chain moieties of from about 3 to about 10 carbon atoms.

[0018] The term "aryl" as employed herein refers to single and multi-ring aromatic compounds that may include alkyl, alkenyl, alkylaryl, amino, hydroxyl, alkoxy, halo substituents, and/or heteroatoms including, but not limited to, nitrogen, oxygen, and sulfur.

[0019] Lubricants, combinations of components, or individual components of the present description may be suitable for use in various types of internal combustion engines. Suitable engine types may include, but are not limited to heavy duty diesel, passenger car, light duty diesel, medium speed diesel, or marine engines. An internal combustion engine may be a diesel fueled engine, a gasoline fueled engine, a natural gas fueled engine, a bio-fueled engine, a mixed diesel/biofuel fueled engine, a mixed gasoline/biofuel fueled engine, an alcohol fueled engine, a mixed gasoline/alcohol fueled engine, a compressed natural gas (CNG) fueled engine, or mixtures thereof. A diesel engine may be a compression ignited engine. A gasoline engine may be a spark-ignited engine. An internal combustion engine may also be used in combination with an electrical or battery source of power. An engine so configured is commonly known as a hybrid engine. The internal combustion engine may be a 2-stroke, 4-stroke, or rotary engine. Suitable internal combustion engines include marine diesel engines (such as inland marine), aviation piston engines, low-load diesel engines, and motorcycle, automobile, locomotive, and truck engines.

[0020] The internal combustion engine may contain components of one or more of an aluminum-alloy, lead, tin, copper, cast iron, magnesium, ceramics, stainless steel, composites, and/or mixtures thereof. The components may be coated, for example, with a diamond-like carbon coating, a lubrited coating, a phosphorus-containing coating, molybdenum-containing coating, a graphite coating, a nano-particle-containing coating, and/or mixtures thereof. The aluminum-alloy may include aluminum silicates, aluminum oxides, or other ceramic materials. In one embodiment the aluminum-alloy is an aluminum-silicate surface. As used herein, the term "aluminum alloy" is intended to be synonymous with "aluminum composite" and to describe a component or surface comprising aluminum

and another component intermixed or reacted on a microscopic or nearly microscopic level, regardless of the detailed structure thereof. This would include any conventional alloys with metals other than aluminum as well as composite or alloy-like structures with non-metallic elements or compounds such with ceramic-like materials.

[0021] The lubricating oil composition for an internal combustion engine may be suitable for any engine lubricant irrespective of the sulfur, phosphorus, or sulfated ash (ASTM D-874) content. The sulfur content of the engine oil lubricant may be about 1 wt.% or less, or about 0.8 wt.% or less, or about 0.5 wt.% or less, or about 0.3 wt.% or less, or about 0.2 wt.% or less. In one embodiment the sulfur content may be in the range of about 0.001 wt.% to about 0.5 wt.%, or about 0.01 wt.% to about 0.3 wt.%. The phosphorus content may be about 0.2 wt.% or less, or about 0.1 wt.% or less, or about 0.06 wt.% to about 0.2 wt.%. In one embodiment the phosphorus content may be about 500 ppmw to about 1250 ppmw, or about 600 ppmw to about 1200 ppmw. The total sulfated ash content may be about 2 wt.% or less, or about 1.5 wt.% or less, or about 1.1 wt.% or less, or about 1 wt.% or less, or about 0.8 wt.% or less, or about 0.5 wt.% or less. In one embodiment the sulfated ash content may be about 0.05 wt.% to about 0.9 wt.%, or about 0.1 wt.% or about 0.2 wt.% to about 0.45 wt.%. In another embodiment, the sulfur content may be about 0.4 wt.% or less, the phosphorus content may be about 0.12 wt.% or less, and the sulfated ash is about 1 wt.% or less. In yet another embodiment the sulfur content may be about 0.3 wt.% or less, the phosphorus content is about 0.11 wt.% or less, and the sulfated ash may be about 0.8 wt.% or less.

[0022] In one embodiment the lubricating oil composition is an engine oil, wherein the lubricating oil composition may have (i) a sulfur content of about 0.5 wt.% or less, (ii) a phosphorus content of about 0.1 wt.% or less, and (iii) a sulfated ash content of about 1.5 wt.% or less.

[0023] In one embodiment the lubricating oil composition is suitable for a 2-stroke or a 4-stroke marine diesel internal combustion engine. In one embodiment the marine diesel combustion engine is a 2-stroke engine. In some embodiments, the lubricating oil composition is not suitable for a 2-stroke or a 4-stroke marine diesel internal combustion engine for one or more reasons, including but not limited to, the high sulfur content of fuel used in powering a marine engine and the high TBN required for a marine-suitable engine oil (e.g., above about 40 TBN in a marine-suitable engine oil).

[0024] In some embodiments, the lubricating oil composition is suitable for use with engines powered by low sulfur fuels, such as fuels containing about 1 to about 5% sulfur. Highway vehicle fuels contain about 15 ppmw sulfur (or about 0.0015% sulfur).

[0025] Low speed diesel typically refers to marine engines, medium speed diesel typically refers to locomotives, and high speed diesel typically refers to highway vehicles. The lubricating oil composition may be suitable for only one of these types or all.

[0026] Further, lubricants of the present description may be suitable to meet one or more industry specification requirements such as ILSAC GF-3, GF-4, GF-5, GF-5+, GF-6, PC-11, CF, CF-4, CH-4, CK-4, FA-4, CJ-4, CI-4 Plus, CI-4, API SG, SJ, SL, SM, SN, SN PLUS, ACEA A1/B1, A2/B2, A3/B3, A3/B4, A5/B5, A7/B7, C1, C2, C3, C4, C5, C6 E4/E6/E7/E9, Euro 5/6, JASO DL-1, Low SAPS, Mid SAPS, or original equipment manufacturer specifications such as Dexos1™, Dexos2™, MB-Approval 229.1, 229.3, 229.5, 22.51/229.31, 229.52, 229.6, 229.71, 226.5, 226.51, 228.0/1, 228.2/3, 228.31, 228.5, 228.51, 228.61, VW 501.01, 502.00, 503.00/503.01, 504.00, 505.00, 505.01, 506.00/506.01, 507.00, 508.00, 509.00, 508.88, 509.99, BMW Longlife-01, Longlife-01 FE, Longlife-04, Longlife-12 FE, Longlife-14 FE+, Longlife-17 FE+ Porsche A40, C30, Peugeot Citroën Automobiles B71 2290, B71 2294, B71 2295, B71 2296, B71 2297, B71 2300, B71 2302, B71 2312, B71 2007, B71 2008, Renault RN0700, RN0710, RN0720, Ford WSS-M2C153-H, WSS-M2C930-A, WSS-M2C945-A, WSS-M2C913A, WSS-M2C913-B, WSS-M2C913-C, WSS-M2C913-D, WSS-M2C948-B, WSS-M2C948-A, GM 6094-M, Chrysler MS-6395, Fiat 9.55535 G1, G2, M2, N1, N2, Z2, S1, S2, S3, S4, T2, DS1, DSX, GH2, GS1, GSX, CR1, Jaguar Land Rover STJLR.03.5003, STJLR.03.5004, STJLR.03.5005, STJLR.03.5006, STJLR.03.5007, STJLR.51.5122, or any past or future PCMO or HDD specifications not mentioned herein. In some embodiments for passenger car motor oil (PCMO) applications, the amount of phosphorus in the finished fluid is 1000 ppmw or less or 900 ppmw or less or 800 ppmw or less.

[0027] Other hardware may not be suitable for use with the disclosed lubricant. A “functional fluid” is a term which encompasses a variety of fluids including but not limited to tractor hydraulic fluids, power transmission fluids including automatic transmission fluids, continuously variable transmission fluids and manual transmission fluids, hydraulic fluids, including tractor hydraulic fluids, some gear oils, power steering fluids, fluids used in wind turbines, compressors, some industrial fluids, and fluids related to power train components. It should be noted that within each of these fluids such as, for example, automatic transmission

fluids, there are a variety of different types of fluids due to the various transmissions having different designs which have led to the need for fluids of markedly different functional characteristics. This is contrasted by the term “lubricating fluid” which is not used to generate or transfer power.

[0028] With respect to tractor hydraulic fluids, for example, these fluids are all-purpose products used for all lubricant applications in a tractor except for lubricating the engine. These lubricating applications may include lubrication of gearboxes, power take-off and clutch(es), rear axles, reduction gears, wet brakes, and hydraulic accessories.

[0029] When the functional fluid is an automatic transmission fluid, the automatic transmission fluids must have enough friction for the clutch plates to transfer power. However, the friction coefficient of fluids has a tendency to decline due to the temperature effects as the fluid heats up during operation. It is important that the tractor hydraulic fluid or automatic transmission fluid maintain its high friction coefficient at elevated temperatures, otherwise brake systems or automatic transmissions may fail. This is not a function of an engine oil.

[0030] Tractor fluids, and for example Super Tractor Universal Oils (STUOs) or Universal Tractor Transmission Oils (UTTOs), may combine the performance of engine oils with transmissions, differentials, final-drive planetary gears, wet-brakes, and hydraulic performance. While many of the additives used to formulate a UTTO or a STUO fluid are similar in functionality, they may have deleterious effect if not incorporated properly. For example, some anti-wear and extreme pressure additives used in engine oils can be extremely corrosive to the copper components in hydraulic pumps. Detergents and dispersants used for gasoline or diesel engine performance may be detrimental to wet brake performance. Friction modifiers specific to quiet wet brake noise, may lack the thermal stability required for engine oil performance. Each of these fluids, whether functional, tractor, or lubricating, are designed to meet specific and stringent manufacturer requirements.

[0031] The present disclosure provides novel lubricating oil blends formulated for use as automotive crankcase lubricants. The present disclosure provides novel lubricating oil blends formulated for use as 2T and/or 4T motorcycle crankcase lubricants. Embodiments of the present disclosure may provide lubricating oils suitable for crankcase applications and having improvements in the following characteristics: air entrainment, alcohol fuel compatibility, antioxidancy, anti-wear performance, biofuel compatibility, foam reducing

properties, friction reduction, fuel economy, preignition prevention, rust inhibition, sludge and/or soot dispersibility, piston cleanliness, deposit formation, and water tolerance.

[0032] Engine oils of the present disclosure may be formulated by the addition of one or more additives, as described in detail below, to an appropriate base oil formulation. The additives may be combined with a base oil in the form of an additive package (or concentrate) or, alternatively, may be combined individually with a base oil (or a mixture of both). The fully formulated engine oil may exhibit improved performance properties, based on the additives added and their respective proportions.

[0033] Additional details and advantages of the disclosure will be set forth in part in the description which follows, and/or may be learned by practice of the disclosure. The details and advantages of the disclosure may be realized and attained by means of the elements and combinations particularly pointed out in the appended claims. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the disclosure, as claimed.

BRIEF DESCRIPTION OF THE DRAWINGS

[0034] Figure 1 is a graph of the amount of zinc (Zn) in weight percent provided to the lubricating oil composition by the one or more ZDDP compounds multiplied by the contribution of the total base number (TBN) of the one or more dispersants to the TBN of the lubricating oil composition versus the Average Engine Sludge.

[0035] Figure 2 is a graph of the amount of phosphorus (P) in weight percent provided to the lubricating oil composition by the one or more ZDDP compounds multiplied by the contribution of the total base number (TBN) of the one or more dispersants to the TBN of the lubricating oil composition versus the Average Engine Sludge.

DETAILED DESCRIPTION

[0036] This disclosure relates to lubricating oil compositions with reduced engine deposits. In particular, this disclosure relates to lubricating oil compositions, and methods for improving resistance to deposits of a lubricating oil in an engine or other mechanical component lubricated with the lubricating oil. The lubricating oils of this disclosure are useful as passenger vehicle engine oil (PVEO) products, commercial vehicle engine oil (CVEO) products, or other applications where lubricating oils are subjected to heat and oxidative conditions.

[0037] In an embodiment, the lubricating oil composition of the invention comprises greater than 50 wt.% of a base oil of lubricating viscosity, and an additive composition comprising: one or more zinc dialkyl dithiophosphates (ZDDP compounds) and one or more dispersants, wherein the amount of zinc (Zn) in weight percent provided to the lubricating oil composition by the one or more ZDDP compounds multiplied by the contribution of the total base number (TBN) of the one or more dispersants to the TBN of the lubricating oil composition is a multiplication factor $Zn*TBNDisp$ of at least about 0.06.

[0038] In another embodiment, the lubricating oil composition of the invention comprises greater than 50 wt.% of a base oil of lubricating viscosity, and an additive composition comprising: one or more zinc dialkyl dithiophosphates (ZDDP compounds) and one or more dispersants, wherein the amount of phosphorus (P) in weight percent provided to the lubricating oil composition by the one or more ZDDP compounds multiplied by the contribution of the total base number (TBN) of the one or more dispersants to the TBN of the lubricating oil composition is a multiplication factor $P*TBNDisp$ of at least about 0.051.

[0039] ZDDP has antioxidant and anti-wear functionalities. Without being bound to theory, it is believed that the ZDDP acts as an oxidation inhibitor to minimize the formation of deposit precursors, such as hydroperoxides and radicals. These species are reactive, and they attack the hydrocarbon base oil and additives, which make up the lubricant, to form sludge, resin, varnish, and hard deposits. The dispersant works in coordination with the ZDDP, by keeping these entities suspended in the bulk lubricant. This not only results in improved deposit control but also minimizes particulate-related abrasive wear and viscosity increase.

[0040] As discussed in detail below, the lubricating oil compositions were tested according to a Sequence VH engine test. The Sequence VH Test (ASTM D8256) is a test method used to evaluate an automotive engine oil's control of engine deposits under operating conditions deliberately selected to accelerate deposit formation. The engine is a spark-ignited engine fueled with gasoline and operated under low-temperature, light-duty conditions. One of the measurements included in the Sequence VH Test is of the Average Engine Sludge. Cleanliness of the engine is measured via sludge merits, whereby a higher score demonstrates increased engine cleanliness.

[0041] In an embodiment, there is improved resistance to engine deposits when the engine oil is formulated with an additive composition having the features of an $Zn*TBNDisp$ multiplication factor of at least about 0.06 and the one or more ZDDP compounds is present

in a sufficient amount to provide greater than about 0.071 wt.% of zinc based on the total weight of the lubricating oil composition. This improvement is seen over engine oil formulations lacking said features.

[0042] In another embodiment, there is improved resistance to engine deposits when the engine oil is formulated with an additive composition having the features of a Zn*TBNDISP multiplication factor is at least about 0.06 and the contribution of TBN of the one or more dispersants to the TBN of the lubricating oil composition is at least 0.79 mg KOH/g. This improvement is seen over engine oil formulations lacking said features.

[0043] In yet another embodiment, there is improved resistance to engine deposits when the engine oil is formulated with an additive composition having the features of a P*TBNDISP multiplication factor is at least about 0.051 and the one or more ZDDP compounds is present in a sufficient amount to provide greater than about 0.065 wt.% of P based on the total weight of the lubricating oil composition. This improvement is seen over engine oil formulations lacking said features.

[0044] In an additional embodiment, there is improved resistance to engine deposits when the engine oil is formulated with an additive composition having the features of a P*TBNDISP multiplication factor is at least about 0.051 and the contribution of TBN of the one or more dispersants to the TBN of the lubricating oil composition is at least 0.79 mg KOH/g. This improvement is seen over engine oil formulations lacking said features.

Base Oil

[0045] The base oil used in the lubricating oil compositions herein may be selected from any of the base oils in Groups I-V as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are shown in Table 1 below:

Table 1

Base oil Category	Sulfur (%)		Saturates (%)	Viscosity Index
Group I	> 0.03	and/or	<90	80 to 120
Group II	≤0.03	and	≥90	80 to 120
Group III	≤0.03	and	≥90	≥120
Group IV	All polyalphaolefins (PAOs)			
Group V	All others not included in Groups I, II, III, or IV			

[0046] Groups I, II, and III are mineral oil process stocks. Group IV base oils contain true synthetic molecular species, which are produced by polymerization of olefinically unsaturated hydrocarbons. Many Group V base oils are also true synthetic products and may include diesters, polyol esters, polyalkylene glycols, alkylated aromatics, polyphosphate esters, polyvinyl ethers, and/or polyphenyl ethers, and the like, but may also be naturally occurring oils, such as vegetable oils. It should be noted that although Group III base oils are derived from mineral oil, the rigorous processing that these fluids undergo causes their physical properties to be very similar to some true synthetics, such as PAOs. Therefore, oils derived from Group III base oils may be referred to as synthetic fluids in the industry. Group II+ may comprise high viscosity index Group II.

[0047] The base oil used in the disclosed lubricating oil composition may be a mineral oil, animal oil, vegetable oil, synthetic oil, synthetic oil blends, or mixtures thereof. Suitable oils may be derived from hydrocracking, hydrogenation, hydrofinishing, unrefined, refined, and re-refined oils, and mixtures thereof.

[0048] Unrefined oils are those derived from a natural, mineral, or synthetic source without or with little further purification treatment. Refined oils are similar to unrefined oils except that they have been treated in one or more purification steps, which may result in the improvement of one or more properties. Examples of suitable purification techniques are solvent extraction, secondary distillation, acid or base extraction, filtration, percolation, and

the like. Oils refined to the quality of an edible may or may not be useful. Edible oils may also be called white oils. In some embodiments, lubricating oil compositions are free of edible or white oils.

[0049] Re-refined oils are also known as reclaimed or reprocessed oils. These oils are obtained similarly to refined oils using the same or similar processes. Often these oils are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

[0050] Mineral oils may include oils obtained by drilling or from plants and animals or any mixtures thereof. For example such oils may include, but are not limited to, castor oil, lard oil, olive oil, peanut oil, corn oil, soybean oil, and linseed oil, as well as mineral lubricating oils, such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types. Such oils may be partially or fully hydrogenated, if desired. Oils derived from coal or shale may also be useful.

[0051] Useful synthetic lubricating oils may include hydrocarbon oils such as polymerized, oligomerized, or interpolymerized olefins (e.g., polybutylenes, polypropylenes, propyleneisobutylene copolymers); poly(1-hexenes), poly(1-octenes), trimers or oligomers of 1-decene, e.g., poly(1-decenes), such materials being often referred to as α -olefins, and mixtures thereof; alkyl-benzenes (e.g. dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)-benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); diphenyl alkanes, alkylated diphenyl alkanes, alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof or mixtures thereof. Polyalphaolefins are typically hydrogenated materials.

[0052] Other synthetic lubricating oils include polyol esters, diesters, liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, and the diethyl ester of decane phosphonic acid), or polymeric tetrahydrofurans. Synthetic oils may be produced by Fischer-Tropsch reactions and typically may be hydroisomerized Fischer-Tropsch hydrocarbons or waxes. In one embodiment oils may be prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid oils.

[0053] The major amount of base oil included in a lubricating composition may be selected from the group consisting of Group I, Group II, a Group III, a Group IV, a Group V, and a combination of two or more of the foregoing, and wherein the major amount of base oil is other than base oils that arise from provision of additive components or viscosity index

improvers in the composition. In another embodiment, the major amount of base oil included in a lubricating composition may be selected from the group consisting of Group II, a Group III, a Group IV, a Group V, and a combination of two or more of the foregoing, and wherein the major amount of base oil is other than base oils that arise from provision of additive components or viscosity index improvers in the composition.

[0054] The amount of the oil of lubricating viscosity present may be the balance remaining after subtracting from 100 wt.% the sum of the amount of the performance additives inclusive of viscosity index improver(s) and/or pour point depressant(s) and/or other top treat additives. For example, the oil of lubricating viscosity that may be present in a finished fluid may be a major amount, such as greater than about 50 wt.%, greater than about 60 wt.%, greater than about 70 wt.%, greater than about 80 wt.%, greater than about 85 wt.%, or greater than about 90 wt.%.

Dispersants

[0055] The lubricating oil composition further comprises one or more dispersants. Dispersants are often known as ashless-type dispersants because, prior to mixing in a lubricating oil composition, they do not contain ash-forming metals and they do not normally contribute any ash when added to a lubricant. Ashless type dispersants are characterized by a polar group attached to a relatively high molecular weight hydrocarbon chain. Typical ashless dispersants include N-substituted long chain alkenyl succinimides. Examples of N-substituted long chain alkenyl succinimides include polyisobutylene succinimide with number average molecular weight of the polyisobutylene substituent in the range about 350 g/mol to about 50,000 g/mol, or to about 5,000 g/mol, or about 500 g/mol to about 3,000 g/mol, as measured by GPC. Succinimide dispersants and their preparation are disclosed, for instance in U.S. Pat. No. 7,897,696 or U.S. Pat. No. 4,234,435. The alkenyl substituent may be prepared from polymerizable monomers containing about 2 to about 16, or about 2 to about 8, or about 2 to about 6 carbon atoms. Succinimide dispersants are typically the imide formed from a polyamine, typically a poly(ethyleneamine).

[0056] Preferred amines are selected from polyamines and hydroxyamines. Examples of polyamines that may be used include, but are not limited to, diethylene triamine (DETA), triethylene tetramine (TETA), tetraethylene pentamine (TEPA), and higher polyethylene amine (PEA) homologues such as pentaethylamine hexamine (PEHA), and the like. In an embodiment, the amine is PEA taken alone or in combination with TEPA.

[0057] A suitable heavy polyamine is a mixture of polyalkylene-polyamines comprising small amounts of lower polyamine oligomers such as TEPA and PEHA (pentaethylene hexamine) but primarily oligomers with 6 or more nitrogen atoms, 2 or more primary amines per molecule, and more extensive branching than conventional polyamine mixtures. A heavy polyamine preferably includes polyamine oligomers containing 7 or more nitrogens per molecule and with 2 or more primary amines per molecule. The heavy polyamine comprises more than 28 wt. % (e.g. >32 wt. %) total nitrogen and an equivalent weight of primary amine groups of 120-160 grams per equivalent.

[0058] In some approaches, suitable polyamines are commonly known as PAM and contain a mixture of ethylene amines where TEPA and pentaethylene hexamine (PEHA) are the major part of the polyamine, usually less than about 80%.

[0059] Typically PAM has 8.7-8.9 milliequivalents of primary amine per gram (an equivalent weight of 115 to 112 grams per equivalent of primary amine) and a total nitrogen content of about 33-34 wt. %. Heavier cuts of PAM oligomers with practically no TEPA and only very small amounts of PEHA but containing primarily oligomers with more than 6 nitrogens and more extensive branching, may produce dispersants with improved dispersancy.

[0060] In an embodiment, the one or more dispersants has 0.1 to 5 wt.% nitrogen; or 0.25 to 3 wt.% nitrogen; or 0.5 to 2 wt.% nitrogen based on the total weight of the one or more dispersants.

[0061] In an embodiment the present disclosure further comprises at least one polyisobutylene succinimide dispersant derived from polyisobutylene with a number average molecular weight in the range about 350 to about 50,000 g/mol, or to about 5000 g/mol, or about 500 g/mol to about 3000 g/mol, as determined by GPC. The polyisobutylene succinimide may be used alone or in combination with other dispersants.

[0062] In some embodiments, polyisobutylene, when included, may have greater than 50 mol%, greater than 60 mol%, greater than 70 mol%, greater than 80 mol%, or greater than 90 mol% content of terminal double bonds. Such PIB is also referred to as highly reactive PIB ("HR-PIB"). HR-PIB having a number average molecular weight ranging from about 800 g/mol to about 5000 g/mol, as determined by GPC, is suitable for use in embodiments of the present disclosure. Conventional PIB typically has less than 50 mol%, less than 40 mol%, less than 30 mol%, less than 20 mol%, or less than 10 mol% content of terminal double bonds.

[0063] An HR-PIB having a number average molecular weight ranging from about 900 g/mol to about 3000 g/mol, as determined by GPC, may be suitable. Such HR-PIB is commercially available, or can be synthesized by the polymerization of isobutene in the presence of a non-chlorinated catalyst such as boron trifluoride, as described in US Patent No. 4,152,499 to Boerzel, et al. and U.S. Patent No. 5,739,355 to Gateau, et al. When used in the aforementioned thermal ene reaction, HR-PIB may lead to higher conversion rates in the reaction, as well as lower amounts of sediment formation, due to increased reactivity. A suitable method is described in U.S. Patent No. 7,897,696.

[0064] In one embodiment, the present disclosure further comprises at least one dispersant derived from polyisobutylene succinic anhydride ("PIBSA"). The PIBSA may have an average of about 1.0 and about 2.0 succinic acid moieties per PIB polymer; or about 1.1 and about 1.8 succinic acid moieties per PIB polymer.

[0065] The % actives of the alkenyl or alkyl succinic anhydride can be determined using a chromatographic technique. This method is described in column 5 and 6 in U.S. Pat. No. 5,334,321.

[0066] The percent conversion of the polyolefin is calculated from the % actives using the equation in column 5 and 6 in U.S. Pat. No. 5,334,321.

[0067] Unless stated otherwise, all percentages are in weight percent and all molecular weights are number average molecular weights determined by gel permeation chromatography (GPC) using commercially available polystyrene standards (with a number average molecular weight of 180 g/mol to about 18,000 g/mol as the calibration reference).

[0068] In one embodiment, the dispersant may be derived from a polyalphaolefin (PAO) succinic anhydride. In one embodiment, the dispersant may be derived from olefin maleic anhydride copolymer. As an example, the dispersant may be described as a poly-PIBSA. In an embodiment, the dispersant may be derived from an anhydride which is grafted to an ethylene-propylene copolymer.

[0069] The TBN of a suitable dispersant may be from about 10 mg/KOH/g to about 65 mg/KOH/g on an oil-free basis, which is comparable to about 5 mg/KOH/g to about 30 mg/KOH/g TBN if measured on a dispersant sample containing about 50% diluent oil. TBN is measured by the method of ASTM D2896.

[0070] The contribution of TBN of the total dispersant to the TBN of the lubricating oil composition is at least 0.79 mg KOH/g; or is at least 0.85 mg KOH/g; or is 0.85 mg

KOH/g to 5 mg KOH/g; or is 0.9 mg KOH/g to 2.5 mg KOH/g. TBN is measured by the method of D2896.

[0071] A suitable class of nitrogen-containing dispersants may be derived from olefin copolymers (OCP), more specifically, ethylene-propylene dispersants which may be grafted with maleic anhydride. A more complete list of nitrogen-containing compounds that can be reacted with the functionalized OCP are described in U.S. Patent Nos. 7,485,603; 7,786,057; 7,253,231; 6,107,257; and 5,075,383; and/or are commercially available.

[0072] The hydrocarbyl moiety of the hydrocarbyl-dicarboxylic acid or anhydride of Component A) may alternatively be derived from ethylene-alpha olefin copolymers. These copolymers contain a plurality of ethylene units and a plurality of one or more C₃-C₁₀ alpha-olefin units. The C₃-C₁₀ alpha-olefin units may include propylene units.

[0073] One class of suitable dispersants may be Mannich bases. Mannich bases are materials that are formed by the condensation of a higher molecular weight, alkyl substituted phenol, a polyalkylene polyamine, and an aldehyde such as formaldehyde. Mannich bases are described in more detail in U.S. Patent No. 3,634,515.

[0074] A suitable class of dispersants may be high molecular weight esters or half ester amides.

[0075] A suitable dispersant may also be post-treated by conventional methods by a reaction with any of a variety of agents. Among these are boron, urea, thiourea, dimercaptiothiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, carbonates, cyclic carbonates, hindered phenolic esters, and phosphorus compounds. Preferably the dispersant is post-treated with boron and maleic anhydride. US 7,645,726; US 7,214,649; and US 8,048,831 are incorporated herein by reference in their entireties.

[0076] The one or more dispersants can be a mix of at least one dispersant that is post-treated and at least one dispersant that is not post-treated. The weight ratio of dispersants that are post-treated and dispersants that are not post-treated can be about 5:1 to about 1:15; or about 4:1 to about 1:10.

[0077] In addition to the carbonate and boric acids post-treatments both the compounds may be post-treated, or further post-treatment, with a variety of post-treatments designed to improve or impart different properties. Such post-treatments include those summarized in columns 27-29 of U.S. Pat. No. 5,241,003, hereby incorporated by reference. Such treatments include, treatment with:

Inorganic phosphorous acids or anhydrides (e.g., U.S. Pat. Nos. 3,403,102 and 4,648,980);
Organic phosphorous compounds (e.g., U.S. Pat. No. 3,502,677);
Phosphorous pentasulfides;
Boron compounds as already noted above (e.g., U.S. Pat. Nos. 3,178,663 and 4,652,387);
Carboxylic acid, polycarboxylic acids, anhydrides and/or acid halides (e.g., U.S. Pat. Nos. 3,708,522 and 4,948,386);
Epoxides polyepoxiates or thioepoxides (e.g., U.S. Pat. Nos. 3,859,318 and 5,026,495);
Aldehyde or ketone (e.g., U.S. Pat. No. 3,458,530);
Carbon disulfide (e.g., U.S. Pat. No. 3,256,185);
Glycidol (e.g., U.S. Pat. No. 4,617,137);
Urea, thourea or guanidine (e.g., U.S. Pat. Nos. 3,312,619; 3,865,813; and British Patent GB 1,065,595);
Organic sulfonic acid (e.g., U.S. Pat. No. 3,189,544 and British Patent GB 2,140,811);
Alkenyl cyanide (e.g., U.S. Pat. Nos. 3,278,550 and 3,366,569);
Diketene (e.g., U.S. Pat. No. 3,546,243);
A diisocyanate (e.g., U.S. Pat. No. 3,573,205);
Alkane sultone (e.g., U.S. Pat. No. 3,749,695);
1,3-Dicarbonyl Compound (e.g., U.S. Pat. No. 4,579,675);
Sulfate of alkoxylated alcohol or phenol (e.g., U.S. Pat. No. 3,954,639);
Cyclic lactone (e.g., U.S. Pat. Nos. 4,617,138; 4,645,515; 4,668,246; 4,963,275; and 4,971,711);
Cyclic carbonate or thiocarbonate linear monocarbonate or polycarbonate, or chloroformate (e.g., U.S. Pat. Nos. 4,612,132; 4,647,390; 4,648,886; 4,670,170);
Nitrogen-containing carboxylic acid (e.g., U.S. Pat. 4,971,598 and British Patent GB 2,140,811);
Hydroxy-protected chlorodicarbonyloxy compound (e.g., U.S. Pat. No. 4,614,522);
Lactam, thiolactam, thiolactone or dithiolactone (e.g., U.S. Pat. Nos. 4,614,603 and 4,666,460);
Cyclic carbonate or thiocarbonate, linear monocarbonate or polycarbonate, or chloroformate (e.g., U.S. Pat. Nos. 4,612,132; 4,647,390; 4,646,860; and 4,670,170);
Nitrogen-containing carboxylic acid (e.g., U.S. Pat. No. 4,971,598 and British Patent GB 2,440,811);
Hydroxy-protected chlorodicarbonyloxy compound (e.g., U.S. Pat. No. 4,614,522);

Lactam, thiolactam, thiolactone or dithiolactone (e.g., U.S. Pat. Nos. 4,614,603, and 4,666,460);

Cyclic carbamate, cyclic thiocarbamate or cyclic dithiocarbamate (e.g., U.S. Pat. Nos. 4,663,062 and 4,666,459);

Hydroxyaliphatic carboxylic acid (e.g., U.S. Pat. Nos. 4,482,464; 4,521,318; 4,713,189);

Oxidizing agent (e.g., U.S. Pat. No. 4,379,064);

Combination of phosphorus pentasulfide and a polyalkylene polyamine (e.g., U.S. Pat. No. 3,185,647);

Combination of carboxylic acid or an aldehyde or ketone and sulfur or sulfur chloride (e.g., U.S. Pat. Nos. 3,390,086; 3,470,098);

Combination of a hydrazine and carbon disulfide (e.g. U.S. Pat. No. 3,519,564);

Combination of an aldehyde and a phenol (e.g., U.S. Pat. Nos. 3,649,229; 5,030,249; 5,039,307);

Combination of an aldehyde and an O-diester of dithiophosphoric acid (e.g., U.S. Pat. No. 3,865,740);

Combination of a hydroxyaliphatic carboxylic acid and a boric acid (e.g., U.S. Pat. No. 4,554,086);

Combination of a hydroxyaliphatic carboxylic acid, then formaldehyde and a phenol (e.g., U.S. Pat. No. 4,636,322);

Combination of a hydroxyaliphatic carboxylic acid and then an aliphatic dicarboxylic acid (e.g., U.S. Pat. No. 4,663,064);

Combination of formaldehyde and a phenol and then glycolic acid (e.g., U.S. Pat. No. 4,699,724);

Combination of a hydroxyaliphatic carboxylic acid or oxalic acid and then a diisocyanate (e.g. U.S. Pat. No.4,713,191);

Combination of inorganic acid or anhydride of phosphorus or a partial or total sulfur analog thereof and a boron compound (e.g., U.S. Pat. No. 4,857,214);

Combination of an organic diacid then an unsaturated fatty acid and then a nitrosoaromatic amine optionally followed by a boron compound and then a glycolating agent (e.g., U.S. Pat. No. 4,973,412);

Combination of an aldehyde and a triazole (e.g., U.S. Pat. No. 4,963,278);

Combination of an aldehyde and a triazole then a boron compound (e.g., U.S. Pat. No. 4,981,492);

Combination of cyclic lactone and a boron compound (e.g., U.S. Pat. No. 4,963,275 and 4,971,711). The above mentioned patents are herein incorporated in their entireties.

[0078] The one or more dispersants can be used in an amount sufficient to provide up to about 20 wt.%, based upon the final weight of the lubricating oil composition. Another amount of the one or more dispersants that can be used may be about 0.1 wt.% to about 15 wt.%, or about 0.1 wt.% to about 10 wt.%, or about 0.1 to about 8 wt.%, or about 1 wt.% to about 10 wt.%, or about 1 wt.% to about 8 wt.%, or about 1 wt.% to about 7 wt.%, based upon the total weight of the lubricating oil composition. In some embodiments, the lubricating oil composition utilizes a mixed dispersant system. A single type or a mixture of two or more types of dispersants in any desired ratio may be used.

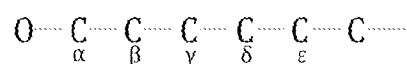
Zinc Dialkyl Dithiophosphate Compound(s)

[0079] The lubricating oil composition of the disclosure for use in an internal combustion engine to reduce engine sludge contains an amount of one or more zinc dialkyl dithiophosphates (ZDDP compounds). The one or more ZDDP compounds can also aid to improve friction and wear properties of the lubricating oil composition.

[0080] The one or more ZDDP compounds can be present in the lubricating oil composition in amounts of from about 0.01 wt.% to about 15 wt.%, or about 0.01 wt.% to about 10 wt.%, or about 0.05 wt.% to about 5 wt.%, or about 0.1 wt.% to about 3 wt.%, or about 0.1 wt.% to about 1.5 wt.% based on the total weight of the lubricating oil composition.

[0081] The one or more ZDDP compounds can comprise ZDDP compounds derived from primary alkyl alcohols, secondary alkyl alcohols, or a combination of primary and secondary alkyl alcohols. The primary alkyl alcohols and secondary alkyl alcohols used to prepare the one or more ZDDP compounds may have an alkyl group including 1 to 20 carbon atoms, or from about 1 to 18 carbon atoms, or from about 1 to about 16 carbon atoms, or 2 to 12 carbon atoms, or about 3 to about 8 carbon atoms. Preferably, the primary alkyl alcohols have branching at the beta carbon relative to the hydroxyl group.

[0082] For example, an alcohol with branching at the beta (β) carbon, would be branching at the second carbon counted from the oxygen atom of the hydroxyl group.



[0083] Suitable examples of primary alkyl alcohols and secondary alkyl alcohols for use in preparing the one or more ZDDP compounds may be selected from the group consisting of n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, 2-butanol, isobutyl alcohol, n-pentyl alcohol, amyl alcohol, hexanol, methyl isobutyl carbinol, isohexanol, n-heptanol, isoheptanol, octanol, nonanol, decanol, undecanol, dodecanol, tridecanol, tetradecanol, pentadecanol, hexadecanol, heptadecanol, octadecanol, nonadecanol, eicosanol, and 2-ethylhexanol.

[0084] The molar ratio of primary alkyl alcohol to secondary alkyl alcohol used to make the one or more ZDDP compounds in the lubricating oil composition can be from about 1:5 to 2:1. The one or more ZDDP compounds may have a P:Zn molar ratio of from about 1.08 to 1.3, or from about 1.08 to 1.2, or from about 1.09 to about 1.15. In some embodiments, the one or more one or more ZDDP compounds may be overbased with zinc oxide.

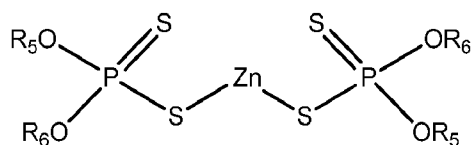
[0085] In some embodiments, the additive composition may comprise at least two different zinc dialkyl dithiophosphate compound(s). The two alkyl groups on the zinc dialkyl dithiophosphate compound(s) may be the same or different.

[0086] In some embodiments, 100 mole percent of the alkyl groups of the one or more one or more ZDDP compounds may be derived from one or more primary alcohol groups. In some embodiments, 100 mole percent of the alkyl groups of the one or more one or more ZDDP compounds may be derived from one or more secondary alcohol groups. In some embodiments, mixtures of one or more all primary alcohol ZDDP compounds and one or more all secondary alcohol ZDDP compounds are provided. In some embodiments, the mixture comprises one or more all primary alcohol ZDDP compounds contributing 15 to 500 ppmw zinc and one or more all secondary alcohol ZDDP compounds contributing 100 to 1000 ppmw zinc to the lubricating oil composition based on the weight of the lubricating oil composition; or the mixture comprises one or more all primary alcohol ZDDP compounds contributing 100 to 400 ppmw zinc and one or more all secondary alcohol ZDDP compounds contributing 300 to 700 ppmw zinc to the lubricating oil composition based on the weight of the lubricating oil composition.

[0087] The alcohols suitable for producing the one or more ZDDP compounds may be primary alkyl alcohols, secondary alkyl alcohols, or a mixture of primary and secondary alcohols. In an embodiment, the additive package comprises one ZDDP compound derived from an alcohol comprising a primary alkyl group and another ZDDP compound derived

from an alcohol comprising a secondary alkyl group. In another embodiment, the ZDDP compound is derived from at least two secondary alcohols. The alcohols may contain any of branched, cyclic, or straight chains.

[0088] The one or more ZDDP compounds may be oil soluble salts of dihydrocarbyl dithiophosphoric acids and may be represented by the following formula:



wherein R₅ and R₆ may be the same or different alkyl groups containing from 1 to 20 carbon atoms, or from about 1 to 18 carbon atoms, or from about 1 to about 16 carbon atoms, or 2 to 12 carbon atoms, or about 3 to about 8 carbon atoms, and including moieties such as alkyl, and cycloalkyl moieties. Thus, the moieties may, for example, be ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, amyl, n-hexyl, i-hexyl, 4-methyl-pentyl, n-octyl, decyl, dodecyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, 2-ethylhexyl, nonadecyl, eicosyl, 2-ethylhexyl, cyclohexyl, or methylcyclopentyl.

[0089] The average number of total number of carbon atoms per mole of phosphorus for a ZDDP compound may be calculated by dividing by two the sum of the carbon atoms in the four alkyl groups R₅ and R₆ provided to the ZDDP compound by alcohol(s) used to make the ZDDP compound. For example, for a single ZDDP compound, if R₅ is a C₃-alkyl group and R₆ is a C₆ alkyl group, the total number of carbon atoms is 3 + 3 + 6 + 6 = 18. Dividing this by two moles of phosphorus per mole of ZDDP gives an average total number of carbon atoms per mole of phosphorus of 9.

[0090] The average total number of carbon atoms per mole of phosphorus (ATCP) for compositions containing one or more ZDDP compounds may be calculated from the alcohol(s) used to make the ZDDP compounds according to the following formula:

$$\text{ATCP} = 2 * [(\text{mol\% of alc1} * \# \text{ of C atoms in alc1}) + (\text{mol\% of alc2} * \# \text{ of C atoms in alc2}) + (\text{mol\% of alc3} * \# \text{ of C atoms in alc3}) + \dots \text{etc.}]$$

wherein alc1, alc2 and alc3 each represent a different alcohol used to make the ZDDP compound(s) and the mol% is the molar percentage of each of the alcohols that was present in the reaction mixture used to make the ZDDP compound(s). The “etc.” indicates that if

more than three alcohols are used to make the ZDDP compounds(s), the formula can be expanded to include each of the alcohols present in the reaction mixture.

[0091] The average total number of carbon atoms from both R₅ and R₆ in the ZDDP is greater than 2 carbon atoms per mole of phosphorus, and in one embodiment in the range from greater than 4 to 40 carbon atoms, or from greater than 6 to about 20 carbon atoms, and in one embodiment in the range from greater than 6 to about 16 carbon atoms, and in one embodiment in the range from about 6 to about 15 carbon atoms, and in one embodiment in the range from about 9 to about 15 carbon atoms, and in one embodiment about 12 carbon atoms per mole of phosphorus.

[0092] The dialkyl dithiophosphate zinc compounds may be prepared in accordance with known techniques by first forming a dialkyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohols and then neutralizing the formed DDPA with a zinc compound. To make the zinc compound, any basic or neutral zinc compound could be used but the oxides, hydroxides, and carbonates are most generally employed. The zinc dialkyl dithiophosphates of component (i) may be made by a process such as the process generally described in U.S. Pat. No. 7,368,596.

[0093] In some embodiments, the one or more ZDDP compounds may be present in the lubricating oil in an amount sufficient to provide from about 100 to about 1500 ppmw phosphorus, or from about 100 to about 1000 ppmw phosphorus, or from about 200 to about 1300 ppmw phosphorus, or from about 300 to about 1200 ppmw phosphorus, or from about 550 to about 1200 ppmw phosphorus, based on the total weight of the lubricating oil composition.

[0094] In some embodiments, the one or more ZDDP compounds may be present in the lubricating oil in an amount sufficient to provide from about 10 ppmw zinc to about 1500 ppmw zinc, or from about 100 ppmw zinc to about 1300 ppmw zinc, or from about 600 ppmw zinc to about 1200 ppmw zinc, based on the total weight of the lubricating oil composition.

[0095] The use of one or more ZDDP compounds derived from a molar ratio of primary alkyl alcohol to secondary alkyl alcohol of from about 100:0 to about 0:100 unexpectedly provides increased viscosity control across a wide variety of ZDDP compounds relative to the same lubricating oil compositions except lacking ZDDP compounds. Specifically, to improve viscosity control the use of one or more ZDDP compounds derived from 100 mole percent of one or more secondary alkyl alcohols, and/or one or more ZDDP

compounds derived from 100 mole percent of one or more primary alkyl alcohols, unexpectedly provided increased resistance to sludge.

[0096] Also, the use of one or more ZDDP compounds derived from all secondary alkyl alcohol to one or more ZDDP compounds derived from all primary alkyl alcohol is in a molar ratio ranging from 100:0 to 0.2:1; or from 10:1 to 0.4:1; or from 6:1 to 0.75:1 provides improved friction and/or wear results and/or viscosity control across a wide variety of ZDDP compounds relative to lubricating oil compositions except lacking ZDDP compounds.

[0097] The present invention can include overbased ZDDP's which are basic ZDDP's. The term basic ZDDP's or equivalent expressions, is used herein to describe those zinc salts wherein the metal substituent is present in stoichiometrically greater amounts than the phosphorus acid radical. For instance, normal or neutral zinc phosphorodithioate has two equivalents (i.e., 1 mole) of zinc per two equivalents (i.e., 2 moles) of a phosphorodithioic acid, whereas a basic zinc diorganophosphorodithioate has more than two equivalents of zinc per two equivalents of the phosphorodithioic acid.

[0098] For instance, the overbasing can be performed with a basic zinc compound such as zinc oxide. The amount of basic zinc compound required to give the desired overbasing is not critical. The essential factor is that there be present in the reaction mixture sufficient zinc compound for the overbasing reaction. Although it is not absolutely essential, it has been found that the reaction proceeds in a more satisfactory way if a slight excess of zinc compound over the amount required for reaction is used. This excess should be kept at a minimum level to the necessity for removing large amounts of solid from the final product. As a general statement, the excess of zinc compound should not exceed 10-15 percent by weight.

Friction Modifiers

[0099] The lubricating oil compositions herein also may optionally contain one or more friction modifiers. Suitable friction modifiers may comprise metal containing and metal-free friction modifiers and may include, but are not limited to, imidazolines, amides, amines, succinimides, alkoxyated amines, alkoxyated ether amines, amine oxides, amidoamines, nitriles, betaines, quaternary amines, imines, amine salts, amino guanidine, alkanolamides, phosphonates, metal-containing compounds, glycerol esters, sulfurized fatty compounds and olefins, sunflower oil other naturally occurring plant or animal oils,

dicarboxylic acid esters, esters or partial esters of a polyol and one or more aliphatic or aromatic carboxylic acids, and the like.

[00100] Suitable friction modifiers may contain hydrocarbyl groups that are selected from straight chain, branched chain, or aromatic hydrocarbyl groups or mixtures thereof, and may be saturated or unsaturated. The hydrocarbyl groups may be composed of carbon and hydrogen or hetero atoms such as sulfur or oxygen. The hydrocarbyl groups may range from about 12 to about 25 carbon atoms. In some embodiments the friction modifier may be a long chain fatty acid ester. In another embodiment the long chain fatty acid ester may be a mono-ester, or a di-ester, or a (tri)glyceride. The friction modifier may be a long chain fatty amide, a long chain fatty ester, a long chain fatty epoxide derivatives, or a long chain imidazoline.

[00101] Other suitable friction modifiers may include organic, ashless (metal-free), nitrogen-free organic friction modifiers. Such friction modifiers may include esters formed by reacting carboxylic acids and anhydrides with alkanols and generally include a polar terminal group (e.g. carboxyl or hydroxyl) covalently bonded to an oleophilic hydrocarbon chain. An example of an organic ashless nitrogen-free friction modifier is known generally as glycerol monooleate (GMO) which may contain mono-, di-, and tri-esters of oleic acid. Other suitable friction modifiers are described in U.S. Pat. No. 6,723,685, herein incorporated by reference in its entirety.

[00102] Aminic friction modifiers may include amines or polyamines. Such compounds can have hydrocarbyl groups that are linear, either saturated or unsaturated, or a mixture thereof and may contain from about 12 to about 25 carbon atoms. Further examples of suitable friction modifiers include alkoxylated amines and alkoxylated ether amines. Such compounds may have hydrocarbyl groups that are linear, either saturated, unsaturated, or a mixture thereof. They may contain from about 12 to about 25 carbon atoms. Examples include ethoxylated amines and ethoxylated ether amines.

[00103] The amines and amides may be used as such or in the form of an adduct or reaction product with a boron compound such as a boric oxide, boron halide, metaborate, boric acid or a mono-, di- or tri-alkyl borate. Other suitable friction modifiers are described in U.S. Pat. No. 6,300,291, herein incorporated by reference in its entirety.

[00104] A friction modifier may optionally be present in ranges such as about 0 wt.% to about 10 wt.%, or about 0.01 wt.% to about 8 wt.%, or about 0.1 wt.% to about 4 wt.%.

Antioxidants

[00105] The lubricating oil compositions herein also may optionally contain one or more antioxidants in addition to the one or more ZDDP compounds. Antioxidant compounds are known and include for example, phenates, phenate sulfides, sulfurized olefins, phosphosulfurized terpenes, sulfurized esters, aromatic amines, alkylated diphenylamines (e.g., nonyl diphenylamine, di-nonyl diphenylamine, octyl diphenylamine, di-octyl diphenylamine), phenyl-alpha-naphthylamines, alkylated phenyl-alpha-naphthylamines, hindered non-aromatic amines, phenols, hindered phenols, oil-soluble molybdenum compounds, macromolecular antioxidants, or mixtures thereof. Antioxidant compounds may be used alone or in combination.

[00106] The hindered phenol antioxidant may contain a secondary butyl and/or a tertiary butyl group as a sterically hindering group. The phenol group may be further substituted with a hydrocarbyl group and/or a bridging group linking to a second aromatic group. Examples of suitable hindered phenol antioxidants include 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tert-butylphenol, 4-propyl-2,6-di-tert-butylphenol or 4-butyl-2,6-di-tert-butylphenol, or 4-dodecyl-2,6-di-tert-butylphenol. In one embodiment the hindered phenol antioxidant may be an ester and may include, e.g., Irganox™ L-135 available from BASF or an addition product derived from 2,6-di-tert-butylphenol and an alkyl acrylate, wherein the alkyl group may contain about 1 to about 18, or about 2 to about 12, or about 2 to about 8, or about 2 to about 6, or about 4 carbon atoms. Another commercially available hindered phenol antioxidant may be an ester and may include Ethanox™ 4716 available from Albemarle Corporation.

[00107] Useful antioxidants may include diarylamines and high molecular weight phenols. In an embodiment, the lubricating oil composition may contain a mixture of a diarylamine and a high molecular weight phenol, such that each antioxidant may be present in an amount sufficient to provide up to about 5%, by weight, based upon the final weight of the lubricating oil composition. In an embodiment, the antioxidant may be a mixture of about 0.3 to about 1.5% diarylamine and about 0.4 to about 2.5% high molecular weight phenol, by weight, based upon the final weight of the lubricating oil composition.

[00108] Examples of suitable olefins that may be sulfurized to form a sulfurized olefin include propylene, butylene, isobutylene, polyisobutylene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene, tridecene, tetradecene, pentadecene, hexadecene, heptadecene, octadecene, nonadecene, eicosene or mixtures thereof. In one embodiment,

hexadecene, heptadecene, octadecene, 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.

[00109] Another class of sulfurized olefin includes sulfurized fatty acids and their esters. The fatty acids are often obtained from vegetable oil or animal oil and typically contain about 4 to about 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. Fatty acids and/or ester may be mixed with olefins, such as α -olefins.

[00110] In another alternative embodiment the antioxidant composition also contains a molybdenum-containing antioxidant in addition to the phenolic and/or aminic antioxidants discussed above. When a combination of these three antioxidants is used, preferably the ratio of phenolic to aminic to molybdenum-containing is (0 to 2) : (0 to 2) : (0 to 1).

[00111] The one or more antioxidant(s) may be present in ranges about 0 wt.% to about 20 wt.%, or about 0.1 wt.% to about 10 wt.%, or about 1 wt.% to about 5 wt.%, of the lubricating oil composition.

Anti-Wear Agents

[00112] The lubricating oil compositions herein also may optionally contain one or more anti-wear agents in addition to the one or more ZDDP compounds. Examples of suitable anti-wear agents include, but are not limited to, a metal thiophosphate; a phosphoric acid ester or salt thereof; a phosphate ester(s); a phosphite; a phosphorus-containing carboxylic ester, ether, or amide; a sulfurized olefin; thiocarbamate-containing compounds including, thiocarbamate esters, alkylene-coupled thiocarbamates, and bis(S-alkyldithiocarbamyl)disulfides; and mixtures thereof. A suitable anti-wear agent may be a molybdenum dithiocarbamate. The phosphorus containing anti-wear agents are more fully described in European Patent 612 839. The metal in the dialkyl dithio phosphate salts may be an alkali metal, alkaline earth metal, aluminum, lead, tin, molybdenum, manganese, nickel, copper, titanium, or zinc. A useful anti-wear agent may be zinc dialkyldithiophosphate.

[00113] Further examples of suitable anti-wear agents include titanium compounds, tartrates, tartrides, oil soluble amine salts of phosphorus compounds, sulfurized olefins,

phosphites (such as dibutyl phosphite), phosphonates, thiocarbamate-containing compounds, such as thiocarbamate esters, thiocarbamate amides, thiocarbamic ethers, alkylene-coupled thiocarbamates, and bis(S-alkyldithiocarbamyl) disulfides. The tartrate or tartramide may contain alkyl-ester groups, where the sum of carbon atoms on the alkyl groups may be at least 8. The anti-wear agent may in one embodiment include a citrate.

[00114] The anti-wear agent may be present in ranges including about 0 wt.% to about 15 wt.%, or about 0.01 wt.% to about 10 wt.%, or about 0.05 wt.% to about 5 wt.%, or about 0.1 wt.% to about 3 wt.% of the lubricating oil composition.

Boron-Containing Compounds

[00115] The lubricating oil compositions herein may optionally contain one or more boron-containing compounds.

[00116] Examples of boron-containing compounds include borate esters, borated fatty amines, borated epoxides, borated detergents, and borated dispersants, such as borated succinimide dispersants, as disclosed in U.S. Patent No. 5,883,057.

[00117] The boron-containing compound, if present, can be used in an amount sufficient to provide up to about 8 wt.%, about 0.01 wt.% to about 7 wt.%, about 0.05 wt.% to about 5 wt.%, or about 0.1 wt.% to about 3 wt.% of the lubricating oil composition.

Detergents

[00118] The lubricating oil composition may comprise one or more detergents. The one or more detergents may be neutral, low based, or overbased detergents, and mixtures thereof. Suitable detergent substrates include phenates, sulfur containing phenates, sulfonates, calixarates, salixarates, salicylates, carboxylic acids, phosphorus acids, mono- and/or di-thiophosphoric acids, alkyl phenols, sulfur coupled alkyl phenol compounds, or methylene bridged phenols. Suitable detergents and their methods of preparation are described in greater detail in numerous patent publications, including U.S. Pat. No. 7,732,390 and references cited therein.

[00119] The one or more detergents may be formed from a detergent substrate salted with an alkali or another alkaline earth metal such as, but not limited to, calcium, magnesium, potassium, sodium, lithium, barium, or mixtures thereof. In some embodiments, the detergent is free of barium.

[00120] A suitable detergent may include salts of petroleum sulfonic acids and long chain mono- or di-alkylarylsulfonic acids with the aryl group being benzyl, tolyl, and xylyl. Examples of suitable detergents include, but are not limited to, calcium phenates, calcium sulfur containing phenates, calcium sulfonates, calcium calixarates, calcium salixarates, calcium salicylates, calcium carboxylic acids, calcium phosphorus acids, calcium mono- and/or di-thiophosphoric acids, calcium alkyl phenols, calcium sulfur coupled alkyl phenol compounds, calcium methylene bridged phenols, magnesium phenates, magnesium sulfur containing phenates, magnesium sulfonates, magnesium calixarates, magnesium salixarates, magnesium salicylates, magnesium carboxylic acids, magnesium phosphorus acids, magnesium mono- and/or di-thiophosphoric acids, magnesium alkyl phenols, magnesium sulfur coupled alkyl phenol compounds, magnesium methylene bridged phenols, sodium phenates, sodium sulfur containing phenates, sodium sulfonates, sodium calixarates, sodium salixarates, sodium salicylates, sodium carboxylic acids, sodium phosphorus acids, sodium mono- and/or di-thiophosphoric acids, sodium alkyl phenols, sodium sulfur coupled alkyl phenol compounds, or sodium methylene bridged phenols.

[00121] The one or more detergents may be an overbased detergent. Such detergent additives may be prepared by reacting a metal oxide or metal hydroxide with a substrate and carbon dioxide gas. The substrate is typically an acid, for example, an acid such as an aliphatic substituted sulfonic acid, an aliphatic substituted carboxylic acid, or an aliphatic substituted phenol.

[00122] The terminology “overbased” relates to metal salts, such as metal salts of sulfonates, carboxylates, and phenates, wherein the amount of metal present exceeds the stoichiometric amount. Such salts may have a conversion level in excess of 100% (i.e., they may comprise more than 100% of the theoretical amount of metal needed to convert the acid to its “normal,” “neutral” salt). The expression “metal ratio,” often abbreviated as MR, is used to designate the ratio of total chemical equivalents of metal in the overbased salt to chemical equivalents of the metal in a neutral salt according to known chemical reactivity and stoichiometry. In a normal or neutral salt, the metal ratio is one and in an overbased salt, MR, is greater than one. They are commonly referred to as overbased, hyperbased, or superbased salts and may be salts of organic sulfur acids, carboxylic acids, or phenols.

[00123] An overbased detergent of the lubricating oil composition may have a total base number (TBN) of about 200 mg KOH/gram or greater, or as further examples, about 225 mg KOH/g or greater, or about 250 mg KOH/gram or greater, or about 300 mg KOH/gram or

greater, or about 350 mg KOH/gram or greater, or about 375 mg KOH/gram or greater, or about 400 mg KOH/gram or greater.

[00124] Preferably, the one or more detergents comprises an overbased calcium-containing detergent. Examples of suitable overbased calcium-containing detergents include, but are not limited to, overbased calcium phenates, overbased calcium sulfur containing phenates, overbased calcium sulfonates, overbased calcium calixarates, overbased calcium salixarates, overbased calcium salicylates, overbased calcium carboxylic acids, overbased calcium phosphorus acids, overbased calcium mono- and/or di-thiophosphoric acids, overbased calcium alkyl phenols, overbased calcium sulfur coupled alkyl phenol compounds, and overbased calcium methylene bridged phenols. Preferably, the overbased calcium-containing detergent is an overbased calcium sulfonate detergent.

[00125] Examples of other suitable overbased detergents include, but are not limited to, overbased magnesium phenates, overbased magnesium sulfur containing phenates, overbased magnesium sulfonates, overbased magnesium calixarates, overbased magnesium salixarates, overbased magnesium salicylates, overbased magnesium carboxylic acids, overbased magnesium phosphorus acids, overbased magnesium mono- and/or di-thiophosphoric acids, overbased magnesium alkyl phenols, overbased magnesium sulfur coupled alkyl phenol compounds, or overbased magnesium methylene bridged phenols.

[00126] The overbased detergent may have a metal to substrate ratio of from 1.1:1, or from 2:1, or from 4:1, or from 5:1, or from 7:1, or from 10:1.

[00127] The one or more detergents may be a low-based/neutral detergent having a TBN of up to 175 mg KOH/g, or up to 150 mg KOH/g. The low-based/neutral detergent can be formed from a detergent substrate salted with an alkali or another alkaline earth metal such as, but not limited to, calcium, magnesium, potassium, sodium, lithium, barium, or mixtures thereof. In some embodiments, the detergent is free of barium. The low-based/neutral detergent may be selected from a sulfonate, phenate or salicylate detergent. In some embodiments, the low-based/neutral detergent is a calcium-containing detergent or a mixture of calcium-containing detergents. In some embodiments, the low-based/neutral detergent is a calcium sulfonate detergent or a calcium phenate detergent. In an embodiment, the one or more detergents comprises a mixture of one or more low-based/neutral calcium-containing detergents and one or more overbased calcium-containing detergents.

[00128] The one or more detergents may comprise an overbased calcium-containing detergent and a low-based/neutral detergent which is a salt of an alkali or alkaline earth metal other than calcium.

[00129] The amount of calcium provided by the one or more calcium-containing detergents is greater than about 0.01 wt.%; or greater than about 0.02 wt.%; or up to about 0.25 wt.%; or about 0.010 wt.% to about 0.25 wt.%; or about 0.02 wt.% to about 0.20 wt.%; or about 0.02 wt.% to about 0.15 wt.%, wherein the amount is based on the total weight of the lubricating oil composition.

[00130] The low-based/neutral detergent may provide calcium in an amount that comprises at least 0.001 wt % of the calcium provided by the total detergent in the lubricating oil composition. In some embodiments, the low-based/neutral detergent may provide calcium in an amount that comprises at least 0.003 wt %, or 0.003 wt % to 0.05 wt.% of the calcium provided by the total detergent in the lubricating oil composition.

[00131] In certain embodiments, the one or more low-based/neutral detergents provide from about 1 to about 400 ppmw calcium by weight to the lubricating oil composition based on a total weight of the lubricating oil composition. In some embodiments, the one or more low-based/neutral calcium-containing detergents provide from 1 to 350 ppmw by weight calcium to the lubricating oil composition based on a total weight of the lubricating oil composition.

[00132] In some embodiments, a detergent is effective at suspending harmful products formed in the lubricating oil composition during engine use.

[00133] The one or more detergents may be present at about 0 wt % to about 10 wt %, or about 0.1 wt % to about 8 wt %, or about 0.2 wt.% to about 4 wt % based on the total weight of the lubricating oil composition.

Molybdenum-containing component

[00134] The lubricating oil compositions herein also may optionally contain one or more molybdenum-containing compounds. An oil-soluble molybdenum compound may have the functional performance of an anti-wear agent, an antioxidant, a friction modifier, or mixtures thereof. An oil-soluble molybdenum compound may include molybdenum dithiocarbamates, molybdenum dialkyldithiophosphates, molybdenum dithiophosphinates, amine salts of molybdenum compounds, molybdenum xanthates, molybdenum thioxanthates, molybdenum sulfides, molybdenum carboxylates, molybdenum alkoxides, a trinuclear

organo-molybdenum compound, and/or mixtures thereof. The molybdenum sulfides include molybdenum disulfide. The molybdenum disulfide may be in the form of a stable dispersion. In one embodiment the oil-soluble molybdenum compound may be selected from the group consisting of molybdenum dithiocarbamates, molybdenum dialkyldithiophosphates, amine salts of molybdenum compounds, and mixtures thereof. In one embodiment the oil-soluble molybdenum compound may be a molybdenum dithiocarbamate.

[00135] Suitable examples of molybdenum compounds which may be used include commercial materials sold under the trade names such as Molyvan 822™, Molyvan™ A, Molyvan 2000™, Molyvan 1055™, and Molyvan 855™ from R. T. Vanderbilt Co., Ltd., and Sakura-Lube™ S-165, S-200, S-300, S-310G, S-525, S-600, S-700, and S-710 available from Adeka Corporation, and mixtures thereof. Suitable molybdenum components are described in US 5,650,381; US RE 37,363 E1; US RE 38,929 E1; and US RE 40,595 E1, incorporated herein by reference in their entireties.

[00136] Additionally, the molybdenum compound may be an acidic molybdenum compound. Included are molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate, and other alkaline metal molybdates and other molybdenum salts, e.g., hydrogen sodium molybdate, MoOCl_4 , MoO_2Br_2 , $\text{Mo}_2\text{O}_3\text{Cl}_6$, molybdenum trioxide or similar acidic molybdenum compounds. Alternatively, the compositions can be provided with molybdenum by molybdenum/sulfur complexes of basic nitrogen compounds as described, for example, in U.S. Pat. Nos. 4,263,152; 4,285,822; 4,283,295; 4,272,387; 4,265,773; 4,261,843; 4,259,195 and 4,259,194; and WO 94/06897, incorporated herein by reference in their entireties.

[00137] Another class of suitable organo-molybdenum compounds are trinuclear molybdenum compounds, such as those of the formula $\text{Mo}_3\text{S}_k\text{L}_n\text{Q}_z$ and mixtures thereof, wherein S represents sulfur, L represents independently selected ligands having organo groups with a sufficient number of carbon atoms to render the compound soluble or dispersible in the oil, n is from 1 to 4, k varies from 4 through 7, Q is selected from the group of neutral electron donating compounds such as water, amines, alcohols, phosphines, and ethers, and z ranges from 0 to 5 and includes non-stoichiometric values. At least 21 total carbon atoms may be present among all the ligands' organo groups, such as at least 25, at least 30, or at least 35 carbon atoms. Additional suitable molybdenum compounds are described in U.S. Pat. No. 6,723,685, herein incorporated by reference in its entirety.

[00138] The oil-soluble molybdenum compound may be present in an amount sufficient to provide about 0.5 ppmw to about 2000 ppmw, about 1 ppmw to about 700 ppmw, about 1 ppmw to about 550 ppmw, about 5 ppmw to about 300 ppmw, or about 20 ppmw to about 250 ppmw of molybdenum.

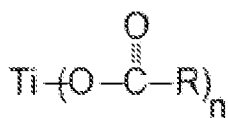
Transition Metal-containing compounds

[00139] In another embodiment, the oil-soluble compound may be a transition metal containing compound or a metalloid. The transition metals may include, but are not limited to, titanium, vanadium, copper, zinc, zirconium, molybdenum, tantalum, tungsten, and the like. Suitable metalloids include, but are not limited to, boron, silicon, antimony, tellurium, and the like.

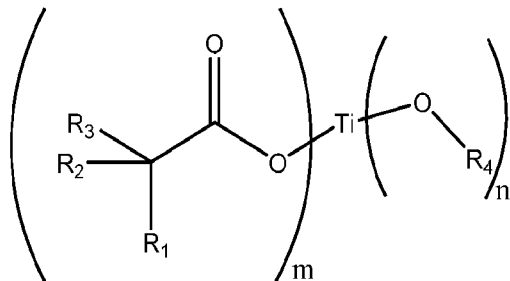
[00140] In an embodiment, an oil-soluble transition metal-containing compound may function as anti-wear agents, friction modifiers, antioxidants, deposit control additives, or more than one of these functions. In an embodiment the oil-soluble transition metal-containing compound may be an oil-soluble titanium compound, such as a titanium (IV) alkoxide. Among the titanium containing compounds that may be used in, or which may be used for preparation of the oils-soluble materials of, the disclosed technology are various Ti (IV) compounds such as titanium (IV) oxide; titanium (IV) sulfide; titanium (IV) nitrate; titanium (IV) alkoxides such as titanium methoxide, titanium ethoxide, titanium propoxide, titanium isopropoxide, titanium butoxide, titanium 2-ethylhexoxide; and other titanium compounds or complexes including but not limited to titanium phenates; titanium carboxylates such as titanium (IV) 2-ethyl-1-3-hexanedioate or titanium citrate or titanium oleate; and titanium (IV) (triethanolaminate)isopropoxide. Other forms of titanium encompassed within the disclosed technology include titanium phosphates such as titanium dithiophosphates (e.g., dialkyldithiophosphates) and titanium sulfonates (e.g., alkylbenzenesulfonates), or, generally, the reaction product of titanium compounds with various acid materials to form salts, such as oil-soluble salts. Titanium compounds can thus be derived from, among others, organic acids, alcohols, and glycols. Ti compounds may also exist in dimeric or oligomeric form, containing Ti--O--Ti structures. Such titanium materials are commercially available or can be readily prepared by appropriate synthesis techniques which will be apparent to the person skilled in the art. They may exist at room temperature as a solid or a liquid, depending on the particular compound. They may also be provided in a solution form in an appropriate inert solvent.

[00141] In one embodiment, the titanium can be supplied as a Ti-modified dispersant, such as a succinimide dispersant. Such materials may be prepared by forming a titanium mixed anhydride between a titanium alkoxide and a hydrocarbyl-substituted succinic anhydride, such as an alkenyl- (or alkyl) succinic anhydride. The resulting titanate-succinate intermediate may be used directly or it may be reacted with any of a number of materials, such as (a) a polyamine-based succinimide/amide dispersant having free, condensable --NH functionality; (b) the components of a polyamine-based succinimide/amide dispersant, i.e., an alkenyl- (or alkyl-) succinic anhydride and a polyamine, (c) a hydroxy-containing polyester dispersant prepared by the reaction of a substituted succinic anhydride with a polyol, aminoalcohol, polyamine, or mixtures thereof. Alternatively, the titanate-succinate intermediate may be reacted with other agents such as alcohols, aminoalcohols, ether alcohols, polyether alcohols or polyols, or fatty acids, and the product thereof either used directly to impart Ti to a lubricant, or else further reacted with the succinic dispersants as described above. As an example, 1 part (by mole) of tetraisopropyl titanate may be reacted with about 2 parts (by mole) of a polyisobutene-substituted succinic anhydride at 140-150° C for 5 to 6 hours to provide a titanium modified dispersant or intermediate. The resulting material (30 g) may be further reacted with a succinimide dispersant from polyisobutene-substituted succinic anhydride and a polyethylenepolyamine mixture (127 grams + diluent oil) at 150° C for 1.5 hours, to produce a titanium-modified succinimide dispersant.

[00142] Another titanium containing compound may be a reaction product of titanium alkoxide and C₆ to C₂₅ carboxylic acid. The reaction product may be represented by the following formula:

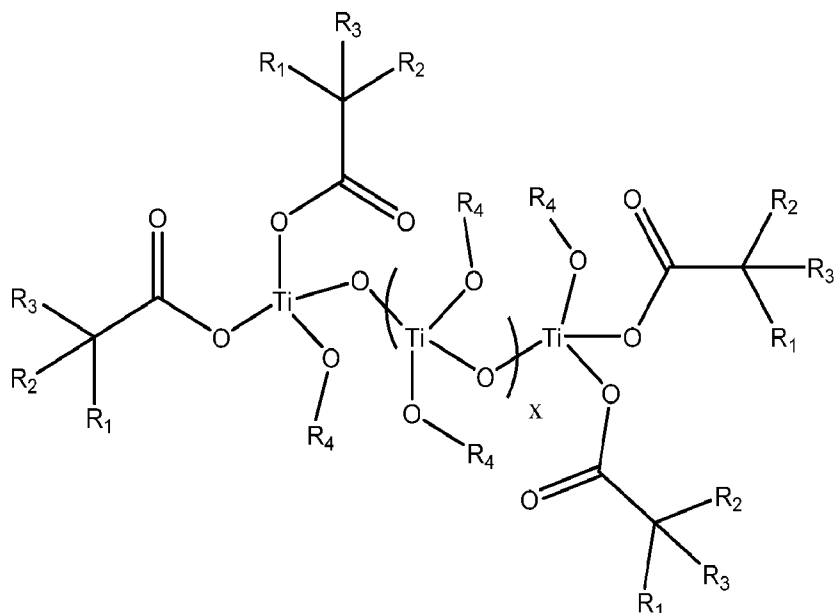


wherein n is an integer selected from 2, 3 and 4, and R is a hydrocarbyl group containing from about 5 to about 24 carbon atoms, or by the formula:



wherein m + n = 4 and n ranges from 1 to 3, R₄ is an alkyl moiety with carbon atoms ranging

from 1-8, R_1 is selected from a hydrocarbyl group containing from about 6 to 25 carbon atoms, and R_2 and R_3 are the same or different and are selected from a hydrocarbyl group containing from about 1 to 6 carbon atoms, or by the formula:



wherein x ranges from 0 to 3, R_1 is selected from a hydrocarbyl group containing from about 6 to 25 carbon atoms, R_2 , and R_3 are the same or different and are selected from a hydrocarbyl group containing from about 1 to 6 carbon atoms, and R_4 is selected from a group consisting of either H, or C_6 to C_{25} carboxylic acid moiety.

[00143] Suitable carboxylic acids may include, but are not limited to caproic acid, caprylic acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, oleic acid, erucic acid, linoleic acid, linolenic acid, cyclohexanecarboxylic acid, phenylacetic acid, benzoic acid, neodecanoic acid, and the like.

[00144] In an embodiment the oil soluble titanium compound may be present in the lubricating oil composition in an amount to provide from 0 to 3000 ppmw titanium by weight or 25 to about 1500 ppmw titanium by weight or about 35 ppmw to 500 ppmw titanium by weight or about 50 ppmw to about 300 ppmw.

Viscosity Index Improvers

[00145] The lubricating oil compositions herein also may optionally contain one or more viscosity index improvers. Suitable viscosity index improvers may include polyolefins, olefin copolymers, ethylene/propylene copolymers, polyisobutenes, hydrogenated styrene-isoprene polymers, styrene/maleic ester copolymers, hydrogenated styrene/butadiene

copolymers, hydrogenated isoprene polymers, alpha-olefin maleic anhydride copolymers, polymethacrylates, polyacrylates, polyalkyl styrenes, hydrogenated alkenyl aryl conjugated diene copolymers, or mixtures thereof. Viscosity index improvers may include star polymers and suitable examples are described in US Publication No. 2012/0101017A1.

[00146] The lubricating oil compositions herein also may optionally contain one or more dispersant viscosity index improvers in addition to a viscosity index improver or in lieu of a viscosity index improver. Suitable viscosity index improvers may include functionalized polyolefins, for example, ethylene-propylene copolymers that have been functionalized with the reaction product of an acylating agent (such as maleic anhydride) and an amine; polymethacrylates functionalized with an amine, or esterified maleic anhydride-styrene copolymers reacted with an amine.

[00147] The total amount of viscosity index improver and/or dispersant viscosity index improver may be about 0 wt.% to about 20 wt.%, about 0.1 wt.% to about 15 wt.%, about 0.1 wt.% to about 12 wt.%, or about 0.5 wt.% to about 10 wt.%, of the lubricating oil composition.

Other Optional Additives

[00148] Other additives may be selected to perform one or more functions required of a lubricating fluid. Further, one or more of the mentioned additives may be multi-functional and provide functions in addition to or other than the function prescribed herein.

[00149] A lubricating oil composition according to the present disclosure may optionally comprise other performance additives. The other performance additives may be in addition to specified additives of the present disclosure and/or may comprise one or more of metal deactivators, viscosity index improvers, detergents, ashless TBN boosters, friction modifiers, anti-wear agents, corrosion inhibitors, rust inhibitors, dispersant viscosity index improvers, extreme pressure agents, antioxidants, foam inhibitors, demulsifiers, emulsifiers, pour point depressants, seal swelling agents and mixtures thereof. Typically, fully-formulated lubricating oil will contain one or more of these performance additives.

[00150] Suitable metal deactivators may include derivatives of benzotriazoles (typically tolyltriazole), dimercaptothiadiazole derivatives, 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles, or 2-alkyldithiobenzothiazoles; foam inhibitors including copolymers of ethyl acrylate and 2-ethylhexylacrylate and optionally vinyl acetate; demulsifiers including trialkyl phosphates, polyethylene glycols, polyethylene oxides,

polypropylene oxides and (ethylene oxide-propylene oxide) polymers; pour point depressants including esters of maleic anhydride-styrene, polymethacrylates, polyacrylates or polyacrylamides.

[00151] Suitable foam inhibitors include silicon-based compounds, such as siloxane.

[00152] Suitable pour point depressants may include a polymethylmethacrylates or mixtures thereof. Pour point depressants may be present in an amount sufficient to provide from about 0 wt.% to about 1 wt.%, about 0.01 wt.% to about 0.5 wt.%, or about 0.02 wt.% to about 0.04 wt.% based upon the final weight of the lubricating oil composition.

[00153] Suitable rust inhibitors may be a single compound or a mixture of compounds having the property of inhibiting corrosion of ferrous metal surfaces. Non-limiting examples of rust inhibitors useful herein include oil-soluble high molecular weight organic acids, such as 2-ethylhexanoic acid, lauric acid, myristic acid, palmitic acid, oleic acid, linoleic acid, linolenic acid, behenic acid, and cerotic acid, as well as oil-soluble polycarboxylic acids including dimer and trimer acids, such as those produced from tall oil fatty acids, oleic acid, and linoleic acid. Other suitable corrosion inhibitors include long-chain alpha, omega-dicarboxylic acids in the molecular weight range of about 600 to about 3000 and alkenylsuccinic acids in which the alkenyl group contains about 10 or more carbon atoms such as, tetrapropenylsuccinic acid, tetradecenylsuccinic acid, and hexadecenylsuccinic acid. Another useful type of acidic corrosion inhibitors are the half esters of alkenyl succinic acids having about 8 to about 24 carbon atoms in the alkenyl group with alcohols such as the polyglycols. The corresponding half amides of such alkenyl succinic acids are also useful. A useful rust inhibitor is a high molecular weight organic acid. In some embodiments, an engine oil is devoid of a rust inhibitor.

[00154] The rust inhibitor, if present, can be used in an amount sufficient to provide about 0 wt.% to about 5 wt.%, about 0.01 wt.% to about 3 wt.%, about 0.1 wt.% to about 2 wt.%, based upon the final weight of the lubricating oil composition.

[00155] In general terms, a suitable crankcase lubricant may include additive components in the ranges listed in the following table.

Table 2

Component	Wt. % (Suitable Embodiments)	Wt. % (Suitable Embodiments)
Dispersant(s)	0.1 – 20.0	1.0 – 10.0
Antioxidant(s)	0.1 – 5.0	0.01 – 3.0
Detergent(s)	0.1 – 15.0	0.2 – 8.0
Ashless TBN booster(s)	0.0 – 1.0	0.00 – 0.5
Corrosion inhibitor(s)	0.0 – 5.0	0.0 – 2.0
Metal dihydrocarbyldithiophosphate(s)	0.1 – 6.0	0.1 – 4.0
Ash-free phosphorus compound(s)	0.0 – 6.0	0.0 – 4.0
Antifoaming agent(s)	0.0 – 5.0	0.001 – 0.15
Anti-wear agent(s)	0.0 – 1.0	0.0 – 0.8
Pour point depressant(s)	0.0 – 5.0	0.01 – 1.5
Viscosity index improver(s) (on a liquid/dilute basis)	0.0 – 25.0	0.1 – 15.0
Dispersant viscosity index improver(s)	0.0 – 10.0	0.0 – 5.0
Friction modifier(s)	0.0 – 5.0	0.01 – 2.0
Base oil(s)	<u>Balance</u>	<u>Balance</u>
Total	100	100

[00156] The percentages of each component above represent the weight percent of each component, based upon the weight of the final lubricating oil composition. The remainder of the lubricating oil composition consists of one or more base oils.

[00157] Additives used in formulating the compositions described herein may be blended into the base oil individually or in various sub-combinations. However, it may be suitable to blend all of the components concurrently using an additive concentrate (i.e., additives plus a diluent, such as a hydrocarbon solvent).

EXAMPLES

[00158] The following examples are illustrative, but not limiting, of the methods and compositions of the present disclosure. Other suitable modifications and adaptations of the variety of conditions and parameters normally encountered in the field, and which are obvious to those skilled in the art, are within the spirit and scope of the disclosure. All patents and publications cited herein are fully incorporated by reference herein in their entirety.

[00159] Each of the lubricating oil compositions contained a major amount of a base oil and a base conventional dispersant inhibitor (DI) package. The DI package contained conventional amounts of dispersant(s), anti-wear additive(s), antioxidant(s), friction

modifier(s), antifoam agent(s), process oil(s), viscosity index improver(s), and pour point depressant(s), as set forth in Table 3. Specifically, the DI package contained a succinimide dispersant, a molybdenum-containing compound, an antioxidant, and an antifoam agent. The major amount of base oil was a mixture of Group II and Group III base oils. The components that were varied are specified in the Tables and discussion of the Examples below. All the values listed are states as weight percent of the component in the lubricating oil compositions (i.e., active ingredient plus diluent oil, if any) unless specified otherwise.

Table 3 – DI Package Composition Ranges

<u>Component</u>	<u>Wt. %</u>
Antioxidant(s)	0.5 to 2.5
Antifoaming agent(s)	0.001 to 0.05
Detergent(s)	0.1 to 2.0
Dispersant(s)	See Table 5
Metal-containing friction modifier(s)	0– 1.5
Metal free friction modifier(s)	0 to 0.5
Pour point depressant(s)	0 to 0.5
Process oil	0.25 to 1.0
ZDDP	See Table 5
Viscosity modifier	0 to 10.0

[00160] The lubricating oil compositions were tested according to a Sequence VH engine test. The Sequence VH Test (ASTM D8256) is a test method used to evaluate an automotive engine oil's control of engine deposits under operating conditions deliberately selected to accelerate deposit formation. The engine is a spark-ignited engine fueled with gasoline and operated under low-temperature, light-duty conditions. Using a 2013 Ford 4.6 L fuel-injected, eight cylinder, gasoline engine with roller followers, coolant-jacketed rocker covers, and camshaft baffles.

[00161] The test duration is 216 hours involving 54 cycles, each cycle consisting of three different operating stages as shown in the following Table 4. Fuel containing sludge precursors is used, and engine blow-by is intentionally increased. The rocker cover jacket temperature is cycled.

Table 4 – Parameters of Test

	Stage 1	Stage 2	Stage 3
Time, minutes	120	75	45
Engine speed, rpm	1200	2900	700
Intake manifold absolute pressure, kPa	69	66	record
Lubricant temp, °C	68	100	45
Coolant temp, °C	57	85	45
Rocker cover temp, °C	29	85	29

[00162] Sludge deposits are rated on the rocker arm covers, rocker arm cover baffles, timing chain cover, oil pan baffle, oil pan, and valve decks.

[00163] One of the measurements included in the Sequence VH Test is of the Average Engine Sludge. Cleanliness of the engine is measured via sludge merits, whereby a higher score demonstrates increased engine cleanliness. The oil passes the Average Engine Sludge test at 7.01 minutes or higher. The results of the Average Engine Sludge test is given in Table 5 below.

Table 5

Example Numbers	Wt.% of Phosphorus from the ZDDP	Wt.% of Zinc from the ZDDP	TBN of dispersant to TBN of Oil ^a	Wt.% of P from ZDDP × (TBN of dispersant to TBN of Oil) ^b	Wt.% of Zn from ZDDP × (TBN of dispersant to TBN of Oil) ^c	Average Engine Sludge (minutes)
CE-1	0.063	0.070	0.748	0.047	0.052	6.71
CE-2	0.062	0.068	0.777	0.048	0.053	6.72
CE-3	0.063	0.070	0.748	0.047	0.052	6.83
CE-4	0.063	0.070	0.747	0.047	0.052	6.96
IE-1	0.077	0.085	0.927	0.072	0.079	7.08
IE-2	0.073	0.080	0.927	0.068	0.074	7.93
IE-3	0.063	0.070	1.023	0.065	0.071	8.34
IE-4	0.077	0.085	1.301	0.100	0.110	9.06
IE-5	0.098	0.108	1.071	0.105	0.116	9.18
IE-6	0.079	0.087	1.529	0.120	0.132	9.57
IE-7	0.078	0.086	1.474	0.115	0.126	9.67

a) Contribution of TBN of the Total Dispersant to the TBN of the Lubricating Oil Composition

b) Wt.% of Phosphorus from the ZDDP × Contribution of TBN of the Total Dispersant to the TBN of the Lubricating Oil Composition (P×TBNDISP - col 2 × col 4)

c) Wt.% of Zinc from the ZDDP × Contribution of TBN of the Total Dispersant to the TBN of the Lubricating Oil Composition (Zn×TBNDISP - col 3 × col 4)

[00164] The data in Table 5 is plotted in the graph of Figure 1. The data in Table 5 and the graph of Figure 1 demonstrate that there is improved cleanliness for lubricating oil compositions comprising: one or more zinc dialkyl dithiophosphates (ZDDP compounds) and one or more dispersants, wherein the amount of zinc (Zn) in weight percent provided to the lubricating oil composition by the one or more ZDDP compounds multiplied by the contribution of the total base number (TBN) of the one or more dispersants to the TBN of the lubricating oil composition is a multiplication factor wt.% of Zn*TBNDISP of at least about

0.06. This is evident from the higher Average Engine Sludge values for Inventive Examples IE-1 to IE-7 when compared to the values for Comparative Examples CE-1 to CE-4.

[00165] The data in Table 5 also demonstrates that there is improved cleanliness for lubricating oil compositions formulated with the multiplication factor $\text{wt. \% Zn} \cdot \text{TBNDisp}$ of at least about 0.06 and an amount of zinc provided by the one or more ZDDP compounds is 0.070 wt.% to 0.11 wt.% based on the total weight of the lubricating oil composition. This is evident from the higher Average Engine Sludge values for Inventive Examples IE-1 to IE-7 when compared to the values for Comparative Examples CE-1 to CE-4.

[00166] In addition, the data in Table 5 also demonstrates that there is improved cleanliness for lubricating oil compositions formulated with the $\text{wt. \% of Zn} \cdot \text{TBNDisp}$ multiplication factor is at least about 0.06 and the contribution of TBN of the one or more dispersants to the TBN of the lubricating oil composition is at least 0.79 mg KOH/g. This is evident from the higher Average Engine Sludge values for Inventive Examples IE-1 to IE-7 when compared to the values for Comparative Examples CE-1 to CE-4.

[00167] The data in Table 5 is also plotted in the graph of Figure 2. The data in Table 5 and the graph of Figure 2 demonstrate that there is improved cleanliness for lubricating oil compositions comprising: one or more zinc dialkyl dithiophosphates (ZDDP compounds) and one or more dispersants, wherein the amount of phosphorus (P) in weight percent provided to the lubricating oil composition by the one or more ZDDP compounds multiplied by the contribution of the total base number (TBN) of the one or more dispersants to the TBN of the lubricating oil composition is a multiplication factor $\text{wt. \% of P} \cdot \text{TBNDisp}$ of at least about 0.051. This is evident from the higher Average Engine Sludge values for Inventive Examples IE-1 to IE-7 when compared to the values for Comparative Examples CE-1 to CE-4.

[00168] The data in Table 5 and Figure 2 also demonstrates that there is improved cleanliness for lubricating oil compositions formulated such that the $\text{wt. \% of P} \cdot \text{TBNDisp}$ multiplication factor is at least about 0.051 and the one or more ZDDP compounds is present in a sufficient amount to provide greater than about 0.065 wt.% of P based on the total weight of the lubricating oil composition. This is evident from the higher Average Engine Sludge values for Inventive Examples IE-1 to IE-7 when compared to the values for Comparative Examples CE-1 to CE-4.

[00169] In addition, the data in Table 5 and Figure 2 demonstrates that there is improved cleanliness for lubricating oil compositions formulated with the $\text{wt. \% of P} \cdot \text{TBNDisp}$ multiplication factor is at least about 0.051 and the contribution of TBN of the

one or more dispersants to the TBN of the lubricating oil composition is at least 0.79 mg KOH/g. This is evident from the higher Average Engine Sludge values for Inventive Examples IE-1 to IE-7 when compared to the values for Comparative Examples CE-1 to CE-4.

[00170] Other embodiments of the present disclosure will be apparent to those skilled in the art from consideration of the specification and practice of the embodiments disclosed herein. As used throughout the specification and claims, “a” and/or “an” and/or “the” may refer to one or more than one. Unless otherwise indicated, all numbers expressing quantities, proportions, percentages, or other numerical values are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in the specification and claims are approximations that can vary depending upon the desired properties sought to be obtained by the present disclosure. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[00171] It is to be understood that each component, compound, substituent or parameter disclosed herein is to be interpreted as being disclosed for use alone or in combination with one or more of each and every other component, compound, substituent or parameter disclosed herein.

[00172] It is further understood that each range disclosed herein is to be interpreted as a disclosure of each specific value within the disclosed range that has the same number of significant digits. Thus, for example, a range from 1-4 is to be interpreted as an express disclosure of the values 1, 2, 3 and 4 as well as any range of such values.

[00173] It is further understood that each lower limit of each range disclosed herein is to be interpreted as disclosed in combination with each upper limit of each range and each specific value within each range disclosed herein for the same component, compounds, substituent or parameter. Thus, this disclosure to be interpreted as a disclosure of all ranges derived by combining each lower limit of each range with each upper limit of each range or with each specific value within each range, or by combining each upper limit of each range with each specific value within each range. That is, it is also further understood that any range between the endpoint values within the broad range is also discussed herein. Thus, a range from 1 to 4 also means a range from 1 to 3, 1 to 2, 2 to 4, 2 to 3, and so forth.

[00174] Furthermore, specific amounts/values of a component, compound, substituent or parameter disclosed in the description or an example is to be interpreted as a disclosure of either a lower or an upper limit of a range and thus can be combined with any other lower or upper limit of a range or specific amount/value for the same component, compound, substituent or parameter disclosed elsewhere in the application to form a range for that component, compound, substituent or parameter.

What is Claimed is:

1. A lubricating oil composition comprising greater than 50 wt.% of a base oil of lubricating viscosity, and an additive composition comprising:
one or more zinc dialkyl dithiophosphates (ZDDP compounds) and one or more dispersants, wherein the amount of zinc (Zn) in weight percent provided to the lubricating oil composition by the one or more ZDDP compounds multiplied by the contribution of the total base number (TBN) of the one or more dispersants to the TBN of the lubricating oil composition is a multiplication factor $Zn*TBNDisp$ of at least about 0.06.
2. The lubricating oil composition of claim 1, wherein the $Zn*TBNDisp$ multiplication factor is more than about 0.07.
3. The lubricating oil composition of claim 1, wherein the $Zn*TBNDisp$ multiplication factor is at least about 0.06 and the one or more ZDDP compounds is present in a sufficient amount to provide greater than about 0.071 wt.% of zinc based on the total weight of the lubricating oil composition.
4. The lubricating oil composition of claim 1, wherein the $Zn*TBNDisp$ multiplication factor is at least about 0.06 and the contribution of TBN of the one or more dispersants to the TBN of the lubricating oil composition is at least 0.79 mg KOH/g.
5. A lubricating oil composition comprising greater than 50 wt.% of a base oil of lubricating viscosity, and an additive composition comprising:
one or more zinc dialkyl dithiophosphates (ZDDP compounds) and one or more dispersants, wherein the amount of phosphorus (P) in weight percent provided to the lubricating oil composition by the one or more ZDDP compounds multiplied by the contribution of the total base number (TBN) of the one or more dispersants to the TBN of the lubricating oil composition is a multiplication factor $P*TBNDisp$ of at least about 0.051.
6. The lubricating oil composition of claim 5, wherein the $P*TBNDisp$ multiplication factor is more than about 0.06 to 0.5.

7. The lubricating oil composition of claim 5, wherein the $P \cdot \text{TBNDisp}$ multiplication factor is at least about 0.051 and the one or more ZDDP compounds is present in a sufficient amount to provide greater than about 0.065 wt.% of P based on the total weight of the lubricating oil composition.
8. The lubricating oil composition of claim 5, wherein the $P \cdot \text{TBNDisp}$ multiplication factor is at least about 0.051 and the contribution of TBN of the one or more dispersants to the TBN of the lubricating oil composition is at least 0.79 mg KOH/g.
9. The lubricating oil composition of claim 1, wherein the one or more ZDDP compounds is derived from one or more secondary alkyl alcohol(s) having an alkyl group with 3 to 8 carbon atoms.
10. The lubricating oil composition of claim 5, wherein the one or more ZDDP compounds is derived from one or more secondary alkyl alcohol(s) having an alkyl group with 3 to 8 carbon atoms.
11. The lubricating oil composition of claim 1, wherein the one or more ZDDP compounds is a mixture of all primary alcohol ZDDP compounds and all secondary alcohol ZDDP compounds.
12. The lubricating oil composition of claim 5, wherein the one or more ZDDP compounds is a mixture of all primary alcohol ZDDP compounds and all secondary alcohol ZDDP compounds.
13. The lubricating oil composition of claim 11, wherein the mixture comprises all primary alcohol ZDDP compounds contributing 15 to 500 ppmw zinc and all secondary alcohol ZDDP compounds contributing 100 to 1000 ppmw zinc to the lubricating oil composition based on the weight of the lubricating oil composition.
14. The lubricating oil composition of claim 12, wherein the mixture comprises all primary alcohol ZDDP compounds contributing 15 to 500 ppmw zinc and all secondary

alcohol ZDDP compounds contributing 100 to 1000 ppmw zinc to the lubricating oil composition based on the weight of the lubricating oil composition.

15. The lubricating oil composition of claim 1, wherein the one or more dispersants comprises at least one dispersant derived from polyisobutylene succinic anhydride (“PIBSA”), and the PIBSA has an average of about 1.0 and about 2.0 succinic acid moieties per polyisobutylene (PIB) polymer.

16. The lubricating oil composition of claim 5, wherein the one or more dispersants comprises at least one dispersant derived from polyisobutylene succinic anhydride (“PIBSA”), and the PIBSA has an average of about 1.0 and about 2.0 succinic acid moieties per polyisobutylene (PIB) polymer.

17. The lubricating oil composition of claim 1, wherein the contribution of TBN of the total dispersant to the TBN of the lubricating oil composition is at least 0.79 mg KOH/g.

18. The lubricating oil composition of claim 5, wherein the contribution of TBN of the total dispersant to the TBN of the lubricating oil composition is at least 0.79 mg KOH/g.

19. The lubricating oil composition of claim 1, wherein the one or more dispersants is a mixture of at least one dispersant that is post-treated and at least one dispersant that is not post-treated.

20. The lubricating oil composition of claim 5, wherein the one or more dispersants is a mixture of at least one dispersant that is post-treated and at least one dispersant that is not post-treated.

21. A method of reducing engine sludge of an internal combustion engine, the method comprising adding to the engine the lubricating oil composition of claim 1 and operating said engine.

22. A method of reducing engine sludge of an internal combustion engine, the method comprising adding to the engine the lubricating oil composition of claim 5 and operating said engine.

23. A method of improving the fuel economy performance and/or piston cleanliness performance of an engine and/or a vehicle, comprising the step of providing the engine and/or the vehicle with a lubricant composition according to claim 1.

24. A method of improving the fuel economy performance and/or piston cleanliness performance of an engine and/or a vehicle, comprising the step of providing the engine and/or the vehicle with a lubricant composition according to claim 5.

AMENDED CLAIMS

received by the International Bureau on 10 April 2023 (10.04.2023)

What is Claimed is:

1. A lubricating oil composition comprising greater than 50 wt.% of a base oil of lubricating viscosity, and an additive composition comprising:
one or more zinc dialkyl dithiophosphates (ZDDP compounds) and one or more dispersants, wherein the amount of zinc (Zn) in weight percent provided to the lubricating oil composition by the one or more ZDDP compounds multiplied by the contribution of the total base number (TBN) of the one or more dispersants to the TBN of the lubricating oil composition is a multiplication factor $Zn*TBNDisp$ of at least about 0.06, and
one or more detergents consisting of one or more overbased calcium sulfonate detergents and optionally one or more low-based/neutral detergents.
2. The lubricating oil composition of claim 1, wherein the $Zn*TBNDisp$ multiplication factor is more than about 0.07.
3. The lubricating oil composition of claim 1, wherein the $Zn*TBNDisp$ multiplication factor is at least about 0.06 and the one or more ZDDP compounds is present in a sufficient amount to provide greater than about 0.071 wt.% of zinc based on the total weight of the lubricating oil composition.
4. The lubricating oil composition of claim 1, wherein the $Zn*TBNDisp$ multiplication factor is at least about 0.06 and the contribution of TBN of the one or more dispersants to the TBN of the lubricating oil composition is at least 0.79 mg KOH/g.
5. A lubricating oil composition comprising greater than 50 wt.% of a base oil of lubricating viscosity, and an additive composition comprising:
one or more zinc dialkyl dithiophosphates (ZDDP compounds) and one or more dispersants, wherein the amount of phosphorus (P) in weight percent provided to the lubricating oil composition by the one or more ZDDP compounds multiplied by the contribution of the total base number (TBN) of the one or more dispersants to the TBN of the lubricating oil composition is a multiplication factor $P*TBNDisp$ of at least about 0.051, and

one or more detergents consisting of one or more overbased calcium sulfonate detergents and optionally one or more low-based/neutral detergents.

6. The lubricating oil composition of claim 5, wherein the P^*TBND_{isp} multiplication factor is more than about 0.06 to 0.5.

7. The lubricating oil composition of claim 5, wherein the P^*TBND_{isp} multiplication factor is at least about 0.051 and the one or more ZDDP compounds is present in a sufficient amount to provide greater than about 0.065 wt.% of P based on the total weight of the lubricating oil composition.

8. The lubricating oil composition of claim 5, wherein the P^*TBND_{isp} multiplication factor is at least about 0.051 and the contribution of TBN of the one or more dispersants to the TBN of the lubricating oil composition is at least 0.79 mg KOH/g.

9. The lubricating oil composition of claim 1, wherein the one or more ZDDP compounds is derived from one or more secondary alkyl alcohol(s) having an alkyl group with 3 to 8 carbon atoms.

10. The lubricating oil composition of claim 5, wherein the one or more ZDDP compounds is derived from one or more secondary alkyl alcohol(s) having an alkyl group with 3 to 8 carbon atoms.

11. The lubricating oil composition of claim 1, wherein the one or more ZDDP compounds is a mixture of all primary alcohol ZDDP compounds and all secondary alcohol ZDDP compounds.

12. The lubricating oil composition of claim 5, wherein the one or more ZDDP compounds is a mixture of all primary alcohol ZDDP compounds and all secondary alcohol ZDDP compounds.

13. The lubricating oil composition of claim 11, wherein the mixture comprises all primary alcohol ZDDP compounds contributing 15 to 500 ppmw zinc and all secondary alcohol ZDDP compounds contributing 100 to 1000 ppmw zinc to the lubricating oil composition based on the weight of the lubricating oil composition.
14. The lubricating oil composition of claim 12, wherein the mixture comprises all primary alcohol ZDDP compounds contributing 15 to 500 ppmw zinc and all secondary alcohol ZDDP compounds contributing 100 to 1000 ppmw zinc to the lubricating oil composition based on the weight of the lubricating oil composition.
15. The lubricating oil composition of claim 1, wherein the one or more dispersants comprises at least one dispersant derived from polyisobutylene succinic anhydride ("PIBSA"), and the PIBSA has an average of about 1.0 and about 2.0 succinic acid moieties per polyisobutylene (PIB) polymer.
16. The lubricating oil composition of claim 5, wherein the one or more dispersants comprises at least one dispersant derived from polyisobutylene succinic anhydride ("PIBSA"), and the PIBSA has an average of about 1.0 and about 2.0 succinic acid moieties per polyisobutylene (PIB) polymer.
17. The lubricating oil composition of claim 1, wherein the contribution of TBN of the total dispersant to the TBN of the lubricating oil composition is at least 0.79 mg KOH/g.
18. The lubricating oil composition of claim 5, wherein the contribution of TBN of the total dispersant to the TBN of the lubricating oil composition is at least 0.79 mg KOH/g.
19. The lubricating oil composition of claim 1, wherein the one or more dispersants is a mixture of at least one dispersant that is post-treated and at least one dispersant that is not post-treated.

20. The lubricating oil composition of claim 5, wherein the one or more dispersants is a mixture of at least one dispersant that is post-treated and at least one dispersant that is not post-treated.

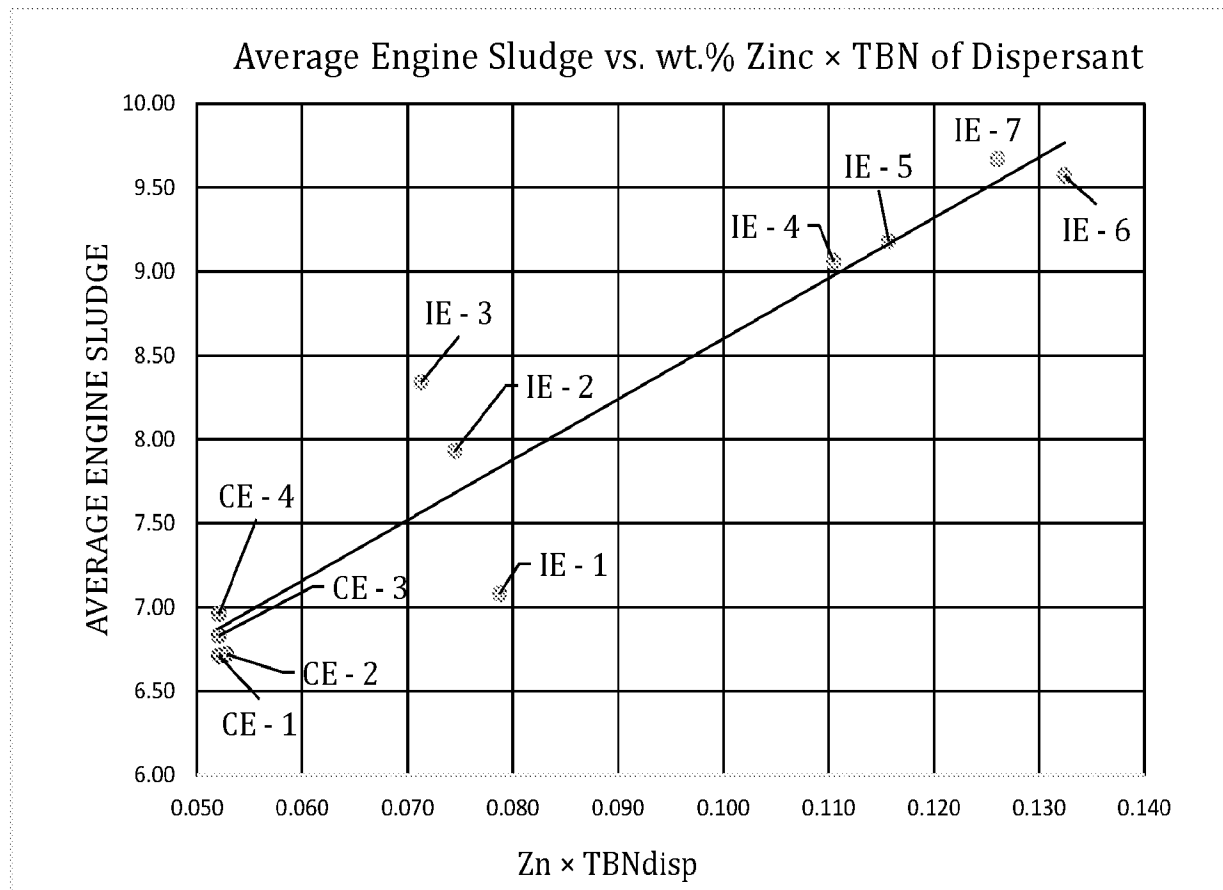
21. A method of reducing engine sludge of an internal combustion engine, the method comprising adding to the engine the lubricating oil composition of claim 1 and operating said engine.

22. A method of reducing engine sludge of an internal combustion engine, the method comprising adding to the engine the lubricating oil composition of claim 5 and operating said engine.

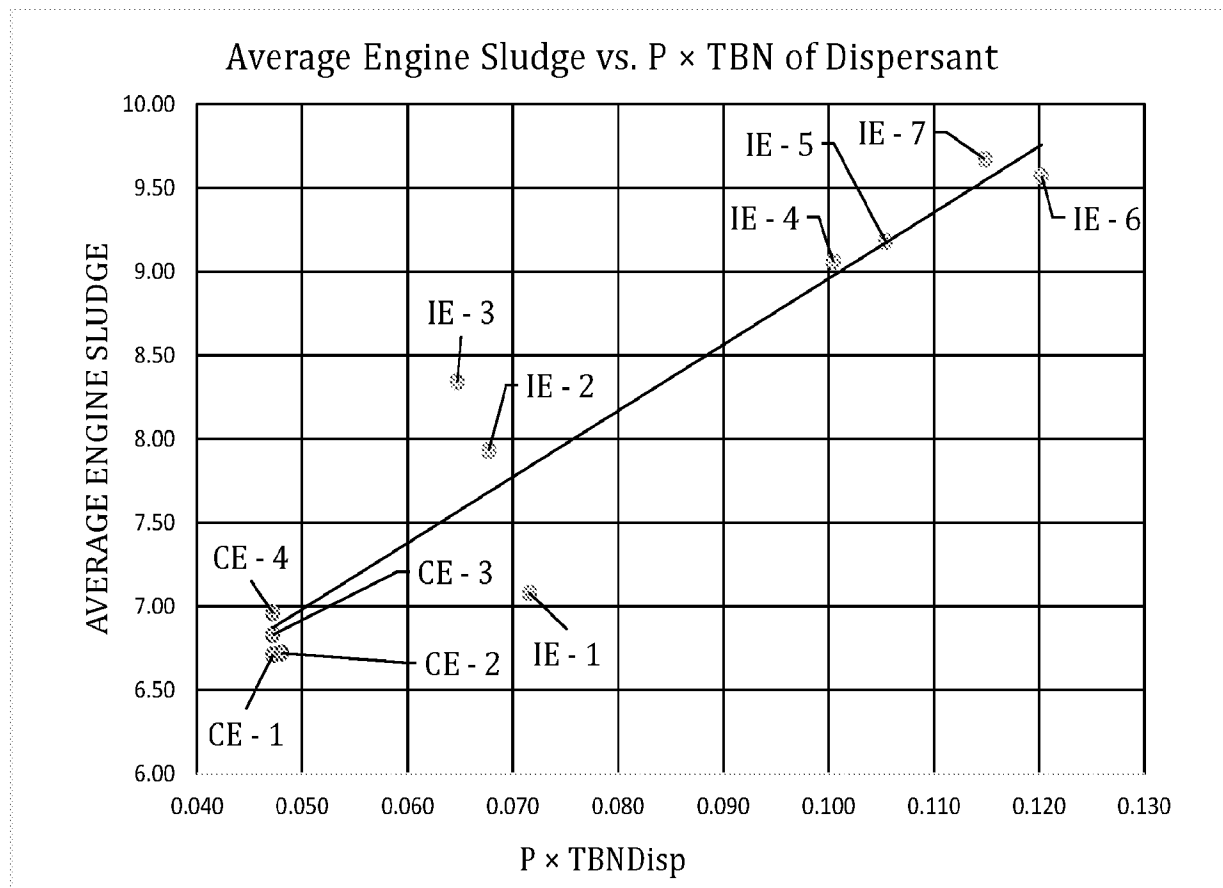
23. A method of improving the fuel economy performance and/or piston cleanliness performance of an engine and/or a vehicle, comprising the step of providing the engine and/or the vehicle with a lubricant composition according to claim 1.

24. A method of improving the fuel economy performance and/or piston cleanliness performance of an engine and/or a vehicle, comprising the step of providing the engine and/or the vehicle with a lubricant composition according to claim 5.

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**Figure 1**

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**FIGURE 2**

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2022/078491

A. CLASSIFICATION OF SUBJECT MATTER C10M 137/10(2006.01)i; C10M 169/04(2006.01)i; C10M 171/00(2006.01)i; C10N 40/25(2006.01)n According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C10M 137/10(2006.01); C10M 133/44(2006.01); C10M 133/52(2006.01); C10M 135/04(2006.01); C10M 141/10(2006.01); C10M 149/12(2006.01); C10M 169/04(2006.01) Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Korean utility models and applications for utility models Japanese utility models and applications for utility models Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) eKOMPASS(KIPO internal) & Keywords: lubricating oil composition, dispersant, total base number, zinc dialkyldithiophosphate		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2020-123438 A1 (THE LUBRIZOL CORPORATION) 18 June 2020 (2020-06-18) claims 1, 12, 14-15; paragraphs [0002]-[0157]; table 1	1-24
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☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "D" document cited by the applicant in the international application "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 21 February 2023		Date of mailing of the international search report 22 February 2023
Name and mailing address of the ISA/KR Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon 35208, Republic of Korea Facsimile No. +82-42-481-8578		Authorized officer HEO, Joo Hyung Telephone No. +82-42-481-5373

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

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