

TRUNK PISTON ENGINE OIL

This invention relates to a trunk piston engine lubricating composition or trunk piston engine oil (TPEO), to an additive pack for such a composition, to associated uses and to a method for the manufacture of the trunk piston engine oil

BACKGROUND

Marine four stroke piston engines typically use a heavy fuel oil for operation and offshore running. Heavy fuel oil is from the heaviest fraction of petroleum distillate and comprises a complex mixture of components which includes asphaltenes, which are defined as the components of the fraction insoluble in light paraffins (such as n-heptane), but soluble in light aromatics (such as toluene or benzene).

Asphaltenes tend to cause fouling in four stroke engines through precipitation in the engine lubricant, which it enters as a contaminant from the heavy fuel oil where it can precipitate to form a sludge or manifests as 'black paint' in the engine. This can inhibit the performance of the lubricant composition and more particularly can lead to degradation of the engine and of the piston, resulting in a shorter component lifespan.

Trunk Piston Engine Oils should ideally inhibit asphaltene precipitation and the formation of 'black paint'. Trunk Piston Engine Oils typically comprise a base stock, which may be a Group I base stock or a higher saturate base stock of Group II or Group III. The base stock is typically treated with an additive pack or booster pack to achieve the performance in terms of asphaltene handling or asphaltene solubility as well as other performance requirements, such as anti-wear agents and anti-foaming agents among others designed to achieve adequate performance in FZG (wear), water shedding and oxidation. The asphaltene handling is typically achieved by addition of detergents. The treat rate of an additive pack (and, in particular of detergent level) to achieve acceptable performances is typically in the region of 16% (for a typical 40 BN TPEO).

There is a continuing drive to provide improved efficiency in marine four stroke piston engine operation and in particular in the TPEOs. It is thus desirable to provide satisfactory performance with choice of base stock and reduced treat rate of additives and, in particular detergent.

The present inventors have developed compositions that addresses these needs.

SUMMARY OF INVENTION

According to a first aspect of the invention, there is provided a trunk piston engine lubricating composition (or a lubricant composition) comprising a base oil of lubricating viscosity and an additive composition comprising an anti-wear additive comprising a zinc dialkyl dithiophosphate (ZDDP) and a detergent composition comprising one or more detergents.

In one embodiment, the ZDDP comprises at least one ester moiety derived from a primary alcohol.

In one embodiment, the additive composition is present in the lubricating composition in a 40 Base Number (BN) equivalent amount of up to 15% w/w of the lubricating composition (or is provided at a 40 BN equivalent treat rate of up to 15% w/w of the lubricating composition).

In one embodiment, the detergent composition is present in the lubricating composition in a 40 BN equivalent amount of up to 14.5% w/w of the lubricating composition (or is provided at a 40 BN equivalent treat rate of up to 14.5% w/w of the lubricating composition). In one embodiment, the ZDDP comprises at least one ester moiety derived from a primary alcohol and preferably the additive composition is present in the lubricating composition in a 40 BN equivalent amount of up to 15% w/w of the lubricating composition.

In a second aspect of the invention, there is provided a use of a zinc dialkyl dithiophosphate (ZDDP) to enhance or improve asphaltene handling in a trunk piston engine lubricating composition (or in a lubricant composition), wherein the ZDDP preferably comprises at least one ester moiety derived from a primary alcohol.

In a third aspect of the invention, there is provided a use of a zinc dialkyl dithiophosphate (ZDDP) preferably comprising at least one ester moiety derived from a primary alcohol to enable reduced detergent treat rate in a trunk piston engine lubricating composition (or in a lubricant composition).

In a fourth aspect of the invention, there is provided a use of an additive pack or additive composition to enhance asphaltene handling in a trunk piston engine lubricating composition (or lubricant composition), the additive pack comprising an anti-wear additive comprising a zinc dialkyl dithiophosphate (ZDDP) comprising at least one ester moiety

derived from a primary alcohol and a detergent composition comprising one or more detergents.

In one embodiment, the use is effected by adding the additive pack to a base oil at a 40 BN equivalent treat rate of up to 15% w/w of a resulting lubricating composition.

5 In a fifth aspect of the invention, there is provided a use of detergent composition in a TPEO detergency amount to improve the asphaltene handling of a trunk piston engine lubricating composition by providing the detergent composition in combination with a zinc dialkyl dithiophosphate (ZDDP) comprising at least one ester moiety derived from a primary alcohol.

10 In one embodiment, the use is effected by adding the detergent composition with the ZDDP to a base oil for a trunk piston engine lubricating composition at a 40 BN treat rate equivalent of up to 14.5% w/w of the resulting lubricating composition.

In a sixth aspect of the invention, there is provided a base oil for use in a trunk piston engine lubricating composition with an additive composition, the base oil comprising in all
15 or in a major part of a primary Group I base stock with a sulfur content of at least 6000 ppm and an aromatic component content of at least 5% by weight and/or the primary Group I base stock having a kinematic viscosity at 100°C of from 12.5 to 17.

In a seventh aspect of the invention, there is provided use of a base oil as defined above to enhance asphaltene handling in a trunk piston engine lubricating composition
20 comprising the base oil and a lubricating composition with an additive composition.

In an eighth aspect of the invention, there is provided a method for the manufacture of a trunk piston engine lubricating composition, the method comprising combining a base oil with an additive composition comprising an anti-wear additive comprising a zinc dialkyl dithiophosphate (ZDDP) comprising at least one ester moiety derived from a
25 primary alcohol and a detergent composition comprising one or more detergents.

In a ninth aspect of the invention, there is provided a method of operating a trunk piston marine engine comprising fuelling the engine with a heavy fuel oil and lubricating the crankcase of the engine with a lubricating composition as defined above.

30 DETAILED DESCRIPTION

The invention, according to a first aspect is directed to a trunk piston engine (preferably trunk piston marine engine) lubricating composition (or to a lubricant

composition). The lubricating composition comprises a base oil and an additive composition. The base oil should be such to provide a lubricating viscosity or the lubricating viscosity in the presence of the additive composition. The base oil composition makes up the major part of the lubricating composition, by which it is meant more than 50% by weight. Preferably, the base oil comprises at least 60% by weight, more preferably at least 70% by weight and still more preferably at least 80% by weight. Most preferably, the lubricating composition is made up of the base oil and an additive composition and optionally other additives. According to the lubricating composition of the invention, the additive composition comprises a zinc dialkyl dithiophosphate (ZDDP) and a detergent composition comprising one or more detergents.

The ZDDP may be any suitable ZDDP that functions to improve the asphaltene handling or cleanliness of the lubricating composition when used as a lubricating composition for an engine running on heavy fuel oil, or which functions to enhance the asphaltene handling of a detergent composition used in the additive composition. Thus, the asphaltene handling of a lubricating composition may be enhanced by selecting such a ZDDP for use (e.g. as an anti-wear additive) in the additive composition. Alternatively, the selection of such a ZDDP for use (e.g. as an anti-wear additive) in the additive composition may enable an asphaltene handling performance of a lubricating composition to remain acceptable with reduced additive composition treat rate and especially with a reduced amount of detergent for a given Base Number composition, or with lower soap content. Thereby, in accordance with an embodiment of the present invention, an acceptable asphaltene handling performance of a lubricating composition can be achieved with a relatively lower amount of additive composition (that is, with a lower treat rate of additive composition).

Thus use of a ZDDP, meeting the functional or structural requirements defined herein, enhances or improves handling in a trunk piston engine lubricating composition and/or enables a reduced amount of detergent composition (or detergent treat rate) to be used whilst maintaining acceptable asphaltene handling.

According to one embodiment, an acceptable asphaltene handling performance or cleanliness may be considered to be the ability of the lubricating composition to handle fuel dilution with heavy fuel oil (high in sulfur and asphaltene) without significant asphaltene precipitation.

An acceptable asphaltene handling performance may, optionally, be defined in terms of a technical assessment of asphaltene handling. For that purpose, there is further described herein and provided as a further aspect of invention, an asphaltene handling test method. An asphaltene handling test method preferably comprises a hot liquid process simulator (HLPS) test under defined conditions. An asphaltene handling HLPS test method comprises providing a lubricating composition to be tested, doping the same with a pre-defined amount of heavy fuel oil (e.g. 1%, but more discriminating tests can be carried out using a doping level of 1.5% or 2% or other according to requirements) to provide a test sample, depositing the test sample in an HLPS apparatus and passing through an HLPS test vessel (e.g. a steel tube, e.g. of 60 mm in length) under suitable flow conditions (e.g. laminar flow) to be subject to thermal treatment and subjecting the HLPS test vessel to a pre-defined temperature (e.g. in the range 100°C to 400°C, preferably 200°C to 300°C and most preferably 250°C) for a pre-defined time (e.g. 1 to 5 hours, preferably 2 to 3 hours and more preferably 2.5 hours). The resulting deposit thickness on the walls of the vessel may then be determined preferably by ellipsometry, preferably the maximum deposit thickness (e.g. by determining the deposit thickness at multiple points along the length of a HLPS test vessel, e.g. every 10 mm). Asphaltene handling is considered to be acceptable if the maximum deposit thickness (as determined by ellipsometry after the predefined time and temperature in the HLPS) meets or is less than a pre-determined threshold. In a preferred embodiment, asphaltene handling is considered to be acceptable when the deposit thickness is 300 nm or less (based on a 1% doped sample heated at 250°C for 2.5h). A preferred asphaltene handling performance is represented for example by a maximum deposit thickness of up to 250 nm and a more preferred asphaltene handling performance by a maximum deposit thickness of up to 200 nm.

A selected ZDDP may be considered to demonstrate the function for use in the present invention, in one embodiment, if it's inclusion allows a lubricating composition to achieve an acceptable asphaltene handling performance (e.g. as defined above) with a detergent composition present in a 40BN equivalent amount of up to 14.5% w/w of the lubricating compositions.

In another embodiment, a ZDDP may be considered to be a ZDDP that meets the requirements for asphaltene handling or maintenance, as discussed above, provided that ZDDP when selected as an anti-wear component is effective in reducing the deposition

thickness determined in the asphaltene handling HLPS test method described above using a lubricating composition comprising the selected ZDDP compared with a comparative lubricating composition that is the same other than its selection of anti-wear component which should be different (e.g. a non-ZDDP anti-wear agent or a ZDDP agent without any primary alcohol-derived ester moieties), preferably effective in reducing the maximum deposition thickness by at least 20 nm, more preferably by at least 30 nm and still more preferably at least 50 nm (e.g. under the preferred test conditions described above of a 1% heavy fuel oil-doped sample heated to 250°C and run for 2.5h). More preferably, in any case, the maximum deposition thickness for the lubricating oil with the selected ZDDP is also 300 nm or less, more preferably 250 nm or less and still more preferably 200 nm or less.

In another embodiment, a ZDDP may be considered to demonstrate such a function as suggested above and thus suitable for use in a composition according to the present invention where a lubricating composition comprising a base oil having a KV100 of 14 cSt, a sulfur content of at least 5000 ppm and an aromatic component content of at least 4% by weight treated with an additive composition comprising the ZDDP and a detergent composition at a treat rate of 14.5 wt% does not precipitate asphaltene particulates in a thickness of greater than 300 nm (preferably not greater than 250 nm) during an asphaltene handling HLPS test method as defined above (with a 1% heavy fuel oil doping rate, thermal treatment of 250°C and run for 2.5 hours, which can be referred to as standard conditions).

In one embodiment, the ZDDP comprises at least one ester moiety derived from a primary alcohol.

The ZDDP preferably comprises at least one ester derived from a primary alcohol. Preferably, the ZDDP comprises at least two ester moieties derived from primary alcohols. Optionally, each dialkyl dithiophosphate moiety comprises at least one ester derived from a primary alcohol and optionally two (both) esters derived from a primary alcohol. In one embodiment, at least 25% of the esters of the ZDDP are derived from a primary alcohol, optionally at least 50% and in one embodiment at least 75%.

Where a ZDDP comprises more than ester derived from a primary alcohol, the ester moieties may be the same or different.

Any suitable primary alcohol may be included. A primary alcohol may comprise a straight chain or branched alkyl group and may be fully saturated or partially unsaturated. Preferably the primary alcohol is a fully saturated. Optionally, the primary alcohol comprises a straight chain alkyl. The primary alcohol from which the one or more ester groups of ZDDP derive preferably comprises a C3 to C10 straight chain or branched alkyl group, more preferably a C3 to C8, still more preferably a C3 to C6 and still more preferably a C4 to C6 alkyl group. Most preferably, each ester that is derived from a primary alcohol comprises a C4-C6 straight chain alcohol. Preferably, the ester derived from a primary alcohol is an n-propyl ester, an n-butyl ester, 1-isobutyl ester, a pentyl ester or a hexyl ester. In one embodiment, all ester moieties in the ZDDP are derived from primary alcohols.

Optionally, according to the embodiment in which at least one ester of the ZDDP (and preferably at least two esters) are derived from primary alcohols, at least one ester may be derived from a secondary alcohol. Suitable secondary alcohols include isopropyl, sec-butyl and other 2-substituted straight chain C5 to C8 alcohols.

In one embodiment, the ZDDP is a mixed primary and secondary alcohol ester ZDDP. Preferably all the esters comprise ester derived from alcohols comprising C3 to C8, preferably C4 to C6.

One exemplary ZDDP for use in aspects of the present invention is mixed isobutyl/pentyl esters.

Another exemplary ZDDP for use in aspects of the present invention is 2-ethyl hexyl esters.

Preferably, the ZDDP used is selected from widely commercially available primary C4/C5 ZDDPs.

The ZDDP is preferably included, with the additive composition, in the lubricating composition in an amount of up to 1% by weight of the lubricating composition, preferably in an amount of up to 0.75%, more preferably up to 0.7%, still more preferably 0.65%, preferably 0.6% and more preferably yet 0.55%. Preferably the ZDDP is provided in an amount of at least 0.4% by weight of the lubricating composition, more preferably 0.45% and still more preferably about 0.5%.

Preferably the ZDDP is selected as an anti-wear additive, which has the added benefit of enhancing asphaltene handling of a lubricating composition for any given treat rate of detergents.

5 In one embodiment, the additive composition is present in the lubricating composition in a 40 Base Number equivalent amount of up to 15% w/w of the lubricating composition (that is, it is provided at a 40 Base Number equivalent treat rate of up to 15% by weight of the resulting lubricating composition).

10 In a preferred embodiment, the lubricating composition comprises an additive composition comprising a zinc dialkyl dithiophosphate (ZDDP), such as defined above, and preferably comprising at least one ester moiety derived from a primary alcohol and a detergent composition comprising one or more detergents, which additive composition is present in the lubricating composition in a 40 BN equivalent amount of up to 15% w/w of the lubricating composition.

15 There is further provided, in a second aspect, a use of an additive pack to enhance asphaltene handling in a trunk piston engine lubricating composition, the additive pack comprising an anti-wear additive comprising a zinc dialkyl dithiophosphate (ZDDP), preferably as defined above and preferably comprising at least one ester moiety derived from a primary alcohol and a detergent composition comprising one or more detergents. The use of the additive pack is preferably put into effect by adding the additive pack to a
20 base oil at a 40 BN treat rate of up to 15% w/w of the resulting lubricating composition.

Preferably, the additive pack or additive composition is present or added in a 40 BN equivalent amount of up to 14.5% w/w of the lubricating composition, more preferably up to 14%, still more preferably up to 13.5% and more preferably still up to 13%. Optionally, the additive composition is present in a lubricating composition of the invention in a 40
25 BN equivalent amount in the range of from 11.5% to 13% w/w of the lubricating composition.

The amount of additive composition and more particularly detergent composition in a trunk piston engine lubricating composition as described herein depends upon the Base Number (BN) of the lubricating composition. The lubricating composition typically will be
30 provided commercially at a BN in the range 20 to 55, having target BN of 20, 30, 40, 50 and 55. Most preferred lubricating compositions have a BN of 40 or lower.

The amount of detergent composition in a lubricating composition is being defined as a 40 BN equivalent amount. By this, it is meant the amount used in a lubricating composition have a Base Number of 40, but also a corresponding amount in lubricating compositions of other Base Number. The amount in lubricating compositions of other Base Number would be proportionate. In other words, a detergent composition present in a 40 BN equivalent amount of 14% by weight of a lubricating composition would be present in an amount of 7% by weight in a 20 BN lubricating composition.

The detergent composition can comprise any suitable detergents for use in a marine piston engine lubricating composition.

The detergent composition may comprise one or more (typically more than one) metal detergent selected from one or a combination of sulphonates, phenates, salicylates, carboxylates, carbonates and naphthenates. More typically, the detergent composition comprises one or more salicylates and/or carboxylates, most preferably salicylates. The detergents may be, for example, calcium or magnesium metal detergents, more preferably calcium salicylates and preferably over-based salicylates.

The metal detergent preferably used in the additive composition and additive pack is an additive based on so-called metal “soaps”, that is metal salts of acidic organic compounds, sometimes referred to as surfactants. They generally comprise a polar head with a long hydrophobic tail. Over-based metal detergents, which comprise neutralized metal detergents as the outer layer of a metal base (e.g. carbonate) micelle, may be provided by including large amounts of metal base by reacting an excess of a metal base, such as an oxide or hydroxide, with an acidic gas such as carbon dioxide. Examples of detergents include metal salicylates, phenates and carboxylates and combinations thereof.

In the present invention, the detergent composition may comprise over-based metal detergents, preferably over-based metal hydrocarbyl-substituted hydroxybenzoate, more preferably hydrocarbyl-substituted salicylate, detergents. The metal may be an alkali metal (e.g. Li, Na, K) or an alkaline earth metal (e.g. Mg, Ca).

“Hydrocarbyl” means a group or radical that contains carbon and hydrogen atoms and that is bonded to the remainder of the molecule via a carbon atom. It may contain hetero atoms, i.e. atoms other than carbon and hydrogen, provided they do not alter the essentially hydrocarbon nature and characteristics of the group. As examples of hydrocarbyl, there may be mentioned alkyl and alkenyl. A preferred over-based metal

hydrocarbyl-substituted hydroxybenzoate is a calcium alkyl-substituted salicylate and has the structure:



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where R is a linear alkyl group.

There may be more than one R group attached to the benzene ring. The COO^- group can be in the ortho, meta or para position with respect to the hydroxyl group; the ortho position is preferred. The R group can be in the ortho, meta or para position with respect to the hydroxyl group.

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Salicylic acids are typically prepared by the carboxylation, by the Kolbe-Schmitt process, of phenoxides, and in that case will generally be obtained (normally in a diluent) in admixture with uncarboxylated phenol. Salicylic acids may be non-sulfurized or sulfurized, and may be chemically modified and/or contain additional substituents.

Processes for sulfurizing an alkyl salicylic acid are well known to those skilled in the art, and are described in, for example, US 2007/0027057.

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The alkyl groups advantageously contain 5 to 100, preferably 9 to 30, especially 14 to 24, carbon atoms.

The term “over-based” is generally used to describe metal detergents in which the ratio of the number of equivalents of the metal moiety to the number of equivalents of the acid moiety is greater than one. The term ‘low-based’ is used to describe metal detergents in which the equivalent ratio of metal moiety to acid moiety is greater than 1, and up to about 2.

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By an “over-based calcium salt of surfactants” is meant an over-based detergent in which the metal cations of the oil-insoluble metal salt are essentially calcium cations. Small amounts of other cations may be present in the oil-insoluble metal salt, but typically at least 80, more typically at least 90, for example at least 95, mole % of the cations in the oil-insoluble metal salt, are calcium ions. Cations other than calcium may be derived, for example, from the use in the manufacture of the over-based detergent of a surfactant salt in which the cation is a metal other than calcium. Preferably, the metal salt of the surfactant is also calcium.

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Carbonated over-based metal detergents typically comprise amorphous

nanoparticles. Additionally, the art discloses nanoparticulate materials comprising carbonate in the crystalline calcite and vaterite forms.

The basicity of the detergents may be expressed as a total base number (TBN), referred to herein as base number (BN). A base number is the amount of acid needed to
5 neutralize all of the basicity of the over-based material. The BN may be measured using ASTM standard D2896 or an equivalent procedure. The test typically measures the change in electrical conductivity, and the results are expressed as mgKOH/g (the equivalent number of milligrams of KOH needed to neutralise 1 gram of a product). The detergent composition (and a detergent used in the detergent composition) as used in the present
10 invention may have a low BN (i.e. a BN of less than 100), a medium BN (i.e. a BN of 100 to 300) or a high BN (i.e. a BN of greater than 300, such as 300-450). The basicity may also be expressed as basicity index (BI), which is the molar ratio of total base to total soap in the over-based detergent.

The skilled person in the art may formulate a detergent composition to meet
15 lubricating composition Base Number requirements, whilst having a soap level meeting the performance requirements for the system, that is, the asphaltene handling performance.

Preferably, the detergent composition comprises one or more over-based calcium salicylate.

In embodiments of the invention, the detergent composition comprises a blend of two
20 or more detergents. The detergents may preferably be selected from a high BN/low soap detergent, a high BN/high soap detergent and a medium or low BN/high soap detergent, the soap levels being relative.

By formulating a detergent composition with detergents of a higher base number and relatively lower soap level, a lower treat rate of detergent composition may be
25 achieved for any given target Base Number (that is, a Base Number of a lubricating composition). Whilst this would normally lead to a lesser performance (e.g. not acceptable asphaltene handling), by forming a composition with a ZDDP of an embodiment of the present invention as defined above (preferably, a ZDDP with at least one ester derived from a primary alcohol), performance can be boosted to a desired and acceptable
30 asphaltene handling performance.

Preferably, a detergent composition is formulated to provide acceptable asphaltene handling in a lubricating composition when the lubricating composition comprises a base

oil as defined above, the detergent composition and a ZDDP with at least one ester derived from a primary alcohol) such that the lubricating composition has acceptable asphaltene handling according to the above-described asphaltene handling test method.

In the lubricating composition of the present invention, there is preferably provided a
5 detergent composition in a 40 BN equivalent amount of up to 14.5% w/w of the resulting lubricating composition. Preferably, the detergent composition is present in a 40 BN equivalent amount of up to 14% w/w of the resulting lubricating composition, more preferably up to 13.5%, still more preferably up to 13% and optionally up to 12.5%. Optionally, the detergent composition is present in a lubricating composition of the
10 invention in a 40 BN equivalent amount in the range of from 11% (e.g. from at least 11.5%) to 12.5% w/w of the lubricating composition.

As discussed above, the amount of detergent composition present in a trunk piston engine lubricating composition as described herein depends upon the Base Number (BN) or target Base Number of the lubricating composition. The lubricating composition
15 typically will be provided commercially at a BN in the range 20 to 55, having target BN of 20, 30, 40, 50 and 55. Most preferred lubricating compositions have a BN of 40 or lower.

Thus, in a 40BN lubricating composition in accordance with the present invention, there is a detergent composition present in an amount of up to 14.5% w/w of the lubricating composition, preferably up to 14% w/w of the resulting lubricating
20 composition, more preferably up to 13.5%, still more preferably up to 13% and optionally up to 12.5%. Optionally, the detergent composition is present in an amount in the range of from 11% (e.g. from at least 11.5%) to 12.5% w/w of the lubricating composition.

In a 30BN lubricating composition in accordance with the present invention, there is a detergent composition present in an amount of up to 10.9% w/w of the lubricating
25 composition, preferably up to 10.5% w/w of the resulting lubricating composition, more preferably up to 10.1%, still more preferably up to 9.75% and optionally up to 9.4%. Optionally, the detergent composition is present in an amount in the range of from 8.25% (e.g. from at least 8.6%) to 9.4% w/w of the lubricating composition.

In a 20 BN lubricating composition in accordance with the present invention, there is
30 a detergent composition present in an amount of up to 7.25% w/w of the lubricating composition, preferably up to 7% w/w of the resulting lubricating composition, more preferably up to 6.75%, still more preferably up to 6.5% and optionally up to 6.25%.

Optionally, the detergent composition is present in an amount in the range of from 5.5% (e.g. from at least 5.75%) to 6.25% w/w of the lubricating composition.

In a 50 BN lubricating composition in accordance with the present invention, there is a detergent composition present in an amount of up to 18.1% w/w of the lubricating composition, preferably up to 17.5% w/w of the resulting lubricating composition, more preferably up to 16.9%, still more preferably up to 16.25% and optionally up to 15.6%. Optionally, the detergent composition is present in an amount in the range of from 13.75% (e.g. from at least 14.4%) to 15.6% w/w of the lubricating composition.

In a 55 BN lubricating composition in accordance with the present invention, there is a detergent composition present in an amount of up to 19.9% w/w of the lubricating composition, preferably up to 19.25% w/w of the resulting lubricating composition, more preferably up to 18.6%, still more preferably up to 17.9% and optionally up to 17.2%. Optionally, the detergent composition is present in an amount in the range of from 15.1% (e.g. from at least 15.8%) to 17.2% w/w of the lubricating composition.

In an aspect of the invention, a method for the manufacture of a trunk piston engine lubricating composition comprising combining a base oil with an additive composition comprising an anti-wear additive comprising a zinc dialkyl dithiophosphate (ZDDP) and a detergent composition comprising one or more detergents. Preferably, the method comprises selecting a ZDDP which is effective in enhancing the asphaltene handling of a detergent composition used in the lubricating composition. Such a ZDDP may be a ZDDP having at least one ester derived from a primary alcohol and/or which enhances the asphaltene handling of a detergent composition in a lubricating composition as determined by the asphaltene handling test method mentioned above. The method preferably further comprises adding a detergent composition at a 40BN equivalent treat rate of up to 14.5% or preferred treat rates mentioned above and preferably formulating a detergent composition for meeting the target Base Number of the lubricating composition and having a soap level to achieve the performance requirement, being an acceptable asphaltene handling in according with the asphaltene handling test method described above, in the presence of the selected ZDDP and a detergent composition treat rate of up to 14.5%. The base oil may preferably be selected according the embodiments for base oil and base stocks described below.

The lubricating composition of the present invention comprises a base oil, which may be any suitable Group I base stock with an appropriate viscosity (in particular kinematic viscosity at 100°C) and suitable solubilising characteristics.

The base oil may more typically comprise a blend of two or more base stocks which together provide the desired performance, viscosity and solubilising (and cleansing) characteristics. Optionally, a base oil comprises a blend of a primary Group I base stock in an amount of more than 50% by weight (or a major part) and a secondary base stock, which is preferably also a Group I base stock, in an amount of less than 50% by weight (or a minor part).

By a Group I base stock, it is meant a Group I base stock as defined by the API (American Petroleum Institute) and more particularly contains less than 90% saturates and/or greater than 3% sulfur and has a viscosity index greater than or equal to 80 and less than 120 according to test methods ASTM D2007 (saturates), ASTM D2270 (viscosity index and ASTM D2622, 4294, 4927, 3120 (sulfur).

A base oil or a primary base stock as defined herein may be used, in accordance with aspects of the present invention, in a lubricating composition of an aspect of the invention, or to enhance the asphaltene handling of a lubricating composition or in combination with a ZDDP defined above for improving the handling of a lubricating composition.

The base oil preferably meets the requirements for viscosity of any SAE grade suitable for use in a trunk piston engine lubrication composition, preferably of SAE grade 30 or grade 40, more preferably SAE grade 40. The base oil of the invention preferably has a kinematic viscosity at 100°C (KV100) in the range 10.5 to 16 cSt, more preferably 11 to 15.5 cSt, still more preferably 11.5 to 15 cSt, more preferably still 12-14.5 cSt.

Preferably, the base oil (and/or the primary base stock) is characterised by a sulfur content of at least 5000 ppm, preferably at least 6000 ppm, still more preferably at least 7000 ppm, more preferably still at least 8000 ppm and optionally in the range 9000 to 12000 ppm.

Preferably, the base oil (and/or the primary base stock) is characterised by an aromatic component content of at least 4% by weight, more preferably at least 5% by weight and still more preferably at least 6% by weight.

Preferably, the base oil comprises one or a blend of base stocks comprising a primary Group I base stock having a sulfur content of at least 7000 ppm (preferably at least 8000

ppm, e.g. at least 10,000 ppm) and an aromatic component content of at least 5% (preferably at least 6%, more preferably at least 8% and optionally at least 10%).

Optionally, in the case of a blend, the base oil comprises the primary base stock in an amount of greater than 50% by weight of the base oil, preferably at least 60%, still more

5 preferably at least 70%, preferably at least 75% and in some embodiments in excess of 80% or even 90%. Preferably the primary base stock has a kinematic viscosity at 100°C of from 12 to 17 cSt, preferably 12.5 to 16.5 cSt, more preferably 13 to 16 cSt. In such
10 embodiments, a secondary base oil is provided, which is preferably a Group I base stock and which comprises a relatively higher or relatively lower viscosity (and in particular a KV100) whereby the viscosity of the base oil and thereby the lubricating composition can
be adjusted (to a target viscosity, e.g. of the SAE Grade 30 or 40). A secondary base stock may be any suitable base stock for blending with the primary base to stock to achieve a target KV100. For example, a secondary base stock may be a base stock having a KV100 of from
15 25 to 35, more preferably 28 to 33..

It is believed that a base oil (composed of a primary Group I base stock) of an embodiment defined above, having a sulfur content of at least 5000 ppm and an aromatic component content of at least 5% by weight provides an enhance asphaltene handling effect when used with a ZDDP anti-wear agent defined above and thus in combination can
20 allow a relatively reduced treat rate of the additive composition comprising the ZDDP and a detergent composition.

Preferably, this allows a 40BN equivalent amount of a lubricating composition of up to 14.5% , preferably up to 14%, more preferably up to 13.5% and still more preferably up to 13% to be used while achieving an acceptable asphaltene handling. Thus a more
25 efficient and cost effective lubricating composition is provided.

The lubricating composition according to this embodiment is capable of maintaining adequate asphaltene handling in use thereof in operation in an engine fuelled by heavy fuel oil.

In one preferred embodiment, the lubricating composition comprises a ZDDP
30 comprising at least one ester moiety derived from a primary alcohol (or a more preferred ZDDP as defined above) and at least 75% by weight of a base stock comprising a sulfur content of at least 6000 ppm, an aromatic component content of at least 5% and having a

kinematic viscosity at 100°C of from 12.5 to 17 cSt (or a more preferred base stock as defined above).

Preferably, according to this embodiment, the lubricating composition comprises an additive composition which comprises the ZDDP and a detergent composition, wherein
5 additive composition is present in a 40 BN equivalent amount of up to 14% (or a more preferred amount as defined above).

Asphaltene handling capability can be assessed by an asphaltene handling test method such as described above. In a particular embodiment, an asphaltene handling test method comprises a hot liquid process simulator (HLPS) test. According to this
10 embodiment, an HLPS system such as an Alcor HLPS 400 may be used. The method comprises providing a 250 ml sample in a reservoir in the Alcor HLPS 400 maintaining a pressure of 200 bar and at a reservoir temperature of 100°C and circulating the sample through a vertically orientated heated tube (e.g. a PAC 1018 steel heater tube available under product code AL91740, having a length of 60 mm and diameter of 3.2 mm) at a
15 circulation setting of 10 rpm to allow slow circulation through the system and with a tube temperature of 250°C. The test is conducted over a 2.5 hour period.

The sample comprises the lubricating oil to be tested doped with a 1% volume of heavy fuel oil (having 8.9% asphaltene content).

At the end of test period, the tube is treated to remove the doped sample and the
20 deposit thickness measured at 10 mm lengths of the tube to characterise the deposit thickness along its length using ellipsometry (e.g. using a Falex 430 Ellipsometer).

A maximum deposit thickness (determining by ellipsometry as mentioned above) of 300 nm or less is considered to represent an acceptable asphaltene handling performance. A maximum deposit thickness of up to 250 nm is considered to represent a preferred
25 asphaltene handling performance and a maximum deposit thickness of up to 200 nm considered to represent a more preferred asphaltene handling performance.

EXAMPLES

30 A control lubricating composition and a number of sample lubricating formulations were prepared to assess asphaltene handling according to an HLPS asphaltene handling test method as described above.

The control lubricating composition comprised a conventionally available additive composition comprising a ZDDP and a detergent composition comprising a combination of calcium salicylate detergents, the additive composition provided to a blend of Group I oil (600 SN and 2500 SN to meet SAE 40 requirements) at a treat rate of 15.9% for a 40 BN composition.

Sample lubricating compositions were prepared having one of two base oils. A first base oil (B1) made of a primary Group I base stock having a sulfur content of 12000 ppm and an aromatic component content of 8% by weight and having a KV100 of about 15 and blended with a secondary base stock having a KV100 of about 5 to provide a lubricating composition KV100 of 14. The primary Group I base stock was present in the base oil in an amount of 92%. A second base oil (B2) made of a Group I base stock blend of a first base stock having a KV100 of around 12 blended with a second base stock having a KV100 of around 31 in a ratio of 90% to 10%.

The base oil in each case was used in the samples in an amount of 87% by weight. In other words, the additive composition was provided at a treat rate of 13%. The samples were prepared with a detergent composition of calcium salicylates to provide a BN of 40.

A ZDDP was provided at a treat rate of 0.47 wt%.

The control and sample were subjected to the HLPS asphaltene test method mentioned above at 1% doping of heavy fuel oil and heated for 2.5 hours at up to 250°C.

The control and samples were then measured for maximum deposit thickness along the length of the tubes. Samples generating a maximum deposit thickness at any point along the length of the tube of greater than 300 nm were considered as not acceptable (designated 'N', also if signal indeterminable) in asphaltene handling, and those exhibiting 300 nm (designated 'Y') or less were considered acceptable, 250 nm or less preferred (designated 'Y*') and 200 nm or less more preferred (designated 'Y**').

The results are set out in Table 1.

Table 1

<u>Sample no</u>	<u>Base oil</u>	<u>ZDDP</u>	<u>Notes</u>	<u>Asphaltene handling</u>
C	B1	ZDDP present but not identified	16% treat rate	Y**
C*	B2	ZDDP present but not identified	16% treat rate	Y*
S1	B1	Isobutyl/pentyl	1y ester; C4-C5	Y*
S1*	B2	Isobutyl/pentyl	1y ester; C4-C5	Y
S2	B1	Dimethylbutyl / isopropyl	1y/2y mix; C3-C5	Y
S2*	B2	Dimethylbutyl / isopropyl	1y/2y mix; C3-C5	N
S3	B1	Dioctyl	1y, C8	Y**
S3*	B2	Dioctyl	1y, C8	Y*
S4	B1	Mixed 1y/2y	Mixed 1y/2y	N
S4*	B2	Mixed 1y/2y	Mixed 1y/2y	N
S5	B1	Octyl 1y/2y	Mixed 1y/2y	Y**
S5*	B2	Octyl 1y/2y	Mixed 1y/2y	N
S6	B1	2y dialkyl	2y	N
S6*	B2	2y dialkyl	2y	N
S7	B1	2y dialkyl	2y	N
S7*	B2	2y dialkyl	2y	N
S8	B1	1y alkyl	1y	Y**
S8*	B2	1y alkyl	1y	Y*
S9	B1	Sec-butyl / 1,3-diemthylbutyl	2y	N
S9*	B2	Sec-butyl / 1,3-diemthylbutyl	2y	N
S10	B1	Bis-2-ethylhexyl	1y	Y**
S10*	B2	Bis-2-ethylhexyl	1y	Y**

As can be seen from Table 1, those lubricating compositions identified as acceptable in asphaltene handling in the above assessment tended to be where the ZDDP comprised a primary ester, preferably all primary esters, was improved with short chain esters, e.g. C3 to C7 and was further enhanced by the use of base oil B1.

The invention has been described with reference to a preferred embodiment. However, it will be appreciated that variations and modifications can be effected by a person of ordinary skill in the art without departing from the scope of the invention.

CLAIMS

1. A trunk piston engine lubricating composition comprising:
a base oil of lubricating viscosity; and
5 an additive composition comprising an anti-wear additive comprising a zinc dialkyl dithiophosphate (ZDDP) and a detergent composition comprising one or more detergents, wherein the ZDDP comprises at least one ester moiety derived from a primary alcohol and wherein the additive composition is present in a 40 Base Number equivalent amount of up to 15% w/w of the lubricating composition.
10
2. A lubricating composition as claimed in claim 1, wherein the additive composition is present in a 40 BN equivalent amount of up to 14% w/w of the lubricating composition.
3. A lubricating composition as claimed in claim 1, wherein the additive composition is
15 in a 40BN equivalent amount of up to 13.5% w/w of the lubricating composition.
4. A lubricating composition as claimed in any one of claims 1 to 3, wherein the ZDDP comprises at least two ester moieties derived from a primary alcohol.
- 20 5. A lubricating composition as claimed in any one of the preceding claims, wherein each dialkyldithiophosphate moiety of the ZDDP comprises at least one ester moiety derived from a primary alcohol.
6. A lubricating composition as claimed in claim 5, wherein each ester moiety of the
25 ZDDP is derived from a primary alcohol.
7. A lubricating composition as claimed in any one of the preceding claims, wherein the ZDDP comprises at least one ester comprising a fully saturated straight chain alkyl group.
- 30 8. A lubricating composition as claimed in any one of the preceding claims, wherein each ester group of the ZDDP is derived from a C4 to C6 alcohol.

9. A lubricating composition as claimed in any one of the preceding claims, wherein the ZDDP comprises mixed isobutyl and pentyl esters.

10. A lubricating composition as claimed in any one of the preceding claims, wherein the ZDDP is provided with the additive composition in a lubricating oil composition treat rate equivalent of up to 0.75%.

11. A lubricating composition as claimed in claim 10, wherein the ZDDP is provided with the additive composition in a lubricating oil composition treat rate equivalent of up to 0.6%.

12. A lubricating composition as claimed in claim 11, wherein the ZDDP is provided with the additive composition in a lubricating oil composition treat rate equivalent of up to 0.55%.

13. A lubricating composition as claimed in any one of the preceding claims, wherein the detergent composition comprises one or more over-based calcium salicylate.

14. A lubricating composition as claimed in any one of the preceding claims, wherein the base oil comprises a major part of one or more Group I base stocks.

15. A lubricating composition as claimed in any one of the preceding claims, wherein the base oil comprises a sulfur content of at least 5000 ppm and an aromatic component content of at least 4% by weight.

16. A lubricating composition as claimed in claim 15, wherein the base oil comprises a sulfur content of at least 7000 ppm and an aromatic component content of at least 6% by weight.

17. A lubricating composition as claimed in any one of the preceding claims, wherein the base oil comprises a blend of a primary Group I base stock making up more than 50% of the base oil and a secondary base stock making up less than 50% of the base oil.

18. A lubricating composition as claimed in claim 17, wherein the primary Group I base stock has a sulfur content of at least 7000 ppm and an aromatic component of at least 5%.
- 5 19. A lubricating composition as claimed in claim 17 or claim 18, wherein the primary Group I base stock has a kinematic viscosity at 100°C of from 12.5 to 17 cSt.
20. A lubricating composition as claimed in any one of claims 17 to 19, wherein the primary Group I base stock makes up to 80% of the base oil.
- 10 21. A lubricating composition as claimed in any one of claims 17 to 20, wherein the secondary base stock is a Group I base stock of viscosity suitable for adjusting the viscosity of the base oil to a target viscosity.
- 15 22. A lubricating composition as claimed in any one of the preceding claims having additive treat rate of up to 14% whilst maintaining adequate asphaltene handling in use thereof in operation in an engine fuelled by heavy fuel oil.
- 20 23. A lubricating composition as claimed in any one of the preceding claims, whereby acceptable asphaltene handling is achieved.
24. Use of a zinc dialkyl dithiophosphate (ZDDP) to enhance asphaltene handling in a trunk piston engine lubricating composition, wherein the ZDDP comprises at least one ester moiety derived from a primary alcohol.
- 25 25. Use of a zinc dialkyl dithiophosphate (ZDDP) comprising at least one ester moiety derived from a primary alcohol to enable reduced detergent treat rate in a trunk piston engine lubricating composition.
- 30 26. A use as claimed in claim 24 or claim 25, wherein the ZDDP is as further defined in any one of claims 4 to 12.

27. A use as claimed in any one of claims 24 to 26 by including the ZDDP in an additive composition for a trunk piston engine lubricating composition.

5 28. A use as claimed in any one of claims 24 to 27 by selecting the ZDDP as an anti-wear additive for a trunk piston engine lubricating composition.

29. Use of detergent composition for a trunk piston engine lubricating composition in combination with a zinc dialkyl dithiophosphate (ZDDP) comprising at least one ester moiety derived from a primary alcohol for enhancing asphaltene handling in said
10 lubricating composition.

30. A base oil for use in a trunk piston engine lubricating composition with an additive composition, the base oil comprising in all or in a major part of a primary Group I base stock with a sulfur content of at least 6000 ppm and an aromatic component content of at
15 least 5% by weight.

31. A base oil as claimed in claim 30, which comprises a major part of the primary Group I base stock and which comprises a sulfur content of at least 5000 ppm and an aromatic component content of at least 4% by weight.
20

32. A base oil as claimed in claim 30 or claim 31, wherein the primary Group I base stock comprises a sulfur content of at least 7000 ppm and an aromatic component content of at least 6% by weight.

25 33. A base oil as claimed in any one of claims 30 to 32, wherein the primary Group I base stock has a kinematic viscosity at 100 °C of from 12.5 to 17 cSt.

34. A base oil as claimed in any one of claims 30 to 33, which comprises the primary Group I base stock in an amount of at least 60% by weight.

30

35. A base oil as claimed in claim 34, which comprise the primary Group I base stock in an amount of at least 75% by weight.

36. A base oil as claimed in claim 35, which comprises the primary Group I base stock in an amount of at least 80% by weight.

5 37. A base oil as claimed in any one of claims 30 to 36, which comprises a blend of a major part of the primary Group I base stock and a minor part of a secondary Group I base stock of lesser or greater kinematic viscosity at 100°C than the primary Group I base stock.

38. A method of operating a trunk piston marine engine comprising:

- 10 i) fuelling the engine with a heavy fuel oil; and
ii) lubricating the crankcase of the engine with a lubricating composition as defined in any one of claims 1 to 23.