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— *as to the identity of the inventor (Rule 4.17(i))*
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
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(54) Title: AFTERTREATMENT SYSTEM FRIENDLY ENGINE OIL FORMULATION

(57) Abstract: This disclosure describes a method of reducing catalyst poisoning in a diesel engine equipped with an aftertreatment system comprising a selective catalytic reduction device. The method includes lubricating the engine with a lubricating oil composition. The lubricating oil composition includes a major amount of oil of lubricating viscosity and a phosphorus-containing additive.

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AFTERTREATMENT SYSTEM FRIENDLY ENGINE OIL FORMULATION

CROSS REFERENCE TO RELATED APPLICATIONS

[001] This application claims the priority benefit of U.S. Provisional Application No. 63/451,749, filed March 13, 2023, the disclosure of which is incorporated herein by reference.

TECHNICAL FIELD

[002] This disclosure relates to engine oil formulations. More specifically, this disclosure relates to engine oil formulated with phosphorus-containing additive designed to reduce emissions from an internal combustion engine.

BACKGROUND

[003] There are ongoing efforts to reduce emissions such as carbon monoxide (CO) and nitrogen oxide (NO_x) from compression ignited internal combustion engines. Aftertreatment system is a method or device that aims to reduce harmful exhaust emissions from internal combustion engines. Some aftertreatment systems (ATS) may employ a diesel particulate filter (DPF) which trap emission particles.

[004] Another ATS approach (which may be used in combination with DPF) is selective catalytic reduction (SCR). SCR catalytically converts tailpipe nitrogen oxide (NO_x) to diatomic nitrogen (N_2) and water. Potential drawbacks of SCR are its susceptibility to plugging and poisoning from soot and ash. In particular, the presence of metals from engine oil can poison the catalysts used in selective catalytic reduction.

SUMMARY

[005] In one aspect, there is provided a method of reducing catalyst poisoning in a diesel engine aftertreatment system comprising a selective catalytic reduction device, the method comprising: lubricating the engine with a lubricating oil

composition comprising: a major amount of oil of lubricating viscosity; and a phosphorus-containing additive.

[006] In another aspect, there is provided a use of a lubricating oil composition in a diesel engine aftertreatment system comprising a selective catalytic reduction device, the lubricating oil composition comprising: a major amount of oil of lubricating viscosity; and a phosphorus-containing additive.

DETAILED DESCRIPTION

[007] It is understood that when combinations, subsets, groups, etc. of elements are disclosed (e.g., combinations of components in a composition, or combinations of steps in a method), that while specific reference of each of the various individual and collective combinations and permutations of these elements may not be explicitly disclosed, each is specifically contemplated and described herein.

[008] Modern engines are often equipped with an aftertreatment system which aims to reduce harmful exhaust emissions from internal combustion engines. Aftertreatment systems may feature selective catalytic reduction which is a means of converting nitrogen oxide (NO_x) with the aid of a catalyst into diatomic nitrogen (N_2) and water (H_20). This reduction chemistry takes place as exhaust gases pass through a catalyst chamber. Just prior to entering the chamber, a reductant is injected and mixed with the exhaust gases. The reductant (typically ammonia) or its precursors (e.g., aqueous ammonia, urea) are usually provided by diesel exhaust fluid (DEF). Catalysts include oxides of base metals (such as molybdenum and tungsten), zeolites, metals, or activated carbon.

[009] The present disclosure relates to a lubricating oil composition formulated to enhance or improve the performance of an aftertreatment system, particularly one that is equipped with selective catalytic reduction system. The specific formulation of these lubricating oil compositions is critical because metals from commonly used lubricant additives such as detergents (e.g., salicylates, sulfonates, phenates) or anti-wear agents (e.g., zinc dithiophosphates) are considered catalyst

poisoning compounds. In an embodiment, the lubricating oil composition of the present disclosure includes base oil and a phosphorus-containing additive.

[010] The present disclosure provides a method of lubricating a diesel engine or reducing catalyst poisoning in a diesel engine equipped with an aftertreatment system comprising a selective catalytic reduction system. In some embodiments, the present disclosure provides a method for improving the performance of a diesel engine equipped with an aftertreatment system comprising a selective catalytic reduction system. In some embodiments, the present disclosure provides a use of a lubricating oil composition for a diesel engine equipped with an aftertreatment system comprising a selective catalytic reduction system.

[011] As an advantage, the lubricating oil composition of this disclosure reduces harmful emissions by reducing the poisoning of catalysts which are used to convert harmful emissions into less harmful compounds. In another aspect, the lubricating oil composition improves the performance of the selective catalytic reduction system. Other advantages will be apparent from the disclosure herein.

Phosphorus-containing additive

[012] The lubricating oil composition of the present invention includes a phosphorus-containing additive. The one or more phosphorus-containing additives may be a metal-containing phosphorus-containing compound such as zinc dithiophosphate (ZnDTP) which is also referred to as zinc dihydrocarbyldithiophosphate (ZDDP) or an ashless phosphorus-containing compound such as dithiophosphoric acid or ashless dithiophosphate.

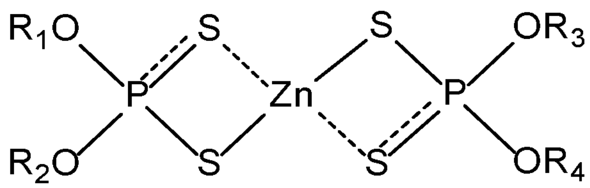
[013] In general, phosphorus-containing additive is present in the lubricating oil composition in an amount necessary to provide a desirable performance benefit. The phosphorus-containing additive may be present in about 4 mM to about 40 mM based on total weight of the lubricating oil composition, such as from about 4 mM to about 40 mM, about 4 mM to about 35 mM, about 4 mM to about 30 mM, about 4 mM to about 25 mM, about 4 mM to about 20 mM, about 4 mM to about 15 mM, about 4 mM to about 10 mM, about 6 mM to about 40 mM, about 6 mM to about 35

mM, about 6 mM to about 30 mM, about 6 mM to about 25 mM, about 6 mM to about 20 mM, about 6 mM to about 15 mM, about 6 mM to about 10 mM, about 10 mM to about 40 mM, about 10 mM to about 35 mM, about 10 mM to about 30 mM, about 10 mM to about 25 mM, about 10 mM to about 20 mM, about 10 mM to about 15 mM, about 15 mM to about 40 mM, about 15 mM to about 35 mM, about 15 mM to about 30 mM, about 15 mM to about 25 mM, about 15 mM to about 20 mM, about 20 mM to about 40 mM, about 20 mM to about 35 mM, about 20 mM to about 30 mM, about 20 mM to about 25 mM, about 25 mM to about 40 mM, about 25 mM to about 35 mM, about 25 mM to about 30 mM, about 30 mM to about 40 mM, about 30 mM to about 35 mM, and from about 35 mM to about 40 mM.

[014] In some embodiments, the lubricating oil composition includes about 250 to about 2500 ppm of Zn based on total weight of the lubricating oil composition such as from about 250 to about 2250 ppm, about 250 to about 2000 ppm, about 250 to about 1750 ppm, about 250 to about 1500 ppm, about 250 to about 1250 ppm, about 250 to about 1000 ppm, about 500 to about 2500 ppm, about 500 to about 2250 ppm, about 500 to about 2000 ppm, about 500 to about 1750 ppm, about 500 to about 1500 ppm, about 500 to about 1250 ppm, about 500 to about 1000 ppm, about 750 to about 2500 ppm, about 750 to about 2250 ppm, about 750 to about 2000 ppm, about 750 to about 1750 ppm, about 750 to about 1500 ppm, about 750 to about 1250 ppm, about 750 to about 1000 ppm, about 1000 to about 2500 ppm, about 1000 to about 2250 ppm, about 1000 to about 2000 ppm, about 1000 to about 1750 ppm, about 1000 to about 1500 ppm, about 1000 to about 1250 ppm, about 1250 to about 2500 ppm, about 1250 to about 2250 ppm, about 1250 to about 2000 ppm, about 1250 to about 1750 ppm, about 1250 to about 1500 ppm, about 1500 to about 2500 ppm, about 1500 to about 2250 ppm, about 1500 to about 2000 ppm, about 1500 to about 1750 ppm, about 1750 to about 2500 ppm, about 1750 to about 2250 ppm, about 1750 to about 2000 ppm, about 2000 to about 2500 ppm, 2000 to about 2250 ppm, or about 2250 to about 2500 ppm.

[015] In some embodiments, the lubricating oil composition includes about 250 to about 2500 ppm of P based on total weight of the lubricating oil composition such as from about 250 to about 2250 ppm, about 250 to about 2000 ppm, about 250 to about 1750 ppm, about 250 to about 1500 ppm, about 250 to about 1250 ppm, about 250 to about 1000 ppm, about 500 to about 2500 ppm, about 500 to about 2250 ppm, about 500 to about 2000 ppm, about 500 to about 1750 ppm, about 500 to about 1500 ppm, about 500 to about 1250 ppm, about 500 to about 1000 ppm, about 750 to about 2500 ppm, about 750 to about 2250 ppm, about 750 to about 2000 ppm, about 750 to about 1750 ppm, about 750 to about 1500 ppm, about 750 to about 1250 ppm, about 750 to about 1000 ppm, about 1000 to about 2500 ppm, about 1000 to about 2250 ppm, about 1000 to about 2000 ppm, about 1000 to about 1750 ppm, about 1000 to about 1500 ppm, about 1000 to about 1250 ppm, about 1250 to about 2500 ppm, about 1250 to about 2250 ppm, about 1250 to about 2000 ppm, about 1250 to about 1750 ppm, about 1250 to about 1500 ppm, about 1500 to about 2500 ppm, about 1500 to about 2250 ppm, about 1500 to about 2000 ppm, about 1500 to about 1750 ppm, about 1750 to about 2500 ppm, about 1750 to about 2250 ppm, about 1750 to about 2000 ppm, about 2000 to about 2500 ppm, 2000 to about 2250 ppm, or about 2250 to about 2500 ppm.

[016] Suitable zinc dithiophosphate (ZnDTP) can have the following formula:



wherein R_1, R_2, R_3, and R_4 are alkyl groups, wherein at least one of R_1, R_2, R_3, or R_4 has 3 carbon atoms and at least one of R_1, R_2, R_3, or R_4 has 8 carbon atoms.

[017] In some embodiments, at least one of R_1, R_2, R_3, or R_4 is a primary alkyl group. In some embodiments, at least one of R_1, R_2, R_3, or R_4 is a secondary alkyl group.

[018] Illustrative examples of the alkyl groups include n-propyl, isopropyl, n-octyl, isooctyl, 2-octyl, 3-octyl, 4-octyl, methylheptyl, 2-ethylhexyl, dimethylhexyl, cyclohexylethyl, ethylcyclohexyl, and vinylhexyl groups.

[019] Zinc dithiophosphates are coordination compounds that can be synthesized from phosphorodithioic acids from which metal salts can be prepared. Examples of dihydrocarbyl phosphorodithioic acids and zinc salts, and processes for preparing such acids and salts are found in, for example, U.S. Pat. Nos. 4,101,428; 4,215,067; 4,263,150; and 4,495,075. These patents are hereby incorporated by reference for such disclosures.

[020] Without being limited by theory, it is believed that the specific combination of the alcohols described herein leads to the desirable performance characteristics demonstrated in the Examples. Particularly useful ZDDPs include those derived from a mixture of alcohols. In some embodiments, the mixture of alcohols include C3 and C8 (C3/C8) alcohols.

[021] Phosphorodithioic or dithiophosphoric acids (DTPA) are typically prepared by the reaction of phosphorous pentasulfide with an alcohol or phenol or mixtures of alcohols and/or phenols. The reaction involves at least four moles of the alcohol or phenol per mole of phosphorous pentasulfide, and may be carried out within the temperature range from about 50° C to about 200° C.

[022] For example, the preparation of O,O-di-(isopropyl/ 2-ethylhexyl) phosphorodithioic acid involves the reaction of phosphorous pentasulfide with at least four moles of a mixture of isopropanol and 2-ethylhexanol at about 100° C for up to 5 hours. Hydrogen sulfide is liberated, and the residue is the defined acid. The preparation of the zinc salt of this acid may be by reaction with zinc oxide in the presence of a promoter (for example acetic acid) at elevated reaction temperature and extended reaction period.

[023] When derived from alkyl alcohols, the zinc dithiophosphate can also be referred to as zinc dialkyldithiophosphate.

[024] The R groups (i.e., R^1, R^2, etc.) derived from a mixture of alcohols having either 3 or 8 carbon atoms may provide performance benefits over other R groups. In some embodiments, the ZDDP comprises a specific ratio of C3 to C8 alcohols. Suitable ratios can range from about 95/5 molar ratio of C3 to C8 alcohols down to about 5/95

of C3 to C8 alcohols, such as a 90/10 ratio of C3 to C8 alcohols, 85/15 ratio of C3 to C8 alcohols, 80/20 ratio of C3 to C8 alcohols, 75/25 ratio of C3 to C8 alcohols, 70/30 ratio of C3 to C8 alcohols, 60/40 ratio of C3 to C8 alcohols, 50/50 ratio of C3 to C8 alcohols, 40/60 ratio of C3 to C8 alcohols, 30/70 ratio to C3 to C8 alcohols, 25/75 ratio of C3 to C8 alcohols, 20/80 ratio of C3 to C8 alcohols, 10/90 ratio of C3 to C8 alcohols and so forth.

Other Additives

[025] The present lubricating oil compositions may also contain conventional lubricant additives for imparting auxiliary functions to give a finished lubricating oil composition in which these additives are dispersed or dissolved. For example, the lubricating oil compositions can be blended with antioxidants, ashless dispersants, anti-wear agents, rust inhibitors, dehazing agents, demulsifying agents, friction modifiers, metal deactivating agents, pour point depressants, viscosity modifiers, antifoaming agents, co-solvents, package compatibilizers, corrosion-inhibitors, dyes, extreme pressure agents and the like and mixtures thereof. A variety of the additives are known and commercially available. These additives, or their analogous compounds, can be employed for the preparation of the lubricating oil compositions of the invention by the usual blending procedures.

[026] Each of the foregoing additives, when used, is used at a functionally effective amount to impart the desired properties to the lubricant. Thus, for example, if an additive is an ashless dispersant, a functionally effective amount of this ashless dispersant would be an amount sufficient to impart the desired dispersancy characteristics to the lubricant. Generally, the concentration of each of these additives, when used, may range, unless otherwise specified, from about 0.001 to about 20 wt. %, such as about 0.01 to about 10 wt. %.

Antioxidants

[027] In one embodiment, the lubricating oil composition may optionally comprise an antioxidant compound. In one embodiment, the antioxidant is an aromatic amine antioxidant. Typical aromatic amine antioxidants have at least two

aromatic groups attached directly to one amine nitrogen. Typical aromatic amine antioxidants have alkyl substituent groups of at least 6 carbon atoms.

[028] Examples of aromatic amine antioxidants useful herein include 4,4′-dioctyldiphenylamine, 4,4′-dinonyldiphenylamine, N-phenyl-1-naphthylamine, N-(4-tert-octyphenyl)-1-naphthylamine, and N-(4-octylphenyl)-1-naphthylamine. Antioxidants may be present at 0.01 to 5 wt. % (e.g., 0.1 to 2 wt. %) of the lubricating oil composition.

Lubricating Oil

[029] The oil of lubricating viscosity (sometimes referred to as “base stock” or ”base oil”) is the primary liquid constituent of a lubricant, into which additives and possibly other oils are blended, for example to produce a final lubricant (or lubricant composition). A base oil, which is useful for making concentrates as well as for making lubricating oil compositions therefrom, may be selected from natural (vegetable, animal or mineral) and synthetic lubricating oils and mixtures thereof.

[030] Oils used as the base oil will be selected or blended depending on the desired end use and the additives in the finished oil to give the desired grade of engine oil, e.g. a lubricating oil composition having an Society of Automotive Engineers (SAE). In one embodiment, the lubricating oil composition is a multi-grade oil for heavy duty or passenger car. The multi-grade oil may have a viscosity grade SAE of 0W-8, 0W-12, 0W-16, 0W-20, 0W-30, 0W-40, 0W-50, 0W-60, 5W, 5W-20, 5W-30, 5W-40, 5W- 50, 5W-60, 10W, 10W-20, 10W-30, 10W-40, 10W-50, 15W, 15W-20, 15W-30, or 15W-40.

[031] Definitions for the base stocks and base oils in this disclosure are the same as those found in American Petroleum Institute (API) Publication 1509 Annex E (“API Base Oil Interchangeability Guidelines for Passenger Car Motor Oils and Diesel Engine Oils,” December 2016). Group I base stocks contain less than 90% saturates and/or greater than 0.03% sulfur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table E-1. Group II base stocks contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 80 and less than 120 using the test

methods specified in Table E-1. Group III base stocks contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 120 using the test methods specified in Table E-1. Group IV base stocks are polyalphaolefins (PAO). Group V base stocks include all other base stocks not included in Group I, II, III, or IV.

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

[033] Synthetic oils include hydrocarbon oil. Hydrocarbon oils include oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene isobutylene copolymers, ethylene-olefin copolymers, and ethylene-alphaolefin copolymers). Polyalphaolefin (PAO) oil base stocks are commonly used synthetic hydrocarbon oil. By way of example, PAOs derived from C_8 to C_{14} olefins, e.g., C_8, C_{10}, C_{12}, C_{14} olefins or mixtures thereof, may be utilized.

[034] Other useful fluids for use as base oils include non-conventional or unconventional base stocks that have been processed, preferably catalytically, or synthesized to provide high performance characteristics.

[035] Non-conventional or unconventional base stocks/base oils include one or more of a mixture of base stock(s) derived from one or more Gas-to-Liquids (GTL) materials, as well as isomerate/isodewaxate base stock(s) derived from natural wax or waxy feeds, mineral and or non-mineral oil waxy feed stocks such as slack waxes, natural waxes, and waxy stocks such as gas oils, waxy fuels hydrocracker bottoms, waxy raffinate, hydrocrackate, thermal crackates, or other mineral, mineral oil, or even non-petroleum oil derived waxy materials such as waxy materials received from coal

liquefaction or shale oil, and mixtures of such base stocks. Other base oils include Coal to liquid (CTL) products and alkyl-naphthalene.

[036] Base oils for use in the lubricating oil compositions of present disclosure are any of the variety of oils corresponding to API Group I, Group II, Group III, Group IV, and Group V oils, and mixtures thereof, preferably API Group II, Group III, Group IV, and Group V oils, and mixtures thereof, more preferably the Group III to Group V base oils due to their exceptional volatility, stability, viscometric and cleanliness features.

[037] The lubricating oil composition may have a high temperature shear (HTHS) viscosity at 150° C of 3.7 cP or less, such as 3.6 cP or less, 3.5 cP or less, 3.4 cP or less, 3.3 cP or less, 3.2 cP or less, 3.1 cP or less, 3.0 cP or less, 2.9 cP or less, 2.8 cP or less, 2.7 cP or less, 2.6 cP or less, 2.5 cP or less, 2.4 cP or less, 2.3 cP or less, 2.2 cP or less, 2.1 cP or less, 2.0 cP or less, 1.9 cP or less, 1.8 cP or less, 1.7 cP or less, 1.6 cP or less, 1.5 cP or less, 1.4 cP or less, 1.3 cP or less, 1.2 cP or less, 1.1 cP or less, 1.0 cP or less, 1.0 to 2.9 cP, 1.3 to 2.9 cP) 1.0 to 2.6 cP, 1.3 to 2.6 cP, 1.0 cP to 2.3 cP, 1.3 cP to 2.3 cP, 1.0 cP to 2.0 cP, 1.3 cP to 2.3 cP, 1.0 cP to 1.7 cP, or 1.3 cP to 1.7 cP.

[038] The lubricating oil composition may have a viscosity index of at least 135 (e.g., 135 to 400, or 135 to 250), at least 150 (e.g., 150 to 400, 150 to 250), at least 165 (e.g., 165 to 400, or 165 to 250), at least 190 (e.g., 190 to 400, or 190 to 250), or at least 200 (e.g., 200 to 400, or 200 to 250). If the viscosity index of the lubricating oil composition is less than 135, it may be difficult to improve fuel efficiency while maintaining the HTHS viscosity at 150° C. If the viscosity index of the lubricating oil composition exceeds 400, evaporation properties may be reduced, and deficits due to insufficient solubility of the additive and matching properties with a seal material may be caused.

[039] The base oil may have a kinematic viscosity at 100°C (ASTM D445) in a range of 1.4 to 20 mm^2/s such as 3 to 12 mm^2/s, such as 3 to 11 mm^2/s, 3 to 10 mm^2/s, 3 to 9 mm^2/s, 3 to 8 mm^2/s, 3 to 7 mm^2/s, 3 to 6 mm^2/s, 3 to 5 mm^2/s, 3 to 4 mm^2/s, 4 to 12 mm^2/s, 4 to 11 mm^2/s, 4 to 10 mm^2/s, 4 to 9 mm^2/s, 4 to 8 mm^2/s, 4 to 7 mm^2/s, 4 to 6 mm^2/s, 4 to 5 mm^2/s, 5 to 12 mm^2/s, 5 to 11 mm^2/s, 5 to 10 mm^2/s, 5 to 9 mm^2/s,

5 to 8 mm^2/s, 5 to 7 mm^2/s, 5 to 6 mm^2/s, 6 to 12 mm^2/s, 6 to 11 mm^2/s, 6 to 10 mm^2/s, 6 to 9 mm^2/s, 6 to 8 mm^2/s, 6 to 7 mm^2/s, 7 to 12 mm^2/s, 7 to 11 mm^2/s, 7 to 10 mm^2/s, 7 to 9 mm^2/s, 7 to 10 mm^2/s, 7 to 9 mm^2/s, 7 to 8 mm^2/s, 8 to 12 mm^2/s, 8 to 11 mm^2/s, 8 to 10 mm^2/s, 8 to 9 mm^2/s, 9 to 12 mm^2/s, 9 to 11 mm^2/s, 9 to 10 mm^2/s, 10 to 12 mm^2/s, 10 to 11 mm^2/s, or 11 to 12 mm^2/s.

[040] In some embodiments, the lubricating oil composition contains 0.8 to 1.5 wt% of ash, such as 0.8 to 1.4 wt%, 0.8 to 1.3 wt%, 0.8 to 1.2 wt%, 0.8 to 1.1 wt%, 0.8 to 1.0 wt%, 0.8 to 0.9 wt%, 0.9 to 1.5 wt%, 0.9 to 1.4 wt%, 0.9 to 1.3 wt%, 0.9 to 1.2 wt%, 0.9 to 1.1 wt%, 0.9 to 1.0 wt%, 1.0 to 1.5 wt%, 1.0 to 1.4 wt%, 1.0 to 1.3 wt%, 1.0 to 1.2 wt%, 1.0 to 1.1 wt%, 1.1 to 1.5 wt%, 1.1 to 1.4 wt%, 1.1 to 1.3 wt%, 1.1 to 1.2 wt%, 1.2 to 1.5 wt%, 1.2 to 1.4 wt%, 1.2 to 1.3 wt%, 1.3 to 1.5 wt%, 1.3 to 1.4 wt%, and 1.4 to 1.5 wt%.

[041] The following non-limiting examples are illustrative of the present invention. Brief descriptions of how the examples were prepared are provided.

EXAMPLES

Baseline Formulation

[042] All samples include the following baseline formulation: SAE 10-30W viscosity grade heavy duty diesel lubricating oil composition prepared by blending the following components base oil and at least one of the following: one or more ZDDP, zinc dithiocarbamate (ZnDTC) and ashless dithiophosphate (DTP). The ZDDP is a C3/C8 ZDDP, C4/C6 ZDDP, or C8 ZDDP.

[043] The remainder of the lubricating oil composition includes commonly known/used additives such as detergent, viscosity index improver, and pour point depressant. Each sample was subjected to NOx conversion bench test as described below.

NOx Conversion Bench Test

[044] This test measures the reduction of the NOx conversion rate in a SCR catalyst after contamination with a lubricating oil. Before the SCR tests can be

performed, the catalyst must be prepared, which involves taking solid vanadium EU6 catalyst monolith and crushing, filtering, hydrothermally aging, and impregnating/calcinating the material.

[045] Once the catalyst material has been crushed & filtered, it is soaked in the oil samples and hot filtered until there is no visible oil. The oil impregnated catalyst is calcinated under positive airflow to remove hydrocarbons. The SCR tests were performed in typical diesel exhaust conditions (temperature ramped from 175 to 550°C). More specifically, the SCR catalyst materials came into contact with a simulated gas feed which is a mixture of NO (500ppm), NH_3 (500ppm), H_2O (5%), O_2 (10%) and balancing amount of N_2.

[046] The SCR runs were performed at 10 different temperature steps (200, 220, 240, 260, 280, 300, 320, 350, 400, 500°C). NOx conversion efficiency (ATS Conversion %) was evaluated from the outflow based on ICP analysis.

Ex.	C3/C8 ZDDP (mM)	C4/C6 ZDDP (mM)	C8 ZDDP (mM)	ZnDTC (mM)	Ashless DTP (mM)	Zn (ppm)	P (ppm)	ATS Conversion %
1	8	0	0	0	0	570	500	66
2	12.5	0	0	0	0	890	770	70
3	16	0	0	0	0	1140	1000	90
4	32	0	0	0	0	2280	2000	86
5	0	0	0	0	34	0	944	70
6	1	0	0	0	62	70	62	29
7	0	0	0	30	0	1000	0	37

[047] For the sake of brevity, only certain ranges are explicitly disclosed herein. However, ranges from any lower limit may be combined with any upper limit to recite a range not explicitly recited, as well as, ranges from any lower limit may be combined with any other lower limit to recite a range not explicitly recited, in the same way,

ranges from any upper limit may be combined with any other upper limit to recite a range not explicitly recited. Additionally, within a range includes every point or individual value between its end points even though not explicitly recited. Thus, every point or individual value may serve as its own lower or upper limit combined with any other point or individual value or any other lower or upper limit, to recite a range not explicitly recited.

[048] Likewise, the term "comprising" is considered synonymous with the term "including." Likewise whenever a composition, an element or a group of elements is preceded with the transitional phrase "comprising," it is understood that we also contemplate the same composition or group of elements with transitional phrases "consisting essentially of," "consisting of," "selected from the group of consisting of," or "is" preceding the recitation of the composition, element, or elements and vice versa.

[049] The terms "a" and "the" as used herein are understood to encompass the plural as well as the singular.

[050] Various terms have been defined above. To the extent a term used in a claim is not defined above, it should be given the broadest definition persons in the pertinent art have given that term as reflected in at least one printed publication or issued patent. Furthermore, all patents, test procedures, and other documents cited in this application are fully incorporated by reference to the extent such disclosure is not inconsistent with this application and for all jurisdictions in which such incorporation is permitted.

[051] The foregoing description of the disclosure illustrates and describes the present disclosure. Additionally, the disclosure shows and describes only the preferred embodiments but, as mentioned above, it is to be understood that the disclosure is capable of use in various other combinations, modifications, and environments and is capable of changes or modifications within the scope of the concept as expressed herein, commensurate with the above teachings and/or the skill or knowledge of the relevant art. While the foregoing is directed to embodiments of the present disclosure,

other and further embodiments of the disclosure may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

[052] It is understood that when combinations, subsets, groups, etc. of elements are disclosed (e.g., combinations of components in a composition, or combinations of steps in a method), that while specific reference of each of the various individual and collective combinations and permutations of these elements may not be explicitly disclosed, each is specifically contemplated and described herein.

[053] The embodiments described hereinabove are further intended to explain best modes known of practicing it and to enable others skilled in the art to utilize the disclosure in such, or other, embodiments and with the various modifications required by the particular applications or uses. Accordingly, the description is not intended to limit it to the form disclosed herein. Also, it is intended that the appended claims be construed to include alternative embodiments.

CLAIMS

1. A method of reducing catalyst poisoning in a diesel engine aftertreatment system comprising a selective catalytic reduction device, the method comprising:

lubricating the engine with a lubricating oil composition comprising:

a major amount of oil of lubricating viscosity; and

a phosphorus-containing additive.

2. The method of claim 1, wherein the phosphorus-containing additive is zinc dithiophosphate, dithiophosphoric acid, or ashless dithiophosphate.

3. The method of claim 2, wherein the zinc dithiophosphate or ashless dithiophosphate is derived from a mixture of alcohols.

4. The method of claim 3, wherein the mixture of alcohols includes C3 and C8 alcohols.

5. The method of claim 3, wherein the mixture of alcohols includes primary and secondary alcohols.

6. The method of claim 1, wherein the phosphorus-containing additive is present in about 5 mM to about 40 mM based on the total lubricating oil composition.

7. The method of claim 3, wherein the mixture of alcohols includes alcohols having an alkyl group, wherein the alkyl group is n-propyl, isopropyl, n-octyl, isooctyl, 2-octyl, 3-octyl, 4-octyl, methylheptyl, 2-ethylhexyl, dimethylhexyl, cyclohexylethyl, ethylcyclohexyl, or vinylhexyl groups.

8. The method of claim 1, wherein lubricating oil composition includes about 250 to about 2500 ppm of Zn.

9. The method of claim 1, wherein the lubricating oil composition includes about 250 to about 2500 ppm of P.

10. Use of a lubricating oil composition in a diesel engine aftertreatment system comprising a selective catalytic reduction device, the lubricating oil composition comprising:

a major amount of oil of lubricating viscosity; and

a phosphorus-containing additive.

11. The use of claim 10, wherein the phosphorus-containing additive is zinc dithiophosphate, dithiophosphoric acid, or ashless dithiophosphate.

12. The use of claim 11, wherein the zinc dithiophosphate or ashless dithiophosphate is derived from a mixture of alcohols.

13. The use of claim 12, wherein the mixture of alcohols includes C3 and C8 alcohols.

14. The use of claim 12, wherein the mixture of alcohols includes primary and secondary alcohols.

15. The use of claim 10, wherein the phosphorus-containing additive is present in about 5 mM to about 40 mM based on the total lubricating oil composition.

16. The use of claim 12, wherein the mixture of alcohols includes alcohols having an alkyl group, wherein the alkyl group is n-propyl, isopropyl, n-octyl, isooctyl, 2-octyl, 3-octyl, 4-octyl, methylheptyl, 2-ethylhexyl, dimethylhexyl, cyclohexylethyl, ethylcyclohexyl, or vinylhexyl groups.

17. The use of claim 10, wherein lubricating oil composition includes about 250 to about 2500 ppm of Zn.

18. The use of claim 10, wherein the lubricating oil composition includes about 250 to about 2500 ppm of P.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2024/019558

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10M137/10
ADD. C10N10/04 C10N30/00 C10N40/25

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 C10N

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	EP 1 803 793 A1 (INFINEUM INT LTD [GB]) 4 July 2007 (2007-07-04) paragraphs [0002]-[0005], [0039]-[0041], [0059], [0060], [0063], claims 1, 9, examples	1-18
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[x] Further documents are listed in the continuation of Box C.

[x] 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

"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)

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 June 2024	26/06/2024

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INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 2017/073613 A1 (GALIC RAGUZ MARY [US] ET AL) 16 March 2017 (2017-03-16) paragraphs [0002], [0105];examples, claims 34-35, 56, table 1 -----	1-3, 6-12, 15-18
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A	KROCHER ET AL: "Chemical deactivation of V"2O"5/WO"3-TiO"2 SCR catalysts by additives and impurities from fuels, lubrication oils, and urea solution", APPLIED CATALYSIS B. ENVIRONMENTAL, ELSEVIER, AMSTERDAM, NL, vol. 77, no. 3-4, 29 November 2007 (2007-11-29), pages 215-227, XP022369681, ISSN: 0926-3373, DOI: 10.1016/J.APCATB.2007.04.021 page 217: 2.3 doping of catalysts; figure 2 -----	1-18

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INTERNATIONAL SEARCH REPORT

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International application No
PCT/US2024/019558

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