

5 MARINE DIESEL CYLINDER LUBRICANT OIL COMPOSITIONS

Technical field

The present invention generally relates to lubricating oil compositions for marine engines that are designed for use with varying fuel sources.

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Background of the Invention

Diesel engines may generally be classified as low-speed, medium-speed, or high-speed engines, with the low-speed variety being used for the largest, deep draft marine vessels and certain other industrial applications such as power generation applications.

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Low-speed diesel engines are unique in size and method of operation. The engines themselves are massive, the output of these engines can reach as high as 100,000 brake horsepower with engine revolutions of 60 to about 200 revolutions per minute. A low-speed diesel engine operates on the two-stroke cycle and is typically a direct-coupled and direct-reversing engine of crosshead construction, with a diaphragm and one or more stuffing boxes separating the power cylinders from the crankcase to prevent combustion products from entering the crankcase and mixing with the crankcase oil. Marine two-stroke diesel cylinder lubricants must meet performance demands in order to comply with severe operating conditions required for more modern larger bore, two-stroke cross-head engines which are run at high outputs and severe loads and higher temperatures of the cylinder liner. The complete separation of the crankcase from the combustion zone has led persons skilled in the art to lubricate the combustion chamber and the crankcase with different lubricating oils.

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In large diesel engines of the crosshead type used in marine applications, the cylinders are lubricated on a total loss basis with the cylinder oil being injected separately on each cylinder, often into quills, by means of lubricators positioned around the cylinder liner. Oil is distributed to the lubricators by means of pumps, which are, in modern engine designs, often actuated to apply the oil directly onto the rings to reduce wastage of the oil.

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5 The typical use of sulfur-containing fuels for operation of these engines creates the need for lubricants with high detergency and neutralizing capability even though the oils are exposed to thermal and other stresses only for short periods of time. Residual fuels commonly used in these engines can contain significant quantities of sulfur, which, in the combustion process, combine with water to form sulfuric acid, the presence
10 of which leads to corrosive wear. In particular, in two-stroke engines for ships, areas around the cylinder liners and piston rings can be corroded and worn by the acid. Therefore, it is important for diesel engine lubricating oils to have the ability to resist such corrosion and wear.

 Accordingly, one of the primary functions of a marine diesel cylinder
15 lubricant is to neutralize sulfur-based acidic components of sulfur-containing fuel combusted. This neutralization has typically been accomplished by the inclusion in the marine diesel cylinder lubricant of basic species such as overbased metallic detergents. An oil's neutralization capacity is characterized by its basicity and is measured by its Total Base Number (TBN).

20 Recently, driven by health and environmental concerns, regulations currently exist in certain areas, mandating the use of low sulfur fuels for the operation of marine diesel engines. As a result, manufacturers are now designing marine diesel engines for use with a variety of fuels including gaseous fuels (compressed natural gas or liquefied natural gas, LNG), high quality distillate fuel with low sulfur and low asphaltene content
25 to poorer quality intermediate or heavy fuel such as marine residual fuel with generally high sulfur and higher asphaltene content. For gaseous or distillate fuel operation, the fuel contains no significant asphaltenes present in the fuels and contains much lower sulfur levels. When the more refined and lower sulfur fuel is combusted, less acid is formed in the combustion chamber. Therefore, the requirements for lubricants used for the operation
30 of engines using gaseous and low sulfur distillate fuels versus marine residual fuels can be very different.

 The TBN is a standard criterion making it possible to adjust the basicity of the cylinder oils to the sulfur content of the fuel used, in order to be able to neutralize all of the sulfur contained in the fuel. Thus, the higher the sulfur content of a fuel, the higher

5 the TBN a marine lubricant must have. This is why lubricating oils having TBNs varying from 5 to 150 mg KOH/g are found in the marine market. Typically in marine formulating, the basicity is provided by overbased detergents which are overbased using metallic carbonates. However, excess of overbased detergent present in the marine diesel cylinder lubricant creates a significant excess of basic sites and a risk of destabilization of the
10 micelles of unused overbased detergent, which contain insoluble metallic salts. This destabilization results in the formation of deposits of insoluble metallic salts in ash formation which plates out onto cylinder walls and other engine components. In the case of large multi-fuel marine engines the quality of exhaust gas is strongly dependent on the fuel used. In order to comply with severe exhaust gas regulations in coastal waters, among
15 other measures SCR catalytic converters are used in marine engines for the reduction of nitrous gases. Engines which contain excessive quantities of ash can result in ash deposit on the surface of the SCR catalyst and potentially block the access of exhaust gas to the catalyst surface preventing the catalyst from functioning.

Therefore, the optimization of the cylinder lubrication of a slow-speed two-
20 stroke engine then requires the selection of the lubricant with the TBN adapted to the fuel and to the operating conditions of the engine. This optimization has challenges as it reduces the flexibility of operation of the engine and requires a significant degree of technical expertise during ship operation in defining the conditions under which the switching from one type of lubricant to the other must be carried out. In order to simplify the operations,
25 it would therefore be desirable to have a single cylinder lubricant for two-stroke marine engines which can accommodate variations in fuel types and fuel sulfur levels.

The present invention relates to a marine diesel cylinder lubricant composition, having a source of ashless base, which can ensure good lubrication of the cylinder of a marine engine and can accommodate the constraints of variations in fuel type
30 and fuel sulfur levels. The present invention further relates to the use of a non-sulfur containing aromatic amine to deliver basicity to a lubricant while reducing and/or limiting detrimental effects.

5 SUMMARY OF THE INVENTION

In accordance with one embodiment of the present invention, there is provided a marine diesel cylinder lubricating oil composition which comprises (a) a major amount of an oil of lubricating viscosity, and (b) a non-sulfur containing aromatic amine having a total base number of from about 100-600 mg KOH/g; wherein the marine diesel
10 cylinder lubricating oil composition has a TBN of about 5 to about 100; and further wherein the TBN contribution of the non-sulfur containing aromatic amine to TBN of the lubricant composition is greater than about 30%.

In accordance with a second embodiment of the present invention, there is provided a marine diesel cylinder lubricant composition comprising (a) a major amount of
15 an oil of lubricating viscosity, (b) a non-sulfur containing aromatic amine having a total base number of from about 100-600 mg KOH/g, and (c) one or more polyalkenyl succinimide dispersants, wherein the polyalkenyl substituent is derived from a polyalkene group having a number average molecular weight of from about 1500 to about 3000; wherein the marine diesel cylinder lubricating oil composition has a TBN of about 5 to
20 about 100; and further wherein the TBN contribution of the non-sulfur containing aromatic amine to TBN of the lubricant composition is greater than about 30%.

The present invention is based on the surprising discovery that the lubricant composition of this invention advantageously improves oxidation, detergency and dispersancy performance of a marine diesel cylinder lubricating oil composition used in a
25 two-stroke crosshead marine diesel engine. Cylinder oils that have high oxidation stability not in bulk fluid but rather in thin film conditions will exhibit a smaller viscosity increase, and anti-scuffing performance. The invention further relates to the use of a non-sulfur containing aromatic amine, in an amount providing greater than about 30% of the TBN contribution of a marine diesel cylinder lubricant, the use being to reduce the rate of
30 depletion of basicity (loss of BN) as determined by ASTM D2896 and provide ashless TBN to the lubricant composition with relatively little impact on seal material which can be used in the engine lubricating systems or the lubricant handling systems.

5 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the present invention, non-sulfur containing aromatic amines are an alternative to ash containing over-based metallic detergents, as a source of BN for the lubricant. The present invention therefore relates to a marine diesel cylinder lubricating oil composition which comprises (a) a major amount of an oil of lubricating viscosity, and
 10 (b) a non-sulfur containing aromatic amine having a total base number of from about 100-600 mg KOH/g; wherein the marine diesel cylinder lubricating oil composition has a TBN of about 5 to about 100; and further wherein the TBN contribution of the non-sulfur containing aromatic amine to TBN of the lubricant composition is greater than about 30%.

In an embodiment of the present invention, the TBN provided by the non-sulfur containing aromatic amine represents at least 30%, or at least 35%, or at least 40%
 15 of the TBN of said marine diesel cylinder lubricant.

In an embodiment of the present invention, the marine diesel cylinder lubricant is used for lubrication of a marine 2-stroke engine operated using low sulfur fuel which comprises less than 1.0 wt. % sulfur, or less than 0.5 wt. % sulfur, or less than 0.1
 20 wt. % sulfur.

According to an embodiment of the present invention, the non-sulfur containing aromatic amine compounds are known as aminic antioxidants which are typically used at lower concentrations in marine diesel cylinder lubricants, since cylinders are lubricated on a total loss basis with the cylinder oil. Examples of aminic antioxidants which may be
 25 conveniently used include diarylamines, alkylated diphenylamines, phenyl- α -naphthylamines, phenyl- β -naphthylamines and alkylated α -naphthylamines.

In one particular embodiment, aminic antioxidants include straight-chain or branched dialkyldiphenylamines such as p,p'-dinonyl-diphenylamine; p,p'-dioctyl-diphenylamine; p,p'-di- α -methylbenzyl-diphenylamine; N-p-butylphenyl-N-p'-octylphenylamine; monoalkyldiphenylamines, such as mono-t-butyl-diphenylamine and mono-octyldiphenylamine; bis(dialkylphenyl) amines, such as di-(2,4-diethylphenyl)amine and di(2-ethyl-4-nonylphenyl)amine; alkylphenyl-1-naphthylamines, such as octylphenyl-1-naphthylamine and n-t-dodecylphenyl-1-

5 naphthylamine; 1-naphthylamine; aryl naphthylamines, such as phenyl-1-naphthylamine, phenyl-2-naphthylamine, N-hexylphenyl-2-naphthylamine and N-octylphenyl-2-naphthylamine; phenylenediamines, such as N,N'-diisopropyl-p-phenylenediamine and N,N'-diphenyl-p-phenylenediamine.

In one embodiment, the non-sulfur containing aromatic amine of the present
10 invention is a diarylamine. In one embodiment, the non-sulfur containing aromatic amine of the present invention is an alkylated diphenylamine. In one particular embodiment, the non-sulfur containing aromatic amine of the present invention is dialkyldiphenylamine.

The non-sulfur containing aromatic amine of the present invention will typically
15 have TBN, as measured according to standard ASTM D-2896, of about 100 to about 600 mg KOH/g, preferably about 100 to about 300 mg KOH/g, preferably about 100 to about 200 mg KOH/g, preferably about 120 to about 500 mg KOH/g, more preferably about 120 to about 300 mg KOH/g and more preferably about 120 to about 250 mg KOH/g on an actives, oil free, basis.

20 In a preferred embodiment, said one or more non-sulfur containing aromatic amine compounds are present in an amount of at least 1.0 wt. %, of at least 1.5 wt. %, of at least 2.0 wt. %, of at least 2.5 wt. %, of at least 3.0 wt. %, of at least 3.5 wt. %, of at least 4.0 wt. %, of at least 4.5 wt. %, of at least 5.0 wt. %, or about 1.0 to 25.0 wt. %, or about 1.0 to 20.0 wt. %, or about 1.0 to 18 wt. %, or about 1.0 to 15.0 wt. %, or about 1.0
25 to about 12.0 wt. %, or about 2.0 to 25.0 wt. %, or about 2.0 to 20.0 wt. %, or about 2.0 to 18 wt. %, or about 2.0 to 15.0 wt. %, or about 2.0 to about 12.0 wt. %, 3.0 to 25.0 wt. %, or about 3.0 to 20.0 wt. %, or about 3.0 to 18 wt. %, or about 3.0 to 15.0 wt. %, or about 3.0 to about 12.0 wt. %, on an actives basis, based on the total weight of the lubricating oil composition.

30 The lubricant composition of the present invention will include at least one non-metal containing additive. A non-metal containing additive may also be referred to as

- 5 “ashless”, since it will typically not produce any sulfated ash when subjected to the conditions of ASTM D 874.

The term “marine diesel cylinder lubricant” or “marine diesel cylinder lubricating oil” as used herein shall be understood to mean a lubricant used in the cylinder lubrication of a low speed or medium speed two-stroke crosshead marine diesel engine.

- 10 The marine diesel cylinder lubricant is fed to the cylinder walls through a number of injection points. Marine diesel cylinder lubricants are capable of providing a film between the cylinder liner and the piston rings and holding partially burned fuel residues in suspension, to thereby promote engine cleanliness and neutralize acids formed by, for example, the combustion of sulfur compounds in the fuel.

- 15 A “marine residual fuel” refers to a material combustible in large marine engines which has a carbon residue, as defined in International Organization for Standardization (ISO) 10370) of at least 2.5 wt. % (e.g., at least 5 wt. %, or at least 8 wt. %) (relative to the total weight of the fuel), a viscosity at 50°C of greater than 14.0 cSt, such as the marine residual fuels defined in the International Organization for
20 Standardization specification ISO 8217:2005, “Petroleum products - Fuels (class F) - Specifications of marine fuels,” the contents of which are incorporated herein in their entirety.

- A “residual fuel” refers to a fuel meeting the specification of a residual marine fuel as set forth in the ISO 8217:2010 international standard. A “low sulfur marine
25 fuel” refers to a fuel meeting the specification of a residual marine fuel as set forth in the ISO 8217:2010 specification that, in addition, has about 1.5 wt. % or less, or even about 0.5% wt.% or less, of sulfur, relative to the total weight of the fuel.

- A “distillate fuel” refers to a fuel meeting the specification of a distillate marine fuel as set forth in the ISO 8217:2010 international standard. A “low sulfur
30 distillate fuel” refers to a fuel meeting the specification of a distillate marine fuel set forth in the ISO 8217:2010 international standard that, in addition, has about 0.1 wt. % or less or even about 0.005 wt. % or less, of sulfur, relative to the total weight of the fuel.

5 Low sulfur gaseous fuel, such as liquid natural gas (LNG), predominantly consists of methane, with the balance made up of other hydrocarbons. Methane, which is the main component of LNG, is generally kept in a liquid state.

 The term “Total Base Number” or “TBN” refers to the level of alkalinity in an oil sample, which indicates the ability of the composition to continue to neutralize
10 corrosive acids, in accordance with ASTM Standard No. D2896 or equivalent procedure. The test measures the change in electrical conductivity, and the results are expressed as mg·KOH/g (the equivalent number of milligrams of KOH needed to neutralize 1 gram of a product). Therefore, a high TBN reflects strongly overbased products and, as a result, a higher base reserve for neutralizing acids.

15 The term “on an actives basis” refers to additive material that is not diluent oil or solvent.

 The marine diesel cylinder lubricating oil composition of the present invention can have any TBN that is suitable for use as a marine diesel cylinder lubricant. In some embodiments, the TBN of the marine diesel cylinder lubricating oil composition
20 of the present invention is less than about 100 mg·KOH/g. In other embodiments, the TBN of the marine diesel cylinder lubricating oil composition of the present disclosure can range from about 5 to about 100, or from about 5 to about 80, or from about 5 to about 70, or from about 5 to about 50, or from about 5 to about 40, or from about 5 to about 30, or from about 5 to 25, or from about 10 to about 100, or from about 10 to about 80, or from about
25 10 to about 70, or from about 10 to about 50, or from 10 to about 40, or from 10 to about 30, or from about 10 to about 25, or from about 15 to about 100, or from about 15 to about 80, or from about 15 to about 70, or from about 15 to about 50, or from about 15 to about 40, or from about 15 to about 30, or from about 20 to about 100, or from about 20 to about 80, or from about 20 to about 70, or from about 20 to about 40, or from about 20 to about
30 30 mg KOH/g.

 Due to low-operating speeds and high loads in marine engines, high viscosity oils (SAE 40, 50, and 60) are typically required. The marine diesel cylinder lubricating oil compositions of this invention can have a kinematic viscosity ranging from about 12.5 to about 26.1 cSt, or about 12.5 to about 21.9, or about 16.3 to about 21.9 cSt

5 at 100°C. The kinematic viscosity of the marine diesel cylinder lubricating oil compositions is measured by ASTM D445.

The marine diesel cylinder lubricating oil compositions of the present invention can be prepared by any method known to a person of ordinary skill in the art for making marine diesel cylinder lubricating oil compositions. The ingredients can be added
10 in any order and in any manner. Any suitable mixing or dispersing equipment may be used for blending, mixing or solubilizing the ingredients. The blending, mixing or solubilizing may be carried out with a blender, an agitator, a disperser, a mixer, a homogenizer, a mil, or any other mixing or dispersing equipment known in the art.

The marine diesel cylinder lubricant composition of the present invention
15 includes a major amount of an oil of lubricating viscosity. By “a major amount” it is meant that the marine diesel cylinder lubricant composition suitably includes at least about 40 wt. %, or at least about 50 wt. %, or at least about 60 wt. %, and particularly at least about 70 wt. %, of an oil of lubricating viscosity as described below, based on the total weight of the marine diesel cylinder lubricant oil composition.

20 The oil of lubricating viscosity may be any oil suitable for the lubrication of large diesel engines including, for example, cross-head engines. The oil of lubricating viscosity may be a base oil derived from natural lubricating oils, synthetic lubricating oils or mixtures thereof. Suitable base oil includes base stocks obtained by isomerization of synthetic wax and slack wax, as well as hydrocracked base stocks produced by
25 hydrocracking (rather than solvent extracting) the aromatic and polar components of the crude.

Suitable natural oils include mineral lubricating oils such as, for example, liquid petroleum oils, solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types, oils derived from coal or shale, animal oils, vegetable oils (e.g., rapeseed oils, castor oils and lard oil), and the like.
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Suitable synthetic lubricating oils include, but are not limited to, hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins, e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-

5 decenes), and the like and mixtures thereof; alkylbenzenes such as dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)-benzenes, and the like; polyphenyls such as biphenyls, terphenyls, alkylated polyphenyls, and the like; alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivative, analogs and homologs thereof and the like.

10 Other synthetic lubricating oils include, but are not limited to, oils made by polymerizing olefins of less than 5 carbon atoms such as ethylene, propylene, butylenes, isobutene, pentene, and mixtures thereof. Methods of preparing such polymer oils are well known to those skilled in the art. Additional synthetic hydrocarbon oils include liquid polymers of alpha olefins having the proper viscosity. Especially useful synthetic
15 hydrocarbon oils are the hydrogenated liquid oligomers of C₆ to C₁₂ alpha olefins such as, for example, 1-decene trimer.

Another class of synthetic lubricating oils include, but are not limited to, alkylene oxide polymers, i.e., homopolymers, interpolymers, and derivatives thereof where the terminal hydroxyl groups have been modified by, for example, esterification or
20 etherification. These oils are exemplified by the oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and phenyl ethers of these polyoxyalkylene polymers (e.g., methyl poly propylene glycol ether having an average molecular weight of 1,000, diphenyl ether of polyethylene glycol having a molecular weight of 500-1000, diethyl ether of polypropylene glycol having a molecular weight of 1,000-1,500, etc.) or
25 mono- and polycarboxylic esters thereof such as, for example, the acetic esters, mixed C₃-C₈ fatty acid esters, or the C₁₃ oxo acid diester of tetraethylene glycol.

Yet another class of synthetic lubricating oils include, but are not limited to, the esters of dicarboxylic acids e.g., phthalic acid, succinic acid, alkyl succinic acids, alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid,
30 adipic acid, linoleic acid dimer, malonic acids, alkyl malonic acids, alkenyl malonic acids, etc., with a variety of alcohols, e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol, etc. Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl)sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate,

5 didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid and the like.

 The oil of lubricating viscosity may be derived from unrefined, refined and rerefined oils, either natural, synthetic or mixtures of two or more of any of these of the type disclosed hereinabove. Unrefined oils are those obtained directly from a natural or
10 synthetic source (e.g., coal, shale, or tar sands bitumen) without further purification or treatment. Examples of unrefined oils include, but are not limited to, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from distillation or an ester oil obtained directly from an esterification process, each of which is then used without
15 further treatment. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. These purification techniques are known to those of skill in the art and include, for example, solvent extractions, secondary distillation, acid or base extraction, filtration, percolation, hydrotreating, dewaxing, etc. Rerefined oils are obtained by treating used oils in processes
20 similar to those used to obtain refined oils. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

 Lubricating oil base stocks derived from the hydroisomerization of wax may also be used, either alone or in combination with the aforesaid natural and/or synthetic
25 base stocks. Such wax isomerate oil is produced by the hydroisomerization of natural or synthetic waxes or mixtures thereof over a hydroisomerization catalyst. Natural waxes are typically the slack waxes recovered by the solvent dewaxing of mineral oils; synthetic waxes are typically the wax produced by the Fischer-Tropsch process.

 In one embodiment, the oil of lubricating viscosity is a Group I basestock.
30 In general, a Group I basestock for use herein can be any petroleum derived base oil of lubricating viscosity as defined in API Publication 1509, 16th Edition, Addendum I, Oct., 2009. API guidelines define a base stock as a lubricant component that may be manufactured using a variety of different processes. Group I base oils generally refer to a petroleum derived lubricating base oil having a saturates content of less than 90 wt. % (as

5 determined by ASTM D 2007) and/or a total sulfur content of greater than 300 ppm (as determined by ASTM D 2622, ASTM D 4294, ASTM D 4297 or ASTM D 3120) and has a viscosity index (VI) of greater than or equal to 80 and less than 120 (as determined by ASTM D 2270).

10 Group I base oils can comprise light overhead cuts and heavier side cuts from a vacuum distillation column and can also include, for example, Light Neutral, Medium Neutral, and Heavy Neutral base stocks. The petroleum derived base oil also may include residual stocks or bottoms fractions, such as, for example, brightstock. Brightstock is a high viscosity base oil which has been conventionally produced from residual stocks or bottoms and has been highly refined and dewaxed. Brightstock can have a kinematic
15 viscosity greater than about 180 cSt at 40°C, or even greater than about 250 cSt at 40°C, or even ranging from about 500 to about 1100 cSt at 40°C.

In one embodiment, the one or more basestocks can be a blend or mixture of two or more, three or more, or even four or more Group I basestocks having different molecular weights and viscosities, wherein the blend is processed in any suitable manner
20 to create a base oil having suitable properties (such as the viscosity and TBN values, discussed above) for use in a marine diesel engine. In one embodiment, the one or more basestocks comprises ExxonMobil CORE®100, ExxonMobil CORE®150, ExxonMobil CORE®600, ExxonMobil CORE®2500, or a combination or mixture thereof.

In another embodiment, the oil of lubricating viscosity is a Group II
25 basestock as defined in API Publication 1509, 16th Edition, Addendum I, Oct., 2009. A Group II basestock generally refer to a petroleum derived lubricating base oil having a total sulfur content equal to or less than 300 parts per million (ppm) (as determined by ASTM D 2622, ASTM D 4294, ASTM D 4927 or ASTM D 3120), a saturates content equal to or greater than 90 weight percent (as determined by ASTM D 2007), and a viscosity index
30 (VI) of between 80 and 120 (as determined by ASTM D 2270).

In another embodiment, the oil of lubricating viscosity is a Group III basestock as defined in API Publication 1509, 16th Edition, Addendum I, Oct., 2009. A Group III basestock generally has a total sulfur content less than or equal to 0.03 wt.% (as determined by ASTM D 2270), a saturates content of greater than or equal to 90 wt.% (as

5 determined by ASTM D 2007), and a viscosity index (VI) of greater than or equal to 120 (as determined by ASTM D 4294, ASTM D 4297 or ASTM D 3120). In one embodiment, the basestock is a Group III basestock, or a blend of two or more different Group III basestocks.

10 In general, Group III basestocks derived from petroleum oils are severely hydrotreated mineral oils. Hydrotreating involves reacting hydrogen with the basestock to be treated to remove heteroatoms from the hydrocarbon, reduce olefins and aromatics to alkanes and cycloparaffins respectively, and in very severe hydrotreating, open up naphthenic ring structures to non-cyclic normal and iso-alkanes ("paraffins"). In one embodiment, a Group III basestock has a paraffinic carbon content (% C_p) of at least about 70 %, as determined by test method ASTM D 3238-95 (2005), "Standard Test Method for Calculation of Carbon Distribution and Structural Group Analysis of Petroleum Oils by the n-d-M Method". In another embodiment, a Group III basestock has a paraffinic carbon content (% C_p) of at least about 72 %. In another embodiment, a Group III basestock has a paraffinic carbon content (% C_p) of at least about 75 %. In another embodiment, a Group 20 III basestock has a paraffinic carbon content (% C_p) of at least about 78 %. In another embodiment, a Group III basestock has a paraffinic carbon content (% C_p) of at least about 80 %. In another embodiment, a Group III basestock has a paraffinic carbon content (% C_p) of at least about 85 %.

25 In another embodiment, a Group III basestock has a naphthenic carbon content (% C_n) of no more than about 25 %, as determined by ASTM D 3238-95 (2005). In another embodiment, a Group III basestock has a naphthenic carbon content (% C_n) of no more than about 20 %. In another embodiment, a Group III basestock has a naphthenic carbon content (% C_n) of no more than about 15 %. In another embodiment, a Group III basestock has a naphthenic carbon content (% C_n) of no more than about 10 %.

30 In one embodiment, a Group III basestock for use herein is a Fischer-Tropsch derived base oil. The term "Fischer-Tropsch derived" means that the product, fraction, or feed originates from or is produced at some stage by a Fischer-Tropsch process. For example, a Fischer Tropsch base oil can be produced from a process in which the feed is a waxy feed recovered from a Fischer-Tropsch synthesis, see, e.g., U.S. Patent

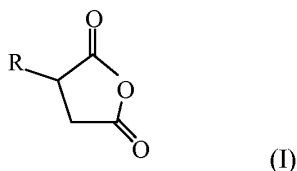
5 Application Publication Nos. 2004/0159582; 2005/0077208; 2005/0133407;
2005/0133409; 2005/0139513; 2005/0139514; 2005/0241990 each of which are
incorporated herein by reference. In general, the process involves a complete or partial
hydroisomerization dewaxing step, employing a dual-functional catalyst or a catalyst that
can isomerize paraffins selectively. Hydroisomerization dewaxing is achieved by
10 contacting the waxy feed with a hydroisomerization catalyst in an isomerization zone under
hydroisomerizing conditions.

In another embodiment, the oil of lubricating viscosity is a Group IV
basestock as defined in API Publication 1509, 16th Edition, Addendum I, Oct., 2009. A
Group IV basestock, or polyalphaolefin (PAO) are typically made by the oligomerization
15 of low molecular weight alpha-olefins, e.g., alpha-olefins containing at least 6 carbon
atoms. In one embodiment, the alpha-olefins are alpha-olefins containing 10 carbon atoms.
PAOs are mixtures of dimers, trimers, tetramers, etc., with the exact mixture depending
upon the viscosity of the final basestock desired. PAOs are typically hydrogenated after
oligomerization to remove any remaining unsaturation.

20 As stated above, the marine cylinder lubricants for use in marine diesel
engines typically have a kinematic viscosity in the range of 9.3 to 26.1 cSt at 100°C. In
order to formulate such a lubricant, a brightstock may be combined with a low viscosity
oil, e.g., an oil having a viscosity from 4 to 6 cSt at 100°C. However, supplies of
brightstock are dwindling and therefore brightstock cannot be relied upon to increase the
25 viscosity of marine cylinder lubricants to the desired ranges that manufacturers
recommend. One solution to this problem is to use thickeners such as polyisobutylene
(PIB) or viscosity index improvers such as olefin copolymers to thicken marine cylinder
lubricants. PIB is a commercially available material from several manufacturers. The PIB
is typically a viscous oil-miscible liquid, having a weight average molecular weight in the
30 range of about 1,000 to about 8,000, or from about 1,500 to about 6,000, and a viscosity in
the range of about 2,000 to about 5,000 or about 6,000 cSt (100°C). The amount of PIB
added to the marine cylinder lubricants will normally be from about 1 to about 20 wt. % of
the finished oil, or from about 2 to about 15 wt. % of the finished oil, or from about 4 to
about 12 wt. % of the finished oil.

5 In one embodiment, the marine diesel cylinder lubricating oil composition of the present invention further includes one or more polyalkenyl bis-succinimide dispersants wherein the polyalkenyl substituent is derived from a polyalkene group having a number average molecular weight of from about 1500 to about 3000. In general, a bis-succinimide is the completed reaction product from the reaction between a polyalkenyl-substituted succinic acid or anhydride and one or more polyamine reactants, and is intended to encompass compounds wherein the product may have amide, amidine, and/or salt linkages in addition to the imide linkage of the type that results from the reaction of a primary amino group and anhydride moiety. The bis-succinimide dispersants is prepared according to methods that are well known in the art, e.g., certain fundamental types of succinimides and related materials encompassed by the term of art "succinimide" are taught in, for example, U.S. Pat. Nos. 2,992,708; 3,018,291; 3,024,237; 3,100,673; 3,219,666; 3,172,892; and 3,272,746, the content of which are hereby incorporated by reference.

20 In one embodiment, the one or more polyalkenyl bis-succinimide dispersants can be obtained by reacting a polyalkenyl-substituted succinic anhydride of formula I:



wherein R is a polyalkenyl substituent is derived from a polyalkene group having a number average molecular weight of from about 1500 to about 3000 with a polyamine. In one embodiment, R is a polyalkenyl substituent is derived from a polyalkene group having a number average molecular weight of from about 1500 to about 2500. In one embodiment, R is a polybutenyl substituent derived from a polybutene having a number average molecular weight of from about 1500 to about 3000. In another embodiment, R is a polybutenyl substituent derived from a polybutene having a number average molecular weight of from about 1500 to about 2500.

5 The preparation of the polyalkenyl-substituted succinic anhydride by reaction with a polyolefin and maleic anhydride has been described in, e.g., U.S. Pat. Nos. 3,018,250 and 3,024,195. Such methods include the thermal reaction of the polyolefin with maleic anhydride and the reaction of a halogenated polyolefin, such as a chlorinated polyolefin, with maleic anhydride. Reduction of the polyalkenyl-substituted succinic
10 anhydride yields the corresponding alkyl derivative. Alternatively, the polyalkenyl substituted succinic anhydride may be prepared as described in, e.g., U.S. Pat. Nos. 4,388,471 and 4,450,281, the contents of which are incorporated by reference herein.

 The size of the polyalkenyl substituent is advantageously one that is derived from a polyalkene group having a number average molecular weight of about 1500 to about
15 3000. In one embodiment, the size of the polyalkenyl substituent is advantageously one that is derived from a polyalkene group having a number average molecular weight of about 1500 to 2500. In another embodiment, the size of the polyalkenyl substituent is advantageously one that is derived from a polyalkene group having a number average molecular weight of about 2300.

20 Polyalkene groups having a number average molecular weight of from about 1500 to about 3000 for reaction with a succinic anhydride such as maleic anhydride are polymers comprising a major amount of C₂ to C₅ mono-olefin, e.g., ethylene, propylene, butylene, isobutylene and pentene. The polymers can be homopolymers such as polyisobutylene as well as copolymers of 2 or more such olefins such as copolymers of:
25 ethylene and propylene, butylene, and isobutylene, etc. Other copolymers include those in which a minor amount of the copolymer monomers, e.g., 1 to 20 mole percent is a C₄ to C₈ nonconjugated diolefin, e.g., a copolymer of isobutylene and butadiene or a copolymer of ethylene, propylene and 1,4-hexadiene, etc.

 A particularly preferred class of polyalkene groups having a number
30 average molecular weight of from about 1500 to about 3000 include polybutenes, which are prepared by polymerization of one or more of 1-butene, 2-butene and isobutene. Especially desirable are polybutenes containing a substantial proportion of units derived from isobutene. The polybutene may contain minor amounts of butadiene which may or may not be incorporated in the polymer. Most often the isobutene units constitute about

5 80%, or at least about 90%, of the units in the polymer. These polybutenes are readily available commercial materials well known to those skilled in the art, e.g., those described in, for example, U.S. Pat. Nos. 3,215,707; 3,231,587; 3,515,669; 3,579,450, and 3,912,764, the contents of which are incorporated by reference herein.

Suitable polyamines for use in preparing the non-borated bis-succinimide
10 dispersants include polyalkylene polyamines. Such polyalkylene polyamines will typically contain about 2 to about 12 nitrogen atoms and about 2 to 24 carbon atoms. Particularly suitable polyalkylene polyamines are those having the formula: $H_2N-(R^1NH)_c-H$ wherein R^1 is a straight- or branched-chain alkylene group having 2 or 3 carbon atoms and c is 1 to 9. Representative examples of suitable polyalkylene polyamines include ethylenediamine,
15 diethylenetriamine, triethylenetetraamine, tetraethylenepentamine and mixtures thereof. Most preferably, the polyalkylene polyamine is tetraethylenepentamine.

Examples of suitable polyamines include tetraethylene pentamine, pentaethylene hexamine, and heavypolyamines (e.g. Dow HPA-X number average molecular weight of 275, available from Dow Chemical Company, Midland, Mich.). Such
20 amines encompass isomers, such as branched-chain polyamines, and the previously mentioned substituted polyamines, including hydrocarbyl-substituted polyamines. HPA-X heavy polyamine ("HPA-X") contains an average of approximately 6.5 amine nitrogen atoms per molecule. Such heavy polyamines generally afford excellent results.

Generally, the polyalkenyl-substituted succinic anhydride of formula I is
25 reacted with the polyamine at a temperature of about 130°C to about 220°C and preferably from about 145°C to about 175°C. The reaction can be carried out under an inert atmosphere, such as nitrogen or argon. The amount of anhydride of formula I employed in the reaction can range from about 30 to about 95 wt. % and preferably from about 40 to about 60 wt. %, based on the total weight of the reaction mixture.

30 Generally, the concentration of the one or more polyalkenyl bis-succinimide dispersants wherein the polyalkenyl substituent is derived from a polyalkene group having a number average molecular weight of from about 1500 to about 3000 in a marine diesel cylinder lubricating oil composition of the present invention is greater than about 0.25 wt. %, or greater than about 0.5 wt. %, or greater than about 1.0 wt. %, or greater than about

5 1.2 wt. %, or greater than about 1.5 wt. %, or greater than about 1.8 wt. %, or greater than
about 2.0 wt. %, or greater than about 2.5 wt. %, or greater than about 2.8 wt. %, on an
active basis, based on the total weight of the marine diesel cylinder lubricating oil
composition. In another embodiment, the amount of the one or more non-borated
polyalkenyl bis-succinimide dispersants wherein the polyalkenyl substituent is derived
10 from a polyalkene group having a number average molecular weight of from about 1500
to about 3000 present in a marine diesel cylinder lubricating oil composition of the present
invention can range from about 0.25 to 10 wt. %, or about 0.25 to 8.0 wt. %, or about 0.25
to 5.0 wt. %, or about 0.25 to 4.0 wt. %, or 0.25 to 3.0 wt. %, or about 0.5 to 10 wt. %, or
about 0.5 to 8.0 wt. %, or about 0.5 to 5.0 wt. %, or about 0.5 to 4.0 wt. %, or about 0.5 to
15 3.0 wt. %, or about 0.5 to 10 wt. %, or about 0.5 to 8.0 wt. %, or about 1.0 to 5.0 wt. %, or
about 1.0 to 4.0 wt. %, or about 1.0 to 3.0 wt. %, or about 1.5 to 10 wt. %, or about 1.5 to
8.0 wt. %, or about 1.5 to 5.0 wt. %, or about 1.5 to 4.0 wt. %, or about 1.5 to 3.0 wt. %, or
about 2.0 to 10 wt. %, or about 2.0 to 8.0 wt. %, or about 2.0 to 5.0 wt. % or about 2.0
to 4.0 wt. % on an active basis, based on the total weight of the marine diesel cylinder
20 lubricating oil composition.

In another embodiment, the marine diesel cylinder lubricating oil
composition of the present invention further includes a cyclic carbonate post-treated
polyalkenyl bis-succinimide dispersant. The polyalkenyl bis-succinimide dispersant of this
embodiment can be prepared as described above, i.e., the reaction of a polyalkenyl-
25 substituted succinic anhydride with a polyamine.

In this embodiment, the polyalkenyl-substituted succinic anhydride can be
a polyalkenyl-substituted succinic anhydride wherein the polyalkenyl substituent is derived
from a polyalkene having a number average molecular weight of from about 500 to about
5000. In another embodiment, the polyalkenyl-substituted succinic anhydride according
30 to the present embodiment can be a polyalkenyl-substituted succinic anhydride wherein the
polyalkenyl substituent is derived from a polyalkene having a number average molecular
weight of from about 700 to about 3000. In another embodiment, the polyalkenyl-
substituted succinic anhydride according to the present embodiment can be a polyalkenyl-
substituted succinic anhydride wherein the polyalkenyl substituent is derived from a

5 polyalkene having a number average molecular weight of from about 1000 to about 3000. In another embodiment, the polyalkenyl-substituted succinic anhydride according to the present embodiment can be a polyalkenyl-substituted succinic anhydride wherein the polyalkenyl substituent is derived from a polyalkene having a number average molecular weight of from about 1300 to about 2500. In another embodiment, the polyalkenyl-substituted succinic anhydride according to the present embodiment can be a polyalkenyl-substituted succinic anhydride wherein the polyalkenyl substituent is derived from a polyalkene having a number average molecular weight of from about 1000 to about 2500. In another embodiment, the polyalkenyl-substituted succinic anhydride according to the present embodiment can be a polyalkenyl-substituted succinic anhydride wherein the polyalkenyl substituent is derived from a polyalkene having a number average molecular weight of from about 1500 to about 2500. In another embodiment, the polyalkenyl-substituted succinic anhydride according to the present embodiment can be a polyalkenyl-substituted succinic anhydride wherein the polyalkenyl substituent is derived from a polyalkene having a number average molecular weight of from about 2000 to about 2500.

20 The polyalkenyl bis-succinimide dispersants of this embodiment is post-treated with a cyclic carbonate to form a cyclic carbonate post-treated polyalkenyl bis-succinimide dispersants. Suitable cyclic carbonates for use in this invention include, but are not limited to, 1,3-dioxolan-2-one (ethylene carbonate); 4-methyl-1,3-dioxolan-2-one (propylene carbonate); 4-hydroxymethyl-1,3-dioxolan-2-one; 4,5-dimethyl-1,3-dioxolan-2-one; 4-ethyl-1,3-dioxolan-2-one (butylene carbonate) and the like. Other suitable cyclic carbonates may be prepared from saccharides, such as sorbitol, glucose, fructose, galactose and the like and from vicinal diols prepared from C₁ to C₃₀ olefins by methods known in the art.

30 The polyalkenyl bis-succinimide dispersant can be post-treated with the cyclic carbonate according to methods well known in the art. For example, a cyclic carbonate post-treated polyalkenyl bis-succinimide dispersant can be prepared by a process comprising charging the bis-succinimide dispersant in a reactor, optionally under a nitrogen purge, and heating at a temperature of from about 80°C to about 170°C. Optionally, diluent oil may be charged under a nitrogen purge in the same reactor. A cyclic

5 carbonate is charged, optionally under a nitrogen purge, to the reactor. This mixture is heated under a nitrogen purge to a temperature in range from about 130°C to about 200°C. Optionally, a vacuum is applied to the mixture for about 0.5 to about 2.0 hours to remove any water formed in the reaction.

The marine diesel cylinder lubricating oil compositions of the
10 present invention may also contain conventional marine diesel cylinder lubricating oil composition additives, other than the foregoing dispersants, for imparting auxiliary functions to give a marine diesel cylinder lubricating oil composition in which these additives are dispersed or dissolved. For example, the marine diesel cylinder lubricating oil compositions can be blended with antioxidants, detergents, anti-wear agents, rust
15 inhibitors, dehazing agents, demulsifying agents, metal deactivating agents, friction modifiers, pour point depressants, antifoaming agents, co-solvents, corrosion-inhibitors, dyes, extreme pressure agents and the like and mixtures thereof. A variety of the additives are known and commercially available. These additives can be employed for the preparation of the marine diesel cylinder lubricating oil compositions of the invention by
20 the usual blending procedures.

In one embodiment, the marine diesel cylinder lubricating oil compositions of the present invention contain essentially no thickener (i.e., a viscosity index improver).

The marine diesel cylinder lubricating oil composition of the present invention can contain one or more antioxidants that can reduce or prevent the oxidation of
25 the base oil. Any antioxidant known by a person of ordinary skill in the art may be used in the lubricating oil composition. Non-limiting examples of suitable antioxidants include amine-based antioxidants (e.g., alkyl diphenylamines such as bis-nonylated diphenylamine, bis-octylated diphenylamine, and octylated/butylated diphenylamine, phenyl- α -naphthylamine, alkyl or arylalkyl substituted phenyl- α -naphthylamine, alkylated
30 p-phenylene diamines, tetramethyl-diaminodiphenylamine and the like), phenolic antioxidants (e.g., 2-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 2,4,6-tri-tert-butylphenol, 2,6-di-tert-butyl-p-cresol, 2,6-di-tert-butylphenol and the like), phosphorous-based antioxidants, zinc dithiophosphate, and combinations thereof.

5 The amount of the antioxidant may vary from about 0.01 wt. % to about 10 wt. %, from about 0.05 wt. % to about 5 wt. %, or from about 0.1 wt. % to about 3 wt. %, based on the total weight of the marine diesel cylinder lubricating oil composition.

 In one embodiment, the marine diesel cylinder lubricating oil compositions of the present invention contain essentially no ashless sulfur-containing compounds.

10 In one embodiment, the marine diesel cylinder lubricating oil compositions of the present invention contain essentially no phenolic antioxidant compounds.

 The marine diesel cylinder lubricating oil composition of the present invention can contain one or more detergents. Metal-containing or ash-forming detergents function as both detergents to reduce or remove deposits and as acid neutralizers or rust
15 inhibitors, thereby reducing wear and corrosion and extending engine life. Detergents generally comprise a polar head with a long hydrophobic tail. The polar head comprises a metal salt of an acidic organic compound. The salts may contain a substantially stoichiometric amount of the metal in which case they are usually described as normal or neutral salts. A large amount of a metal base may be incorporated by reacting excess metal
20 compound (e.g., an oxide or hydroxide) with an acidic gas (e.g., carbon dioxide).

 Detergents that may be used include oil-soluble neutral and overbased sulfonates, phenates, sulfurized phenates, thiophosphonates, salicylates, and naphthenates and other oil-soluble carboxylates of a metal, particularly the alkali or alkaline earth metals, e.g., barium, sodium, potassium, lithium, calcium, and magnesium. The most commonly
25 used metals are calcium and magnesium, which may both be present in detergents used in a lubricant, and mixtures of calcium and/or magnesium with sodium.

 Commercial products are generally referred to as neutral or overbased. Overbased metal detergents are generally produced by carbonating a mixture of hydrocarbons, detergent acid, for example: sulfonic acid, carboxylate etc., metal oxide or
30 hydroxides (for example calcium oxide or calcium hydroxide) and promoters such as xylene, methanol and water. For example, for preparing an overbased calcium sulfonate, in carbonation, the calcium oxide or hydroxide reacts with the gaseous carbon dioxide to form calcium carbonate. The sulfonic acid is neutralized with an excess of CaO or Ca(OH)₂, to form the sulfonate.

5 Overbased detergents may be low overbased, e.g., an overbased salt having a BN below 100. In one embodiment, the BN of a low overbased salt may be from about 5 to about 50. In another embodiment, the BN of a low overbased salt may be from about 10 to about 30. In yet another embodiment, the BN of a low overbased salt may be from about 15 to about 20.

10 Overbased detergents may be medium overbased, e.g., an overbased salt having a BN from about 100 to about 250. In one embodiment, the BN of a medium overbased salt may be from about 100 to about 200. In another embodiment, the BN of a medium overbased salt may be from about 125 to about 175.

Overbased detergents may be high overbased, e.g., an overbased salt having
15 a BN above 250. In one embodiment, the BN of a high overbased salt may be from about 250 to about 550.

In one embodiment, the detergent can be one or more alkali or alkaline earth metal salts of an alkyl-substituted hydroxyaromatic carboxylic acid. Suitable hydroxyaromatic compounds include mononuclear monohydroxy and polyhydroxy
20 aromatic hydrocarbons having 1 to 4, and preferably 1 to 3, hydroxyl groups. Suitable hydroxyaromatic compounds include phenol, catechol, resorcinol, hydroquinone, pyrogallol, cresol, and the like. The preferred hydroxyaromatic compound is phenol.

The alkyl substituted moiety of the alkali or alkaline earth metal salt of an alkyl-substituted hydroxyaromatic carboxylic acid is derived from an alpha olefin having
25 from about 10 to about 80 carbon atoms. The olefins employed may be linear, isomerized linear, branched or partially branched linear. The olefin may be a mixture of linear olefins, a mixture of isomerized linear olefins, a mixture of branched olefins, a mixture of partially branched linear or a mixture of any of the foregoing.

In one embodiment, the mixture of linear olefins that may be used is a
30 mixture of normal alpha olefins selected from olefins having from about 12 to about 30 carbon atoms per molecule. In one embodiment, the normal alpha olefins are isomerized using at least one of a solid or liquid catalyst.

In another embodiment, the olefins are a branched olefinic propylene oligomer or mixture thereof having from about 20 to about 80 carbon atoms, i.e., branched

5 chain olefins derived from the polymerization of propylene. The olefins may also be substituted with other functional groups, such as hydroxy groups, carboxylic acid groups, heteroatoms, and the like. In one embodiment, the branched olefinic propylene oligomer or mixtures thereof have from about 20 to about 60 carbon atoms. In one embodiment, the branched olefinic propylene oligomer or mixtures thereof have from about 20 to about 40
10 carbon atoms.

In one embodiment, at least about 75 mole% (e.g., at least about 80 mole%, at least about 85 mole%, at least about 90 mole%, at least about 95 mole%, or at least about 99 mole%) of the alkyl groups contained within the alkali or alkaline earth metal salt of an alkyl-substituted hydroxyaromatic carboxylic acid such as the alkyl groups of an alkaline
15 earth metal salt of an alkyl-substituted hydroxybenzoic acid detergent are a C₂₀ or higher. In another embodiment, the alkali or alkaline earth metal salt of an alkyl-substituted hydroxyaromatic carboxylic acid is an alkali or alkaline earth metal salt of an alkyl-substituted hydroxybenzoic acid that is derived from an alkyl-substituted hydroxybenzoic acid in which the alkyl groups are the residue of normal alpha-olefins containing at least
20 75 mole% C₂₀ or higher normal alpha-olefins.

In another embodiment, at least about 50 mole % (e.g., at least about 60 mole %, at least about 70 mole %, at least about 80 mole %, at least about 85 mole %, at least about 90 mole %, at least about 95 mole %, or at least about 99 mole %) of the alkyl groups contained within the alkali or alkaline earth metal salt of an alkyl-substituted
25 hydroxyaromatic carboxylic acid such as the alkyl groups of an alkali or alkaline earth metal salt of an alkyl-substituted hydroxybenzoic acid are about C₁₄ to about C₁₈.

The resulting alkali or alkaline earth metal salt of an alkyl-substituted hydroxyaromatic carboxylic acid will be a mixture of ortho and para isomers. In one embodiment, the product will contain about 1 to 99% ortho isomer and 99 to 1% para
30 isomer. In another embodiment, the product will contain about 5 to 70% ortho and 95 to 30% para isomer.

The alkali or alkaline earth metal salts of an alkyl-substituted hydroxyaromatic carboxylic acid can be neutral or overbased. Generally, an overbased alkali or alkaline earth metal salt of an alkyl-substituted hydroxyaromatic carboxylic acid

5 is one in which the TBN of the alkali or alkaline earth metal salts of an alkyl-substituted hydroxyaromatic carboxylic acid has been increased by a process such as the addition of a base source (e.g., lime) and an acidic overbasing compound (e.g., carbon dioxide).

Sulfonates may be prepared from sulfonic acids which are typically obtained by the sulfonation of alkyl substituted aromatic hydrocarbons such as those
10 obtained from the fractionation of petroleum or by the alkylation of aromatic hydrocarbons. Examples included those obtained by alkylating benzene, toluene, xylene, naphthalene, diphenyl or their halogen derivatives. The alkylation may be carried out in the presence of a catalyst with alkylating agents having from about 3 to more than 70 carbon atoms. The alkaryl sulfonates usually contain from about 9 to about 80 or more carbon atoms,
15 preferably from about 16 to about 60 carbon atoms per alkyl substituted aromatic moiety.

The oil soluble sulfonates or alkaryl sulfonic acids may be neutralized with oxides, hydroxides, alkoxides, carbonates, carboxylate, sulfides, hydrosulfides, nitrates, borates and ethers of the metal. The amount of metal compound is chosen having regard to the desired TBN of the final product but typically ranges from about 100 to about 220
20 wt. % (preferably at least about 125 wt. %) of that stoichiometrically required.

In one embodiment, high overbased sulfonate detergents delivers no more than 50 percent of the TBN of the overall composition. In other embodiments, the high overbased sulfonate detergents delivers no more than 40 percent, 30 percent, 25 percent, 10 percent or 5 percent of the TBN of the overall composition. In still other embodiments the
25 compositions of the present invention are substantially free of high overbased sulfonate detergents such that high overbased sulfonate detergents deliver no more than 0.5 percent of the TBN of the overall composition, or even 0 percent of the of the TBN of the overall composition.

Metal salts of phenols and sulfurized phenols, which are sulfurized phenate
30 detergents, are prepared by reaction with an appropriate metal compound such as an oxide or hydroxide and neutral or overbased products may be obtained by methods well known in the art. Sulfurized phenols may be prepared by reacting a phenol with sulfur or a sulfur containing compound such as hydrogen sulfide, sulfur monohalide or sulfur dihalide, to

5 form products which are generally mixtures of compounds in which 2 or more phenols are bridged by sulfur containing bridges.

Additional details regarding the general preparation of sulfurized phenates can be found in, for example, U.S. Pat. Nos. 2,680,096; 3,178,368 and 3,801,507, the contents of which are incorporated herein by reference.

10 Considering now in detail, the reactants and reagents used in the present process, first all allotropic forms of sulfur can be used. The sulfur can be employed either as molten sulfur or as a solid (e.g., powder or particulate) or as a solid suspension in a compatible hydrocarbon liquid.

It is desirable to use calcium hydroxide as the calcium base because of its
15 handling convenience versus, for example, calcium oxide, and also because it affords excellent results. Other calcium bases can also be used, for example, calcium alkoxides.

Suitable alkylphenols which can be used are those wherein the alkyl substituents contain a sufficient number of carbon atoms to render the resulting overbased sulfurized calcium alkylphenate composition oil-soluble. Oil solubility may be provided
20 by a single long chain alkyl substitute or by a combination of alkyl substituents. Typically, the alkylphenol used in the present process will be a mixture of different alkylphenols, e.g., C₂₀ to C₂₄ alkylphenol. Where phenate products having a TBN of 275 or less are desired, it is economically advantageous to use 100% polypropenyl substituted phenol because of its commercial availability and generally lower costs. Where higher TBN phenate products
25 are desired, about 25 to about 100 mole percent of the alkylphenol can have straight-chain alkyl substituent of from about 15 to about 35 carbon atoms and from about 75 to about 0 mole percent in which the alkyl group is polypropenyl of from 9 to 18 carbon atoms. In one embodiment, about 35 to about 100 mole percent of the alkylphenol, the alkyl group will be a straight-chain alkyl of about 15 to about 35 carbon atoms and about from about
30 65 to 0 mole percent of the alkylphenol, the alkyl group will be polypropenyl of from about 9 to about 18 carbon atoms. The use of an increasing amount of predominantly straight chain alkylphenols results in high TBN products generally characterized by lower viscosities. On the other hand, while polypropenylphenols are generally more economical than predominantly straight chain alkylphenols, the use of greater than about 75 mole

5 percent polypropenylphenol in the preparation of calcium overbased sulfurized alkylphenate compositions generally results in products of undesirably high viscosities. However, use of a mixture of from about 75 mole percent or less of polypropenylphenol of from about 9 to about 18 carbon atoms and from about 25 mole percent or more of predominantly straight chain alkylphenol of from about 15 to about 35 carbon atoms allows
10 for more economical products of acceptable viscosities. In one embodiment, suitable alkyl phenolic compounds comprise distilled cashew nut shell liquid or hydrogenated distilled cashew nut shell liquid. Distilled CNSL is a mixture of biodegradable meta-hydrocarbyl substituted phenols, where the hydrocarbyl group is linear and unsaturated, including cardanol. Catalytic hydrogenation of distilled CNSL gives rise to a mixture of meta-
15 hydrocarbyl substituted phenols predominantly rich in 3-pentadecylphenol.

The alkylphenols can be para-alkylphenols, meta-alkylphenols or ortho alkylphenols. Since it is believed that p-alkylphenols facilitate the preparation of highly overbased calcium sulfurized alkylphenate where overbased products are desired, the alkylphenol is preferably predominantly a para alkylphenol with no more than about 45
20 mole percent of the alkylphenol being ortho alkylphenols; and more preferably no more than about 35 mole percent of the alkylphenol is ortho alkylphenol. Alkyl-hydroxy toluenes or xylenes, and other alkyl phenols having one or more alkyl substituents in addition to at least one long chained alkyl substituent can also be used. In the case of distilled cashew nut shell liquid, the catalytic hydrogenation of distilled CNSL gives rise to a mixture of
25 meta-hydrocarbyl substituted phenols.

In general, the selection of alkylphenols can be based on the properties desired for the marine diesel engine lubricating oil compositions, notably TBN, and oil solubility. For example, in the case of alkylphenate having substantially straight chain alkyl substituents, the viscosity of the alkylphenate composition can be influenced by the
30 position of an attachment on alkyl chain to the phenyl ring, e.g., end attachment versus middle attachment. Additional information regarding this and the selection and preparation of suitable alkylphenols can be found, for example, in U.S. Pat. Nos. 5,024,773, 5,320,763; 5,318,710; and 5,320,762, each of which are incorporated herein by reference.

5 Generally, the amount of the detergent can be from about 0.001 wt. % to about 50 wt. %, or from about 0.05 wt. % to about 25 wt. %, or from about 0.1 wt. % to about 20 wt. %, or from about 0.01 to 15 wt. % based on the total weight of the marine diesel cylinder lubricating oil composition.

10 The marine diesel cylinder lubricating oil composition of the present invention can contain one or more friction modifiers that can lower the friction between moving parts. Any friction modifier known by a person of ordinary skill in the art may be used in the marine diesel cylinder lubricating oil composition. Non-limiting examples of suitable friction modifiers include fatty carboxylic acids; derivatives (e.g., alcohol, esters, borated esters, amides, metal salts and the like) of fatty carboxylic acid; mono-, di- or tri-alkyl substituted phosphoric acids or phosphonic acids; derivatives (e.g., esters, amides, metal salts and the like) of mono-, di- or tri-alkyl substituted phosphoric acids or phosphonic acids; mono-, di- or tri-alkyl substituted amines; mono- or di-alkyl substituted amides and combinations thereof. In some embodiments examples of friction modifiers include, but are not limited to, alkoxylated fatty amines; borated fatty epoxides; fatty phosphites, fatty epoxides, fatty amines, borated alkoxylated fatty amines, metal salts of fatty acids, fatty acid amides, glycerol esters, borated glycerol esters; and fatty imidazolines as disclosed in U.S. Patent No. 6,372,696, the contents of which are incorporated by reference herein; friction modifiers obtained from a reaction product of a C₄ to C₇₅, or a C₆ to C₂₄, or a C₆ to C₂₀, fatty acid ester and a nitrogen-containing compound selected from the group consisting of ammonia, and an alkanolamine and the like and mixtures thereof.

25 The marine diesel cylinder lubricating oil composition of the present invention can contain one or more anti-wear agents that can reduce friction and excessive wear. Any anti-wear agent known by a person of ordinary skill in the art may be used in the lubricating oil composition. Non-limiting examples of suitable anti-wear agents include zinc dithiophosphate, metal (e.g., Pb, Sb, Mo and the like) salts of dithiophosphates, metal (e.g., Zn, Pb, Sb, Mo and the like) salts of dithiocarbamates, metal (e.g., Zn, Pb, Sb and the like) salts of fatty acids, boron compounds, phosphate esters, phosphite esters, amine salts of phosphoric acid esters or thiophosphoric acid esters, reaction products of dicyclopentadiene and thiophosphoric acids and combinations thereof.

5 In certain embodiments, the anti-wear agent is or comprises a dihydrocarbyl dithiophosphate metal salt, such as zinc dialkyl dithiophosphate compounds. The metal of the dihydrocarbyl dithiophosphate metal salt may be an alkali or alkaline earth metal, or aluminum, lead, tin, molybdenum, manganese, nickel or copper. In some embodiments, the metal is zinc. In other embodiments, the alkyl group of the dihydrocarbyl
10 dithiophosphate metal salt has from about 3 to about 22 carbon atoms, from about 3 to about 18 carbon atoms, from about 3 to about 12 carbon atoms, or from about 3 to about 8 carbon atoms. In further embodiments, the alkyl group is linear or branched.

 The amount of the dihydrocarbyl dithiophosphate metal salt including the zinc dialkyl dithiophosphate salts in the lubricating oil composition disclosed herein is
15 measured by its phosphorus content. In some embodiments, the phosphorus content of the lubricating oil composition disclosed herein is from about 0.01 wt. % to about 0.14 wt., based on the total weight of the lubricating oil composition.

 The marine diesel cylinder lubricating oil composition of the present invention can contain one or more foam inhibitors or anti-foam inhibitors that can break
20 up foams in oils. Any foam inhibitor or anti-foam known by a person of ordinary skill in the art may be used in the marine diesel cylinder lubricating oil composition. Non-limiting examples of suitable foam inhibitors or anti-foam inhibitors include silicone oils or polydimethylsiloxanes, fluorosilicones, alkoxyated aliphatic acids, polyethers (e.g., polyethylene glycols), branched polyvinyl ethers, alkyl acrylate polymers, alkyl
25 methacrylate polymers, polyalkoxyamines and combinations thereof.

 The marine diesel cylinder lubricating oil composition of the present invention can contain one or more pour point depressants that can lower the pour point of the marine diesel cylinder lubricating oil composition. Any pour point depressant known
30 by a person of ordinary skill in the art may be used in the marine diesel cylinder lubricating oil composition. Non-limiting examples of suitable pour point depressants include polymethacrylates, alkyl acrylate polymers, alkyl methacrylate polymers, di(tetra-paraffin phenol)phthalate, condensates of tetra-paraffin phenol, condensates of a chlorinated paraffin with naphthalene and combinations thereof. In some embodiments, the pour point

5 depressant comprises an ethylene-vinyl acetate copolymer, a condensate of chlorinated paraffin and phenol, polyalkyl styrene or the like.

In another embodiment, the marine diesel cylinder lubricating oil composition of the present invention can contain one or more demulsifiers that can promote oil-water separation in lubricating oil compositions that are exposed to water or steam.

10 Any demulsifier known by a person of ordinary skill in the art may be used in the marine diesel cylinder lubricating oil composition. Non-limiting examples of suitable demulsifiers include anionic surfactants (e.g., alkyl-naphthalene sulfonates, alkyl benzene sulfonates and the like), nonionic alkoxylated alkyl phenol resins, polymers of alkylene oxides (e.g., polyethylene oxide, polypropylene oxide, block copolymers of ethylene oxide, propylene

15 oxide and the like), esters of oil soluble acids, polyoxyethylene sorbitan ester and combinations thereof.

The marine diesel cylinder lubricating oil composition of the present invention can contain one or more corrosion inhibitors that can reduce corrosion. Any corrosion inhibitor known by a person of ordinary skill in the art may be used in the marine

20 diesel cylinder lubricating oil composition. Non-limiting examples of suitable corrosion inhibitor include half esters or amides of dodecylsuccinic acid, phosphate esters, thiophosphates, alkyl imidazolines, sarcosines and combinations thereof.

The marine diesel cylinder lubricating oil composition of the present invention can contain one or more extreme pressure (EP) agents that can prevent sliding

25 metal surfaces from seizing under conditions of extreme pressure. Any extreme pressure agent known by a person of ordinary skill in the art may be used in the marine diesel cylinder lubricating oil composition. Generally, the extreme pressure agent is a compound that can combine chemically with a metal to form a surface film that prevents the welding of asperities in opposing metal surfaces under high loads. Non-limiting examples of

30 suitable extreme pressure agents include sulfurized animal or vegetable fats or oils, sulfurized animal or vegetable fatty acid esters, fully or partially esterified esters of trivalent or pentavalent acids of phosphorus, sulfurized olefins, dihydrocarbyl polysulfides, sulfurized Diels-Alder adducts, sulfurized dicyclopentadiene, sulfurized or co-sulfurized mixtures of fatty acid esters and monounsaturated olefins, co-sulfurized blends of fatty

5 acid, fatty acid ester and alpha-olefin, functionally-substituted dihydrocarbyl polysulfides, thia-aldehydes, thia-ketones, epithio compounds, sulfur-containing acetal derivatives, co-sulfurized blends of terpene and acyclic olefins, and polysulfide olefin products, amine salts of phosphoric acid esters or thiophosphoric acid esters and combinations thereof.

The marine diesel cylinder lubricating oil composition of the present
10 invention can contain one or more rust inhibitors that can inhibit the corrosion of ferrous metal surfaces. Any rust inhibitor known by a person of ordinary skill in the art may be used in the marine diesel cylinder lubricating oil composition. Non-limiting examples of suitable rust inhibitors include nonionic polyoxyalkylene agents, e.g., polyoxyethylene lauryl ether, polyoxyethylene higher alcohol ether, polyoxyethylene nonylphenyl ether,
15 polyoxyethylene octylphenyl ether, polyoxyethylene octyl stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene sorbitol monostearate, polyoxyethylene sorbitol monooleate, and polyethylene glycol monooleate; stearic acid and other fatty acids; dicarboxylic acids; metal soaps; fatty acid amine salts; metal salts of heavy sulfonic acid; partial carboxylic acid ester of polyhydric alcohol; phosphoric esters; (short-chain) alkenyl succinic acids;
20 partial esters thereof and nitrogen-containing derivatives thereof; synthetic alkarylsulfonates, e.g., metal dinonylnaphthalene sulfonates; and the like and mixtures thereof.

The marine diesel cylinder lubricating oil composition of the present invention can contain one or more multifunctional additives. Non-limiting examples of
25 suitable multifunctional additives include sulfurized oxymolybdenum dithiocarbamate, sulfurized oxymolybdenum organophosphorodithioate, oxymolybdenum monoglyceride, oxymolybdenum diethylate amide, amine-molybdenum complex compound, and sulfur-containing molybdenum complex compound.

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Examples

The following examples are intended for illustrative purposes only and do not limit in any way the scope of the present disclosure.

DSC Oxidation Test

10 The DSC oxidation test is used to evaluate thin film oxidation stability of test oils, in accordance with ASTM D-6186. Heat flow to and from test oil in a sample cup is compared to a reference cup during the test. The Oxidation Onset Temperature is the temperature at which the oxidation of the test oil starts. The Oxidation Induction Time is the time at which the oxidation of the test oil starts. A higher oxidation induction time
15 means better performance. The oxidation reaction results in an exothermic reaction which is clearly shown by the heat flow. The Oxidation Induction Time is calculated to evaluate the thin film oxidation stability of the test oil.

Example 1 and Comparative Example A

Example 1 and Comparative Example A were formulated to 25 BN, SAE
20 50 viscosity grade fully formulated marine cylinder lubricating oil compositions comprising majority amount of Esso 600N Group I base oil, Esso 2500 brightstock, a non-sulfur containing aromatic amine, foam inhibitor and additional additives as indicated in Table 1. The non-sulfur containing aromatic amine used in the examples was a nonyl substituted diphenylamine. This additive contained 3.5 wt. % Nitrogen, had
25 a TBN of about 135 mgKOH/g and no diluent oil. The test oils were evaluated using the DSC Oxidation Test. The results are set forth in Table 1 below.

30

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Table 1.

	Example 1	Comparative Example A
Sulfonate ¹ , mass%	-	2.4
Other detergent ² , mass%	9.4	9.4
Nonyl substituted diphenylamine, mass %	8.0	0.3
Succinimide Dispersant ³ , mass %	0.3	0.3
Succinimide Dispersant ⁴ , mass %	5.0	5.0
BN, mgKOH/g	25.0	25.0
DSC, min	36.3	31.8

^{1.} Oil concentrate of a high overbased calcium sulfonate having a TBN of 420 mg KOH/g

^{2.} Combination of an oil concentrate of a medium overbased calcium salicylate having a TBN of 150 mg KOH/g and an oil concentrate of a medium overbased sulfurized calcium phenate detergent having TBN of 116 mg KOH/g

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^{3.} Oil concentrate of polyalkenyl bissuccinimide dispersant derived from a polyalkene group having M_n of about 1000

^{4.} Oil concentrate of polyalkenyl bissuccinimide dispersant derived from a polyalkene group having M_n of about 2300 and post-treated with ethylene carbonate

As is evident from the results illustrated in Table 1, the marine cylinder lubricating oil composition of Example 1 wherein the TBN contribution of the non-sulfur containing aromatic amine to TBN of the lubricant composition is greater than about 30%, exhibited surprisingly better thin film oxidation stability of the test oil, as is evident by the overall higher oxidation induction time, relative to Comparative Example A containing a higher BN contribution from conventional high overbased sulfonate detergent. Cylinder oils that have high oxidation stability not in bulk fluid but rather in thin film conditions will exhibit a smaller viscosity increase, a high spreadability and greater anti-scuffing performance.