

MARINE DIESEL LUBRICANT OIL COMPOSITIONS

Technical field

The present invention generally relates to lubricating oil compositions for marine diesel internal combustion engines.

Background of the Invention

Marine diesel internal combustion 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.

Low-speed diesel engines are unique in size and method of operation. These engines are quite large and typically operate in the range of about 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 engines which are run at high outputs, 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, a cylinder

lubricant and system oil respectively, due to the unique requirements of each type of lubricant.

In two-stroke crosshead engines, the cylinders are lubricated on a total loss basis with the cylinder oil being injected separately on each cylinder, by means of lubricators positioned around the cylinder liner. Cylinder lubricant is not recirculated and is combusted along with the fuel. The cylinder lubricant needs to provide a strong film between the cylinder liner and the piston rings for sufficient lubrication of the cylinder walls to prevent scuffing, be thermally stable in order that the lubricant does not form deposits on the hot surfaces of the piston and the piston rings, and be able to neutralize sulfur-based acidic products of combustion. This neutralization has typically been accomplished by the inclusion of basic species such as metallic detergents. Unfortunately, the basicity of the marine cylinder lubricant can be diminished by oxidation of the marine cylinder lubricant (caused by the thermal and oxidative stress the lubricant undergoes in the engine), thus decreasing the lubricant's neutralization ability. The oxidation can be accelerated if the marine cylinder lubricants contain oxidation catalysts such as wear metals that are generally known to be present in the lubricant during engine operation. In order to prevent the metal catalyzed oxidation and polymerization of lubricating oils, it would be desirable to find a way to complex or sequester the metal ions and prevent the metal ions from acting as oxidation and polymerization catalysts.

The system oil lubricates the crankshaft and the crosshead of a two-stroke engine. It lubricates the main bearings, the crosshead bearings, gears and the camshaft and it cools the piston undercrown and protects the crankcase against corrosion. A

system oil needs to be able to prevent corrosion of metal in the bearing shells and to prevent rust in the crankcase when in the presence of contaminated water. The system oil also needs to provide adequate hydrodynamic lubrication of the bearings and have an anti-wear system sufficient to provide wear protection to the bearings and gears under extreme pressure conditions. In contrast to a cylinder lubricant, system oil is not exposed to the combustion chamber where fuels are being combusted and is formulated to last as long as possible to maximize the lifetime of the oil. Therefore, the primary performance characteristics of system oils are related to wear protection, oxidative stability, viscosity increase control and deposit performance.

Medium-speed engines, typically operate in the range of about 250 to about 1100 rpm and operate on the four-stroke cycle. These engines are typically of the trunk piston design. In trunk piston engines, a single lubricating oil is employed for lubrication of all areas of the engine, as opposed to the crosshead engines. A trunk piston engine oil therefore has unique requirements. Key performance parameters for operating trunk piston engines include: deposit control of the piston cooling gallery and piston ring pack, oxidation and viscosity increase control, and sludge control. For marine residual fuels operation, these performance parameters are almost exclusively driven by asphaltenes contamination from marine residual fuels.

Similar to cylinder lubricants, the system and trunk piston engine oils undergo oxidation in the presence of metal ions. Therefore, a prevention of such type of oxidation is needed by either sequestering or complexing metal ions.

Recent health and environmental concerns, have led to regulations which 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 non-residual gaseous fuels (e.g., compressed or liquefied natural gas) and high quality distillate fuel, to poorer quality intermediate or heavy fuel such as marine residual fuel with generally higher sulfur and higher asphaltene content. For non-residual fuel operation, the fuel contains no significant asphaltenes present in the fuels and contains much lower sulfur levels. When the lower sulfur fuel is combusted, less acid is formed in the combustion chamber. The requirements for lubricants used for the operation of engines using low sulfur gaseous and distillate fuels versus marine residual fuels are very different. For instance, piston deposit control in marine engines running on low sulfur fuel is especially challenging as it has been found that even additions of high amounts of high soap containing detergents has not lead to the level of desired piston deposit control. In addition, basicity of a lubricant can be diminished by oxidation of the marine cylinder lubricant. A decrease in the lubricant's neutralization ability due to oxidation can be especially problematic for marine lubricants designed for use with marine engines running on low sulfur fuel.

Lubricants for the lubrication of marine diesel internal combustion engines have high viscosity industry requirements, due to low-operating speeds and high loads, and are typically high viscosity monograde (i.e. one which exhibits little or no viscosity index improvement properties) lubricants of the SAE 20, SAE 30, SAE 40, SAE 50 or SAE 60 viscosity grade. Because hydrocracking results in a viscosity loss of the base stocks, marine oils generally cannot be formulated solely with hydrocracked base stocks, but require the use of significant amounts of bright stock. However, the reliance on bright stock is not always desirable because of the presence of oxidatively unstable

aromatics. In addition, the availability of brightstock is diminishing, resulting in high volume uses such as those for marine engines, requiring alternative solutions to impart the desired viscometrics in lubricants.

Another important performance aspect of marine diesel lubricants is foaming performance. Foam forms when a large amount of gas is entrained in a liquid. While foaming is desirable in certain applications, such as floatation, washing and cleaning, it can be undesirable in lubricant-related applications where foaming can be an impediment because it leads to ineffective lubrication. The viscosity and surface tension of a lubricant contribute to the stability of the foam. Low-viscosity oils produce foams with large bubbles, which tend to break quickly and be minimally problematic. However, high-viscosity oils, such as those used as marine lubricants, generate stable foams that contain fine bubbles and are difficult to break. Over time, foaming may also accelerate oxidative degradation of the lubricant and in addition may have effects on the transporting and pumping ability of the oil.

In view of restrictive emissions regulations, diminishing supplies of brightstock, changing fuel sources and operating conditions for marine diesel internal combustion engines, there is need for marine diesel lubricating oil technology which sequesters or complexes metal ions in lubricating oil, provides foam control, oxidative stability and enhanced detergency performance across a variety of BN levels, reduces the rate of depletion of basicity (loss of BN), allows for a reduction in the amount of brightstock that is used in the lubricating oil composition, and meets marine lubricant performance demands and requirements for a SAE 20, SAE 30, SAE 40, SAE 50 or SAE 60 monograde lubricating oil composition.

SUMMARY OF THE INVENTION

In one aspect, there is provided a marine diesel lubricating oil composition comprising: (a) a major amount of an oil of lubricating viscosity; and (b) about 0.1 wt. % to about 10 wt. % actives, based on the total weight of the lubricating oil composition, of at least one Mannich reaction product prepared by the condensation of a polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl group is derived from polyisobutene containing at least about 70 wt. % methylvinylidene isomer and has a number average molecular weight of from about 400 to about 2500, an aldehyde, an amino acid or ester derivative thereof, and an alkali metal base; wherein the lubricating oil composition has a BN of 5 to 200 mg KOH/g, and further wherein the marine diesel lubricating oil composition is a monograde lubricating oil composition meeting the specifications for SAE J300 revised January 2015 requirements for a SAE 20, SAE 30, SAE 40, SAE 50 or SAE 60 monograde lubricating oil.

In another aspect, there is provided a marine trunk piston engine oil lubricating oil composition comprising: (a) a major amount of an oil of lubricating viscosity; and (b) about 0.1 wt. % to about 10 wt. % actives, based on the total weight of the marine trunk piston engine lubricating oil composition, of at least one Mannich reaction product prepared by the condensation of a polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl group is derived from polyisobutene containing at least about 70 wt. % methylvinylidene isomer and has a number average molecular weight of from about 400 to about 2500, an aldehyde, an amino acid or ester derivative thereof, and an alkali metal base; wherein the marine trunk piston engine lubricating oil composition has a TBN of 10 to 80 mg KOH/g, and further wherein the marine trunk piston engine oil lubricating oil composition is

a monograde lubricating oil composition meeting the specifications for SAE J300 revised January 2015 requirements for a SAE 30, or SAE 40 monograde lubricating oil.

In yet another aspect, there is provided a marine system lubricating oil composition comprising: (a) a major amount of an oil of lubricating viscosity; and (b) about 0.1 wt. % to about 10 wt. % actives, based on the total weight of the marine system lubricating oil composition, of at least one Mannich reaction product prepared by the condensation of a polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl group is derived from polyisobutene containing at least about 70 wt. % methylvinylidene isomer and has a number average molecular weight of from about 400 to about 2500, an aldehyde, an amino acid or ester derivative thereof, and an alkali metal base; wherein the marine system oil lubricating oil composition has a TBN of 5 to 40 mg KOH/g, and further wherein the marine system oil lubricating oil composition is a monograde lubricating oil composition meeting the specifications for SAE J300 revised January 2015 requirements for a SAE 20, SAE 30 or SAE 40 monograde lubricating oil.

In a further aspect, there is provided a marine diesel cylinder lubricating oil composition comprising: (a) a major amount of an oil of lubricating viscosity; and (b) about 0.1 wt. % to about 10 wt. % actives, based on the total weight of the marine diesel cylinder lubricating oil composition, of at least one Mannich reaction product prepared by the condensation of a polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl group is derived from polyisobutene containing at least about 70 wt. % methylvinylidene isomer and has a number average molecular weight of from about 400 to about 2500, an aldehyde, an amino acid or ester derivative thereof, and an alkali metal base; wherein the marine diesel cylinder lubricating oil composition has a TBN of 5 to 200 mg

KOH/g, and further wherein the marine diesel cylinder lubricating oil composition is a monograde lubricating oil composition meeting the specifications for SAE J300 revised January 2015 requirements for a SAE 30, SAE 40, SAE 50 or SAE 60 monograde lubricating oil.

In another aspect, there is provided a marine diesel cylinder lubricating oil composition comprising: (a) a major amount of an oil of lubricating viscosity; and (b) about 0.1 wt. % to about 10 wt. % actives, based on the total weight of the marine diesel cylinder lubricating oil composition, of at least one Mannich reaction product prepared by the condensation of a polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl group is derived from polyisobutene containing at least about 70 wt. % methylvinylidene isomer and has a number average molecular weight of from about 400 to about 2500, an aldehyde, an amino acid or ester derivative thereof, and an alkali metal base; wherein the marine diesel cylinder lubricating oil composition has a TBN of 5 to 40 mg KOH/g, and further wherein the marine diesel cylinder lubricating oil composition is a monograde lubricating oil composition meeting the specifications for SAE J300 revised January 2015 requirements for a SAE 30, SAE 40, SAE 50 or SAE 60 monograde lubricating oil.

In accordance with one embodiment of the present invention, there is provided a lubricating oil composition comprising:

(a) a major amount of an oil of lubricating viscosity; and

(b) about 0.1 wt. % to about 10 wt. % actives, based on the total weight of the lubricating oil composition, of at least one Mannich reaction product prepared by the condensation of a polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl group is derived from polyisobutene containing at least about 70 wt. %

methylvinylidene isomer and has a number average molecular weight of from about 400 to about 2500, an aldehyde, an amino acid or ester derivative thereof, and an alkali metal base;

wherein the lubricating oil composition has a TBN of 5 to 200 mg KOH/g, and further wherein the lubricating oil composition is a monograde lubricating oil composition meeting the specifications for SAE J300 revised January 2015 requirements for a SAE 20, SAE 30, SAE 40, SAE 50 or SAE 60 monograde lubricating oil.

In accordance with another embodiment of the present invention, there is provided a marine diesel cylinder lubricating oil composition comprising:

(a) a major amount of an oil of lubricating viscosity; and

(b) about 0.1 wt. % to about 10 wt. % actives, based on the total weight of the marine diesel cylinder lubricating oil composition, of at least one Mannich reaction product prepared by the condensation of a polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl group is derived from polyisobutene containing at least about 70 wt.

% methylvinylidene isomer and has a

number average molecular weight of from about 400 to about 2500, an aldehyde, an amino acid or ester derivative thereof, and an alkali metal base; and

wherein the marine diesel cylinder lubricating oil composition has a TBN of 5 to 200 mg KOH/g, and further wherein the marine diesel cylinder lubricating oil composition is a monograde lubricating oil composition meeting the specifications for SAE J300 revised January 2015 requirements for a SAE 30, SAE 40, SAE 50 or SAE 60 monograde lubricating oil.

In accordance with another embodiment of the present invention, there is provided a marine trunk piston engine lubricating oil composition comprising:

(a) a major amount of an oil of lubricating viscosity; and

(b) about 0.1 wt. % to about 10 wt. % actives, based on the total weight of the marine trunk piston engine lubricating oil composition, of at least one Mannich reaction product prepared by the condensation of a polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl group is derived from polyisobutene containing at least about 70 wt. % methylvinylidene isomer and has a number average molecular weight of from about 400 to about 2500, an aldehyde, an amino acid or ester derivative thereof, and an alkali metal base;

wherein the marine trunk piston engine lubricating oil composition has a TBN of 10 to 80 mg KOH/g, and further wherein the marine trunk piston engine lubricating oil composition is a monograde lubricating oil composition meeting the specifications for SAE J300 revised January 2015 requirements for a SAE 30, or SAE 40 monograde lubricating oil.

In accordance with another embodiment of the present invention, there is provided a marine system oil lubricating oil composition comprising:

(a) a major amount of an oil of lubricating viscosity; and

(b) about 0.1 wt. % to about 10 wt. % actives, based on the total weight of the marine system lubricating oil composition, of at least one Mannich reaction product prepared by the condensation of a polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl group is derived from polyisobutene containing at least about 70 wt. % methylvinylidene isomer and has a number average molecular weight of from about 400 to about 2500, an aldehyde, an amino acid or ester derivative thereof, and an alkali metal base;

wherein the marine system oil lubricating oil composition has a TBN of 5 to 40 mg KOH/g, and further wherein the marine system oil lubricating oil composition is a monograde lubricating oil composition meeting the specifications for SAE J300 revised January 2015 requirements for a SAE 20, SAE 30, or SAE 40 monograde lubricating oil.

In accordance with another embodiment of the present invention, there is provided a marine diesel cylinder lubricating oil composition comprising:

(a) a major amount of an oil of lubricating viscosity; and

(b) about 0.1 wt. % to about 10 wt. % actives, based on the total weight of the marine diesel cylinder lubricating oil composition, of at least one Mannich reaction product prepared by the condensation of a polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl group is derived from polyisobutene containing at least about 70 wt. % methylvinylidene isomer and has a

number average molecular weight of from about 400 to about 2500, an aldehyde, an amino acid or ester derivative thereof, and an alkali metal base;

wherein the marine diesel cylinder lubricating oil composition has a TBN of 5 to 40 mg KOH/g, and further wherein the marine diesel cylinder lubricating oil composition is a monograde lubricating oil composition meeting the specifications for SAE J300 revised January 2015 requirements for a SAE 30, SAE 40, SAE 50, or SAE 60 monograde lubricating oil.

In accordance with another embodiment of the present invention, there is provided a marine diesel cylinder lubricating oil composition designed for the lubrication of marine two-stroke crosshead engines operating on low sulfur fuel comprising:

(a) a major amount of an oil of lubricating viscosity; and

(b) about 0.1 wt. % to about 10 wt. % actives, based on the total weight of the marine diesel cylinder lubricating oil composition, of at least one Mannich reaction product prepared by the condensation of a polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl group is derived from polyisobutene containing at least about 70 wt. % methylvinylidene isomer and has a number average molecular weight of from about 400 to about 2500, an aldehyde, an amino acid or ester derivative thereof, and an alkali metal base;

wherein the marine diesel cylinder lubricating oil composition has a TBN of 5 to 40 mg KOH/g, and further wherein the marine diesel cylinder lubricating oil composition is a monograde lubricating oil composition meeting the specifications for SAE J300 revised January 2015 requirements for a SAE 30, SAE 40, SAE 50, or SAE 60 monograde lubricating oil.

In accordance with another embodiment of the present invention, there is provided a marine diesel lubricating oil composition comprising:

(a) a major amount of an oil of lubricating viscosity; and

(b) about 0.1 wt. % to about 10 wt. % actives, based on the total weight of the marine diesel lubricating oil composition, of at least one Mannich reaction product prepared by the condensation of a polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl group is derived from polyisobutene containing at least about 70 wt. % methylvinylidene isomer and has a number average molecular weight of from about 400 to about 2500, an aldehyde, an amino acid or ester derivative thereof, and an alkali metal base;

wherein the marine diesel lubricating oil composition has a TBN of 5 to 40 mg KOH/g, and further wherein the marine diesel lubricating oil composition is a monograde lubricating oil composition meeting the specifications for SAE J300 revised January 2015 requirements for a SAE 20, SAE 30, SAE 40, SAE 50 or SAE 60 monograde lubricating oil.

In accordance with another embodiment of the present invention, there is provided a marine trunk piston engine lubricating oil composition for the lubrication of marine engines operating on low sulfur fuel comprising:

(a) a major amount of an oil of lubricating viscosity; and

(b) about 0.1 wt. % to about 10 wt. % actives, based on the total weight of the marine trunk piston engine lubricating oil composition, of at least one Mannich reaction product prepared by the condensation of a polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl group is derived from polyisobutene containing at least about 70 wt. % methylvinylidene isomer and has a

number average molecular weight of from about 400 to about 2500, an aldehyde, an amino acid or ester derivative thereof, and an alkali metal base;

wherein the marine trunk piston engine lubricating oil composition has a TBN of 10 to 20 mg KOH/g, and further wherein the marine trunk piston engine lubricating oil composition is a monograde lubricating oil composition meeting the specifications for SAE J300 revised January 2015 requirements for a SAE 30 or SAE 40 monograde lubricating oil.

It has been found that about 0.1 wt. % to about 10 wt. % actives, based on the total weight of the lubricating oil composition, of at least one Mannich reaction product prepared by the condensation of a polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl group is derived from polyisobutene containing at least about 70 wt. % methylvinylidene isomer and has a number average molecular weight of from about 400 to about 2500, an aldehyde, an amino acid and an alkali metal base, in a marine diesel lubricating composition can achieve performance benefits such as oil thickening (replacement of brightstock), enhanced detergency performance, reduction in the rate of depletion of basicity, foaming performance, and oxidative stability due to prevention of metal catalyzed oxidation and polymerization of lubricating oils.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

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 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 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.

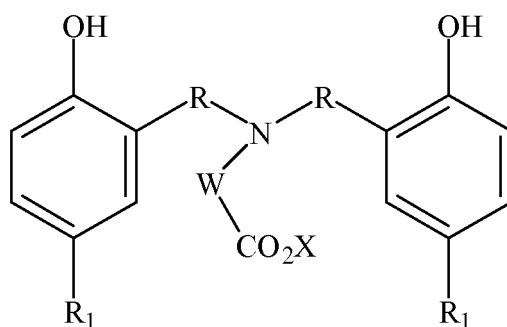
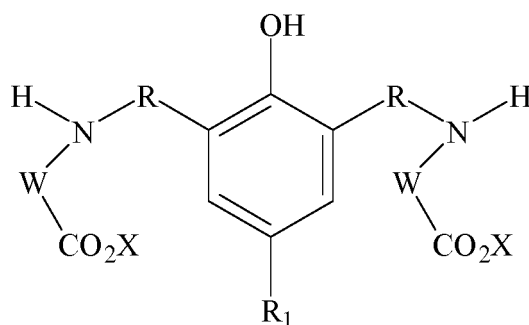
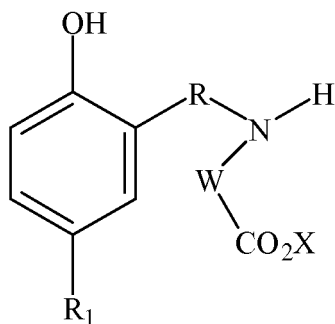
A “distillate fuel” refers to a fuel meeting the specification of a distillate marine fuel as set forth in the ISO 8217:2010 international standard. A “low sulfur distillate fuel” refers to a fuel meeting the specification of a distillate marine fuel set forth in the ISO 8217:2010 international standard 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.

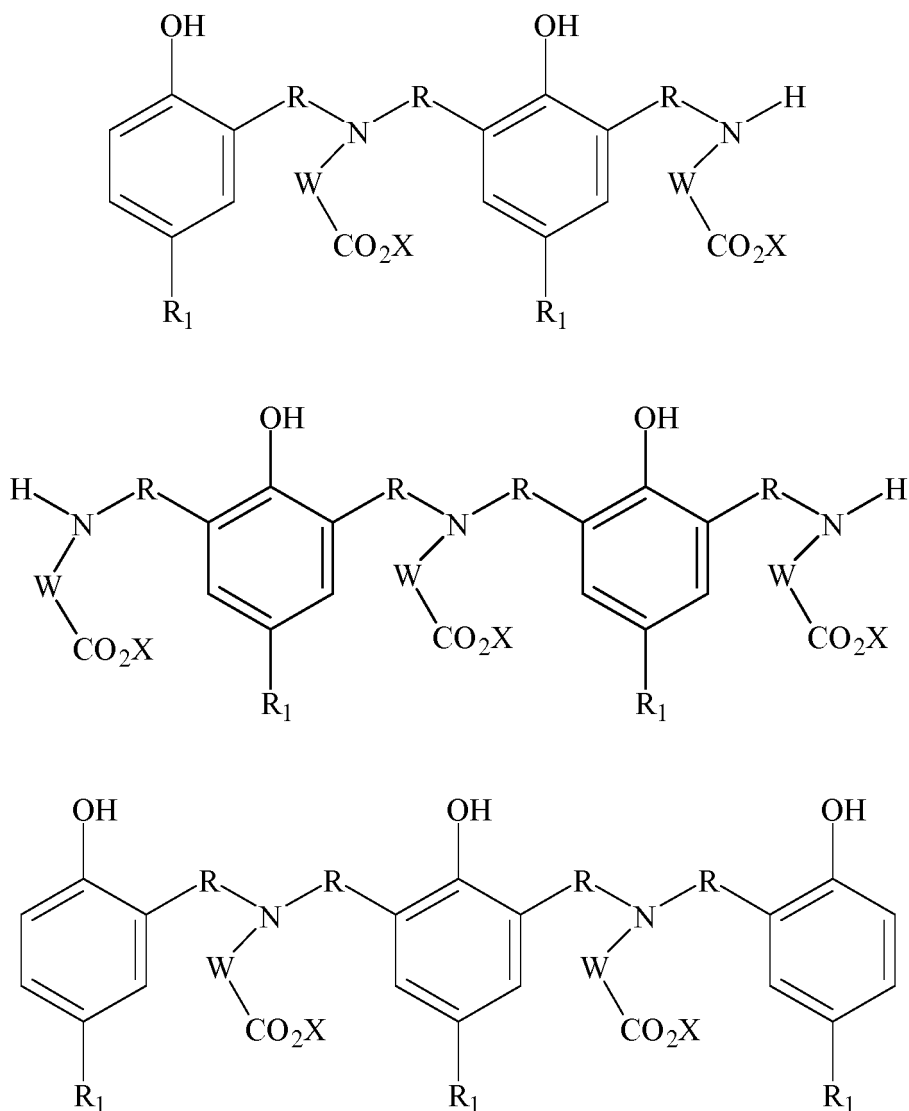
A “low sulfur fuel” refers having about 1.5 wt. % or less, or even about 1.0 wt. % or less, or even 0.5% wt.% or less, or even 0.1 wt. % or less of sulfur, relative to the total weight of the fuel.

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

The term “Mannich condensation product” as used herein refers to a mixture of products obtained by the condensation reaction of a polyisobutyl-substituted hydroxyaromatic compound with an aldehyde and an amino acid as described herein,

to form condensation products having the formulas given below. The formulas given below are provided only as some examples of the Mannich condensation products believed to be of the present invention and are not intended to exclude other possible Mannich condensation products that may be formed using the methods described herein.





wherein R, R_1 , X and W are as defined herein.

The term “Total Base Number” or “TBN” or “BN” refers to the level of alkalinity in an oil sample, which indicates the ability of the composition to continue to neutralize 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 $mg \cdot KOH/g$ (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.

The marine diesel lubricating oil composition of the present invention can have any TBN that is suitable for use as a marine lubricant. In some embodiments, the TBN of the marine lubricating oil composition of the present invention is less than about 200 mg KOH/g. In other embodiments, the TBN of the marine lubricating oil composition of the present disclosure can range from about 5 to about 200, or from about 5 to about 140, or 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 8 to about 200, or from about 8 to about 140, or from about 8 to about 100, or from about 8 to about 80, or from 8 to about 40, or from about 8 to about 30, or from about 10 to about 200, or from about 10 to about 140, or from about 10 to about 100, or from about 10 to about 80, or from about 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 200, or from about 15 to about 140, 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 200, or from about 20 to about 140, 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 mg KOH/g.

The lubricating oil composition may be an SAE 20 monograde lubricating oil composition, or an SAE 30 monograde lubricating oil composition, or an SAE 40 monograde lubricating oil composition, or an SAE 50 monograde lubricating oil composition, or an SAE 60 monograde lubricating oil composition. The monograde of the lubricating oil composition is defined according to the SAE J300 standard Rev. January 2015.

The marine diesel lubricating oil compositions of this invention can have a kinematic viscosity ranging from about 6.9 to about 26.1 cSt @ 100°C, or about 9.3 to about 21.9 cSt @ 100°C, or about 9.3 to about 16.3 cSt @ 100°C, or about 12.5 to about 21.9 cSt @ 100°C, or about 12.5 to about 16.3 cSt @ 100°C, about 16.3 to about 21.9 cSt at 100°C, or about 16.3 to about 26.1 cSt at 100°C. The kinematic viscosity of the marine diesel lubricating oil compositions is measured by ASTM D445.

The marine diesel lubricating oil composition may be a marine diesel cylinder lubricating oil composition. Marine cylinder lubricants are typically made to the SAE 30, SAE 40, SAE 50 or SAE 60 specification in order to provide a sufficiently thick lubricant film at the high temperatures on the cylinder liner wall. Typically, marine cylinder lubricants have a base number higher than 5 mg KOH/g as measured by ASTM D2896 and more recently are being formulated as high as 200 mg KOH/g. The marine diesel cylinder lubricating oil compositions of this invention can have a kinematic viscosity ranging from about 9.3 to about 26.1 cSt at 100°C, or about 12.5 to about 26.1 cSt @ 100°C, or about 12.5 to about 21.9 cSt @ 100°C, about 16.3 to about 21.9 cSt @ 100°C, or about 16.3 to about 26.1 cSt at 100°C. The marine diesel cylinder lubricating composition of this invention can have a base number ranging from about 5 to about 200 mg KOH/g, or from about 5 to about 140 mg KOH/g, or from about 5 to about 100 mg KOH/g, or from about 5 to about 70 mg KOH/g, or from about 5 to about 40 mg KOH/g, or from about 5 to about 30 mg KOH/g, or from about 8 to about 200, or from about 8 to about 140, or from about 8 to about 100, or from about 8 to about 80, or from about 8 to about 40, or from about 8 to about 30, or from about 10 to about 140 mg KOH/g, or from about 10 to about 100 mg KOH/g, or from about 10 to about 80 mg KOH/g, or from about 10 to about 50 mg KOH/g, or from about 10 to about 40 mg KOH/g, or

from about 15 to about 100 mg KOH/g, or from about 15 to about 80 mg KOH/g, or from about 15 to about 40 mg KOH/g, or from about 20 to about 200 mg KOH/g, or from about 20 to about 140 mg KOH/g, or from about 20 to about 100 mg KOH/g, or from about 20 to about 80 mg KOH/g, or from about 25 to about 80 mg KOH/g, or from about 30 to about 80 mg KOH/g.

The marine diesel lubricating oil composition may be a marine system oil lubricating oil composition. Marine system oil lubricants are typically made to the SAE 20, SAE 30 or SAE 40 specification. The viscosity for the marine system oil is set at such a relatively low level in part because a system oil can increase in viscosity during use and the engine designers have set viscosity increase limits to prevent operational problems. The marine system oil lubricating oil compositions of this invention can have a kinematic viscosity ranging from about 6.9 to about 16.3 cSt @ 100°C, or about 6.9 to about 12.5 cSt @ 100°C, or about 6.9 to about 9.3, or about 9.3 to about 16.5 cSt @ 100°C, or about 9.3 to about 12.5 cSt @ 100°C. Typically, marine system oil lubricants have a base number higher than 5 mg KOH/g as measured by ASTM D2896. The marine system oil lubricating composition of this invention can have a base number ranging from about 5 to about 40 mg KOH/g, or from about 5 to about 30 mg KOH/g, or from about 5 to about 25 mg KOH/g, or from about 5 to about 15 mg KOH/g, or from about 10 to about 30 mg KOH/g, or from about 8 to about 40, or from about 8 to about 30, or from about 8 to about 20 mg KOH/g.

The marine diesel lubricating oil composition may be a marine trunk piston engine oil lubricating oil composition. Marine trunk piston engine lubricants are typically made to the SAE 30 or SAE 40 specification. The marine trunk piston engine

oil lubricating oil compositions of this invention can have a kinematic viscosity ranging from about 9.3 to about 16.3 cSt @ 100°C, or about 12.5 to about 16.3 cSt @ 100°C. Typically, marine trunk piston engine oil lubricants have a base number higher than about 10 mg KOH/g as measured by ASTM D2896. The marine trunk piston engine oil can have a base number of 10 to about 80 mg KOH/g, such as from 10 to about 60 mg KOH/g, 20 to 80 mg KOH/g, or from about 20 to about 60 mg KOH/g.

The marine diesel 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 lubricating oil compositions. The ingredients can be added 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 lubricant composition of the present invention includes a major amount of an oil of lubricating viscosity. By “a major amount” it is meant that the marine diesel lubricant composition suitably includes at least about 40 wt. %, or at least about 45 wt. %, or at least about 50 wt. %, or at least about 55 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 lubricant oil composition.

The oil of lubricating viscosity may be any oil suitable for the lubrication of marine diesel 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 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.

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-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.

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 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 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 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, 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, 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 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 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 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 base stocks. Such wax isomerase 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. 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 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).

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 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 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 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 (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 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.

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 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 %.

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 %.

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 Application Publication Nos. 2004/0159582; 2005/0077208; 2005/0133407;

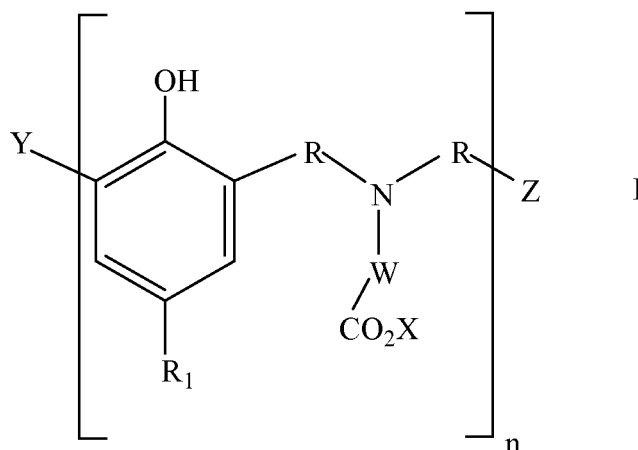
2005/0133409; 2005/0139513; 2005/0139514; 2005/0241990 each of which are incorporated herein by reference. In general, the process involves a complete or partial hydroisomerization dewaxing step, employing a dual-functional catalyst or a catalyst that can isomerize paraffins selectively. Hydroisomerization dewaxing is achieved by 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 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.

As stated above, lubricants for use in marine diesel engines typically have a kinematic viscosity in the range of 6.9 to 26.1 cSt at 100°C. In order to formulate such a lubricant, a brightstock may be combined with a lower viscosity oil. However, supplies of brightstock are dwindling and therefore brightstock cannot be relied upon to increase the viscosity of marine 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 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 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 marine 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.

The lubricating oil composition of the present invention will further contain about 0.1 wt.% to about 10.0 wt.%, or from about 0.5 wt. % to about 10.0 wt. %, or from about 0.5 wt. % to about 8.0 wt. %, or from about 1.0 wt. % to about 10.0 wt. %, or from about 3.0 wt. % to about 10.0 wt. %, or from about 3.0 wt. % to about 8.0 wt. %, or from about 2.5 to about 10.0 wt. %, or from about 2.5 wt. % to about 8.0 wt. % actives based on the total weight of the lubricating oil composition, of at least one Mannich reaction product prepared by the condensation of a polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl group is derived from polyisobutene containing at least about 70 wt. % methylvinylidene isomer and has a number average molecular weight in the range of from about 400 to about 2500, an aldehyde, an amino acid or ester derivative thereof, and an alkali metal base. In general, the principal Mannich condensation product can be represented by the structure of formula I:

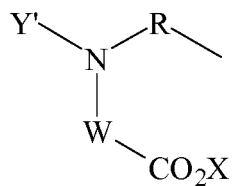


wherein each R is independently -CHR'-, R' is a branched or linear alkyl having one carbon atom to about 10 carbon atoms, a cycloalkyl having from about 3 carbon atoms to about 10 carbon atoms, an aryl having from about 6 carbon atoms to about 10 carbon atoms, an alkaryl having from about 7 carbon atoms to about 20 carbon atoms, or aralkyl having from about 7 carbon atoms to about 20 carbon atoms, R₁ is a polyisobutyl group derived from polyisobutene containing at least about 70 wt. % methylvinylidene isomer and having a number average molecular weight in the range of about 400 to about 2500;

X is hydrogen, an alkali metal ion or alkyl having one to about 6 carbon atoms;

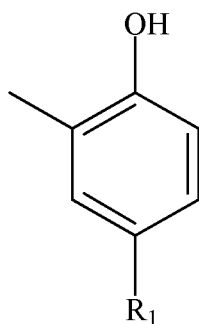
W is -[CHR'']_m wherein each R'' is independently H, alkyl having one carbon atom to about 15 carbon atoms, or a substituted-alkyl having one carbon atom to about 10 carbon atoms and one or more substituents selected from the group consisting of amino, amido, benzyl, carboxyl, hydroxyl, hydroxyphenyl, imidazolyl, imino, phenyl, sulfide, or thiol; and m is an integer from 1 to 4;

Y is hydrogen, alkyl having one carbon atom to about 10 carbon atoms, -CHR'OH, wherein R' is as defined above, or

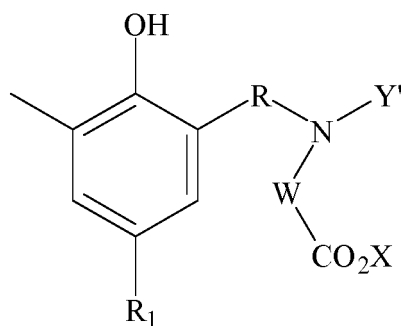


wherein Y' is -CHR'OH, wherein R' is as defined above; and R, X, and W are as defined above;

Z is hydroxyl, a hydroxyphenyl group of the formula:



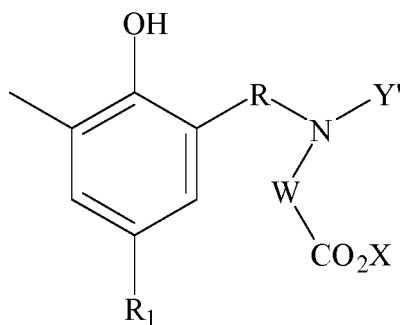
or



wherein R, R₁, Y', X, and W are as defined above,

and n is an integer from 0 to 20, with the proviso that when n = 0, Z must

be:



wherein R, R₁, Y', X, and W are as defined above.

In one embodiment, the R₁ polyisobutyl group has a number average molecular weight of about 500 to about 2500. In one embodiment, the R₁ polyisobutyl group has a number average molecular weight of about 700 to about 1,500. In one embodiment, the R₁ polyisobutyl group has a number average molecular weight of about 700 to about 1,100. In one embodiment, the R₁ polyisobutyl group is derived from polyisobutene containing at least about 70 wt. % methylvinylidene isomer. In one embodiment, the R₁ polyisobutyl group is derived from polyisobutene containing at least about 90 wt. % methylvinylidene isomer.

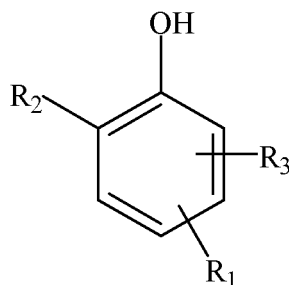
In the compound of formula I above, X is an alkali metal ion and most preferably a sodium or potassium ion. In another embodiment, in the compound of formula I above, X is alkyl selected from methyl or ethyl. In one embodiment, the marine diesel lubricating oil composition of the invention comprises a Mannich reaction product where the alkali metal used in the manufacture of the Mannich product is sodium. In another embodiment, the marine diesel lubricating oil composition of the invention comprises a Mannich reaction product where the alkali metal used in the manufacture of the Mannich product is potassium. In another embodiment, the marine diesel lubricating oil composition of the invention comprises a combination of Mannich

reaction products where the alkali metal used in the manufacture of the Mannich products are potassium and sodium.

In one embodiment, R is CH₂, R₁ is derived from polyisobutene containing at least about 70 wt. % methylvinylidene isomer and a number average molecular weight in the range of about 700 to about 1,100, W is CH₂, X is sodium ion and n is 0 to 20.

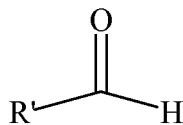
The Mannich condensation products for use in the lubricating oil composition of the present invention can be prepared by combining under reaction conditions a polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl group has a number average molecular weight in the range of from about 400 to about 2500, an aldehyde, an amino acid or ester derivative thereof, and an alkali metal base. In one embodiment, Mannich condensation product prepared by the Mannich condensation of:

(a) a polyisobutyl-substituted hydroxyaromatic compound having the formula:



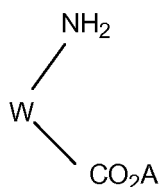
wherein R₁ is a polyisobutyl group derived from polyisobutene containing at least about 70 wt. % methylvinylidene isomer and having a number average molecular weight in the range of about 400 to about 2500, R₂ is hydrogen or lower alkyl having one carbon atom to about 10 carbon atoms, and R₃ is hydrogen or -OH;

(b) a formaldehyde or an aldehyde having the formula:



wherein R' is branched or linear alkyl having one carbon atom to about 10 carbon atoms, cycloalkyl having from about 3 carbon atoms to about 10 carbon atoms, aryl having from about 6 carbon atoms to about 10 carbon atoms, alkaryl having from about 7 carbon atoms to about 20 carbon atoms, or aralkyl having from about 7 carbon atoms to about 20 carbon atoms;

(c) an amino acid or ester derivative thereof having the formula:



wherein W is $-\text{[CHR'']}_m$ wherein each R'' is independently H, alkyl having one carbon atom to about 15 carbon atoms, or a substituted-alkyl having one carbon atom to about 10 carbon atoms and one or more substituents selected from the group consisting of amino, amido, benzyl, carboxyl, hydroxyl, hydroxyphenyl, imidazolyl, imino, phenyl, sulfide, or thiol; and m is an integer from one to 4, and A is hydrogen or alkyl having one carbon atom to about 6 carbon atoms; and

(d) an alkali metal base.

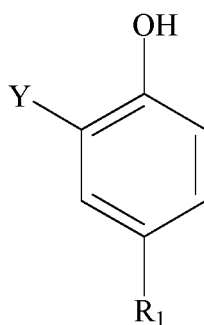
A variety of polyisobutyl-substituted hydroxyaromatic compounds can be utilized in the preparation of the Mannich condensation products of this invention. The critical feature is that the polyisobutyl substituent be large enough to impart oil solubility to the finished Mannich condensation product. In general, the number of

carbon atoms on the polyisobutyl substituent group that are required to allow for oil solubility of the Mannich condensation product is on the order of about C₂₀ and higher. This corresponds to a molecular weight in the range of about 400 to about 2500. It is desirable that the C₂₀ or higher alkyl substituent on the phenol ring be located in the position para to the OH group on the phenol.

The polyisobutyl-substituted hydroxyaromatic compound is typically a polyisobutyl-substituted phenol wherein the polyisobutyl moiety is derived from polyisobutene containing at least about 70 wt. % methylvinylidene isomer and more preferably the polyisobutyl moiety is derived from polyisobutene containing at least about 90 wt. % methylvinylidene isomer. The term “polyisobutyl or polyisobutyl substituent” as used herein refers to the polyisobutyl substituent on the hydroxyaromatic ring. The polyisobutyl substituent has a number average molecular weight in the range of about 400 to about 2500. In one embodiment, the polyisobutyl moiety has a number average molecular weight in the range of about 450 to about 2500. In one embodiment, the polyisobutyl moiety has a number average molecular weight in the range of about 700 to about 1500. In one embodiment, the polyisobutyl moiety has a number average molecular weight in the range of about 700 to about 1100.

Di-substituted phenols are also suitable starting materials for the Mannich condensation products of this invention. Di-substituted phenols are suitable provided that they are substituted in such a way that there is an unsubstituted ortho position on the phenol ring. Examples of suitable di-substituted phenols are o-cresol derivatives substituted in the para position with a C₂₀ or greater polyisobutyl substituent and the like.

In one embodiment, a polyisobutyl-substituted phenol has the following formula:



wherein R₁ is polyisobutyl group derived from polyisobutene containing at least about 70 wt. % methylvinylidene isomer and having a number average molecular weight in the range of about 400 to about 2500, and Y is hydrogen.

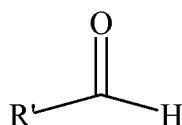
Suitable polyisobutenes may be prepared using boron trifluoride (BF₃) alkylation catalyst as described in U.S. Patent Nos. 4,152,499 and 4,605,808, the contents of each of these references being incorporated herein by reference. Commercially available polyisobutenes having a high alkylvinylidene content include Glissopal® 1000, 1300 and 2300, available from BASF.

The preferred polyisobutyl-substituted phenol for use in the preparation of the Mannich condensation products is a mono-substituted phenol, wherein the polyisobutyl substituent is attached at the para-position to the phenol ring. However, other polyisobutyl-substituted phenols that may undergo the Mannich condensation reaction may also be used for preparation of the Mannich condensation products according to the present invention.

Solvents may be employed to facilitate handling and reaction of the polyisobutyl-substituted phenols in the preparation of the Mannich condensation products. Examples of suitable solvents are hydrocarbon compounds such as heptane, benzene, toluene, chlorobenzene, aromatic solvent, neutral oil of lubricating viscosity, paraffins and naphthenes. Examples of other commercially available suitable solvents that are aromatic mixtures include Chevron® Aromatic 100N, neutral oil, Exxon® 150N, neutral oil.

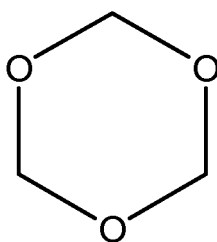
In one embodiment, the Mannich condensation product may be first dissolved in an alkyl-substituted aromatic solvent. Generally, the alkyl substituent on the aromatic solvent has from about 3 carbon atoms to about 15 carbon atoms. In one embodiment, the alkyl substituent on the aromatic solvent has from about 6 carbon atoms to about 12 carbon atoms.

Suitable aldehydes for use in forming the Mannich condensation product include formaldehyde or aldehydes having the formula



wherein R' is branched or linear alkyl having from one carbon atom to about 10 carbon atoms, cycloalkyl having from about 3 carbon atoms to about 10 carbon atoms, aryl having from about 6 carbon atoms to about 10 carbon atoms, alkaryl having from about 7 carbon atoms to about 20 carbon atoms, or aralkyl having from about 7 carbon atoms to about 20 carbon atoms.

Representative aldehydes include, but are not limited to, aliphatic aldehydes such as formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, caproaldehyde and heptaldehyde. Aromatic aldehydes are also contemplated for use in the preparation of the Mannich condensation products, such as benzaldehyde and alkylbenzaldehyde, e.g., para-tolualdehyde. Also useful are formaldehyde producing reagents, such as paraformaldehyde and aqueous formaldehyde solutions such as formalin. In one preferred embodiment, an aldehyde for use in the preparation of the Mannich condensation products is formaldehyde or formalin. By formaldehyde is meant all its forms, including gaseous, liquid and solid. Examples of gaseous formaldehyde is the monomer CH_2O and the trimer, $(\text{CH}_2\text{O})_3$ (trioxane) having the formula given below.



Examples of liquid formaldehyde are the following:

Monomer CH_2O in ethyl ether.

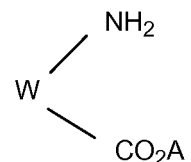
Monomer CH_2O in water which has the formulas $\text{CH}_2(\text{H}_2\text{O})_2$ (methylene glycol) and $\text{HO}(-\text{CH}_2\text{O})_n\text{-H}$.

Monomer CH_2O in methanol which has the formulas $\text{OHCH}_2\text{OCH}_3$ and $\text{CH}_3\text{O}(-\text{CH}_2\text{O})_n\text{-H}$.

Formaldehyde solutions are commercially available in water and various alcohols. In water, it is available as a 37% - 50% solution. Formalin is a 37% solution in water. Formaldehyde is also commercially available as linear and cyclic (trioxane)

polymers. Linear polymers may be low molecular weight or high molecular weight polymers.

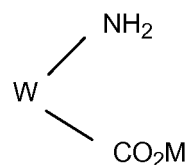
Suitable amino acids or ester derivatives thereof for use in forming the Mannich condensation product include amino acids having the formula



wherein W is $-\text{[CHR'']}_m-$, wherein each R'' is independently H, alkyl having one carbon atom to about 15 carbon atoms, or a substituted-alkyl having one carbon atom to about 10 carbon atoms and one or more substituents selected from the group consisting of amino, amido, benzyl, carboxyl, hydroxyl, hydroxyphenyl, imidazolyl, imino, phenyl, sulfide, or thiol; and m is an integer from one to 4, and A is hydrogen or alkyl having one carbon atom to about 6 carbon atoms. Preferably the alkyl is methyl or ethyl.

In one embodiment, the amino acid is glycine.

The term “amino acid salt” as used herein refers to salts of amino acids having the formula



wherein W is as defined above and M is an alkali metal ion. Preferably M is a sodium ion or a potassium ion. More preferably X is a sodium ion.

Some examples of alpha amino acids contemplated for use in the preparation of the Mannich condensation product are the following: alanine, arginine, asparagine,

aspartic acid, cysteine, cysteine, glutamic acid, glutamine, glycine, histidine, hydroxylysine, isoleucine, leucine, lysine, methionine, phenylalanine, serine, threonine, tyrosine, and valine.

Suitable alkali metal base for use in forming the Mannich condensation product include alkali metal hydroxides, alkali metal alkoxides and the like. In one embodiment, the alkali metal base is an alkali metal hydroxide selected from the group consisting of sodium hydroxide, lithium hydroxide or potassium hydroxide.

In one embodiment, the amino acid may be added in the form of its alkali metal ion salt. In one embodiment, the alkali metal ion is a sodium ion or a potassium ion. In one preferred embodiment, the alkali metal ion is a sodium ion.

The reaction to form the Mannich condensation products can be carried out batch wise, or in continuous or semi-continuous mode. Normally the pressure for this reaction is atmospheric, but the reaction may be carried out under sub atmospheric or super atmospheric pressure if desired.

The temperature for this reaction may vary widely. The temperature range for this reaction can vary from about 10°C to about 200°C, or from about 50°C to about 150°C, or from about 70°C to about 130°C.

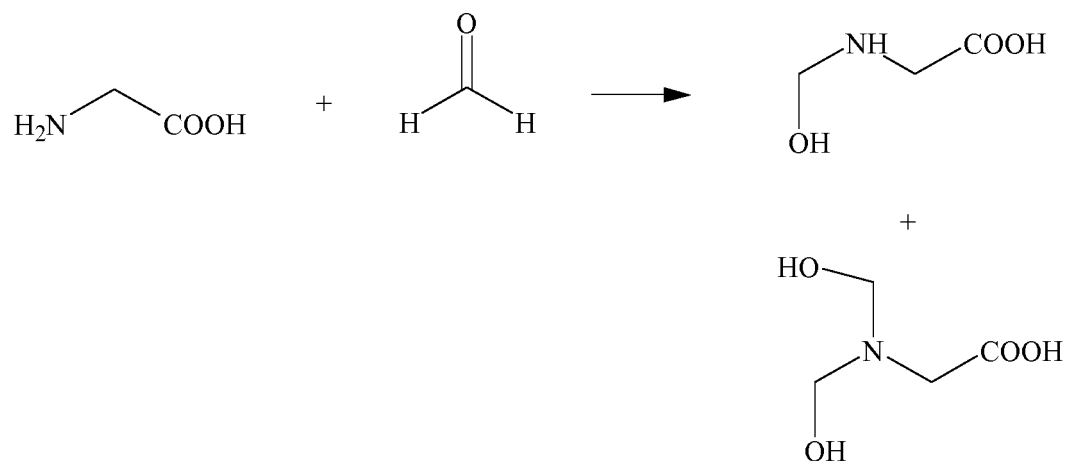
The reaction may be carried out in the presence of a diluent or a mixture of diluents. It is important to ensure that the reactants come into intimate contact with each other in order for them to react. This is an important consideration because the starting materials for the Mannich condensation products include the relatively non polar polyisobutyl-substituted hydroxyl aromatic compounds and the relatively polar

amino acid or ester derivative thereof. It is therefore necessary to find a suitable set of reaction conditions or diluents that will dissolve all the starting materials.

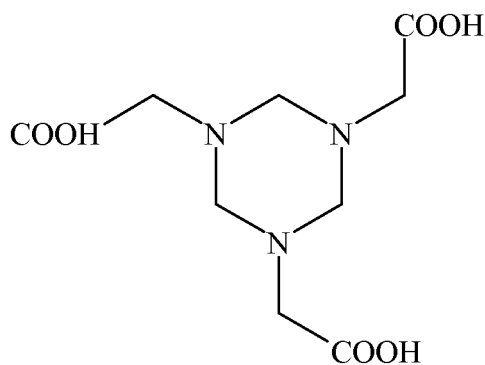
Diluents for this reaction must be capable of dissolving the starting materials of this reaction and allowing the reacting materials to come in contact with each other. Mixtures of diluents can be used for this reaction. Useful diluents for this reaction include water, alcohols, (including methanol, ethanol, isopropanol, 1-propanol, 1-butanol, isobutanol, sec-butanol, butanediol, 2-ethylhexanol, 1-pentanol, 1-hexanol, ethylene glycol, and the like), DMSO, NMP, HMPA, cellosolve, diglyme, various ethers (including diethyl ether, THF, diphenylether, dioxane, and the like), aromatic diluents (including toluene, benzene, o-xylene, m-xylene, p-xylene, mesitylene and the like), esters, alkanes (including pentane, hexane, heptane, octane, and the like), and various natural and synthetic diluent oils (including 100 neutral oils, 150 neutral oils, polyalphaolefins, Fischer-Tropsch derived base oil and the like, and mixtures of these diluents. Mixtures of diluents that form two phases such as methanol and heptane are suitable diluents for this reaction.

The reaction may be carried out by first reacting the hydroxyaromatic compound with the alkali metal base, followed by the addition of the amino acid or ester derivative thereof and the aldehyde, or the amino acid or ester derivative thereof may be reacted with the aldehyde followed by the addition of the hydroxyaromatic compound and the alkali metal base, etc.

It is believed that the reaction of the amino acid, such as glycine, or ester derivative thereof, plus the aldehyde, such as formaldehyde, may produce the intermediate formula

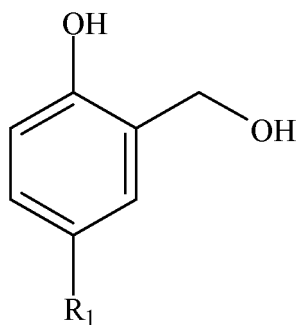


which may ultimately form the cyclic formula



It is believed that these intermediates may react with the hydroxyaromatic compound and the base to form the Mannich condensation products of the present invention.

Alternatively, it is believed that the reaction of the hydroxyaromatic compound with the aldehyde may produce the intermediate formula

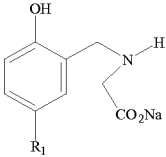
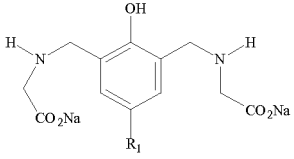
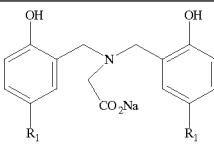
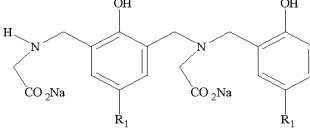
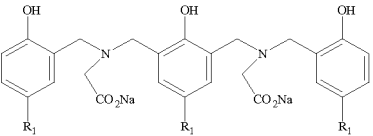


It is also believed that this intermediate may react with the amino acid or ester derivative thereof and the base to form the Mannich condensation product of the present invention.

The time of the reaction can vary widely depending on the temperature. The reaction time can vary between about 0.1 hour to about 20 hours, or from about 2 hours to about 10 hours, or from about 3 hours to about 7 hours.

The charge mole ratio (CMR) of the reagents can also vary over a wide range. Table I below gives a listing of the different formulae that can arise if different charge mole ratios are used. At a minimum, the oil-soluble Mannich condensation products should preferably contain at least one polyisobutyl-substituted phenol ring and one amino acid group connected by one aldehyde group and one alkali metal. The polyisobutyl-substituted phenol/aldehyde/amino acid/base charge mole ratio for this molecule, also shown in Table I below, is 1.0:1.0: 1.0:1.0. Other charge mole ratios are possible and the use of other charge mole ratios can lead to the production of different molecules of different formulas.

TABLE I

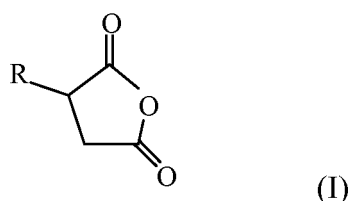
Product	Polyisobutyl-substituted phenol : aldehyde : amino acid : base (CMR)
	1.0 : 1.0 : 1.0 : 10
	1.0 : 2.0 : 2.0 : 2.0
	2.0 : 2.0 : 1.0 : 1.0
	2.0 : 3.0 : 2.0 : 2.0
	3.0 : 4.0 : 2.0 : 2.0

In further embodiments, any of the herein discussed lubricating oil composition of the present invention can further include one or more additives other than the Mannich product. Such additives can be detergents or dispersants.

In one embodiment, the marine diesel 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 900 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.

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 900 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 900 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 polybutenes having a number average

molecular weight of from about 2000 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.

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 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.

Polyalkene groups having a number average molecular weight of from about 900 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: 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 average molecular weight of from about 900 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 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 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: $\text{H}_2\text{N}-(\text{R}^1\text{NH})_c-\text{H}$ 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, 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 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 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 900 to about 3000 in a marine diesel 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 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 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 from a polyalkene group having a number average molecular weight of from about 900 to about 3000 present in a marine diesel 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 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 lubricating oil composition.

In another embodiment, the marine diesel 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-substituted succinic anhydride with a polyamine.

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.

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 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 lubricating oil compositions of the present invention may also contain conventional marine diesel lubricating oil composition additives, other than the foregoing dispersants, for imparting auxiliary functions to give a marine diesel lubricating oil composition in which these additives are dispersed or dissolved. For example, the marine diesel lubricating oil compositions can be blended with antioxidants, detergents, anti-wear agents, rust 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 lubricating oil compositions of the invention by the usual blending procedures.

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

The marine diesel lubricating oil composition of the present invention can contain one or more antioxidants that can reduce or prevent the oxidation of the base oil. 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 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.

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 lubricating oil composition.

The marine diesel 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 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 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 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 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.

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

Overbased detergents may be medium overbased, e.g., an overbased salt having a TBN from about 100 to about 250. In one embodiment, the TBN of a medium overbased salt may be from about 100 to about 200. In another embodiment, the TBN 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 a TBN above 250. In one embodiment, the TBN 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 and is a

“carboxylate” or a “salicylate”. Suitable hydroxyaromatic compounds include mononuclear monohydroxy and polyhydroxy 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 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 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 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 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 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 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 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 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 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 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, 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 wt. % (preferably at least about 125 wt. %) of that stoichiometrically required.

Metal salts of phenols and sulfurized phenols, which are sulfurized phenate 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 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.

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 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 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 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 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 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 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-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 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 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 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.

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 lubricating oil composition.

The marine diesel lubricating oil composition of the present invention can contain one or more friction modifiers that can lower the friction between moving parts. 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, alkoxyated fatty amines; borated fatty epoxides; fatty phosphites, fatty epoxides, fatty amines, borated alkoxyated 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 C_4 to C_{75} , or a C_6 to C_{24} , or a C_6 to C_{20} , fatty acid ester and a nitrogen-containing compound selected from the group consisting of ammonia, and an alkanolamine and the like and mixtures thereof.

The marine diesel 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.

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 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 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 lubricating oil composition of the present invention can contain one or more foam inhibitors or anti-foam inhibitors that can break up foams in oils. 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 methacrylate polymers, polyalkoxyamines and combinations thereof.

The marine diesel 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 lubricating oil composition. Any pour point depressant known by a person of

ordinary skill in the art may be used in the marine diesel 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 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 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. Any demulsifier known by a person of ordinary skill in the art may be used in the marine diesel 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 oxide and the like), esters of oil soluble acids, polyoxyethylene sorbitan ester and combinations thereof.

The marine diesel 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 diesel 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 lubricating oil composition of the present invention can contain one or more extreme pressure (EP) agents that can prevent sliding 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 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 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 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 lubricating oil composition of the present invention can contain one or more rust inhibitors that can inhibit the corrosion of ferrous metal surfaces. Non-limiting examples of suitable rust inhibitors include nonionic polyoxyalkylene agents, e.g., polyoxyethylene lauryl ether, polyoxyethylene higher alcohol ether, polyoxyethylene nonylphenyl ether, 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; partial esters thereof and nitrogen-containing derivatives thereof; synthetic alkarylsulfonates, e.g., metal dinonylnaphthalene sulfonates; and the like and mixtures thereof.

The following non-limiting examples are illustrative of the present invention.

Komatsu Hot Tube (KHT) Test

The Komatsu Hot Tube test is a lubrication industry bench test that measures the degree of high temperature detergency and thermal and oxidative stability of a lubricating oil. During the test, a specified amount of test oil is pumped upwards through a glass tube that is placed inside an oven set at a certain temperature. Air is introduced in the oil stream before the oil enters the glass tube, and flows upward with the oil. Evaluations of the marine trunk piston engine lubricating oils were conducted at temperatures between 300-320°C. After cooling and washing, the test result is determined by comparing the amount of lacquer deposited on the glass test tube to a rating scale ranging from 1.0 (very black) to 10.0 (perfectly clean). The result is reported in multiples of 0.5. In the case the glass tubes are completely blocked with deposits, the test result is recorded as “blocked”. Blockage is deposition below a 1.0 result, in which case the lacquer is very thick and dark but still allows fluid flow, although at a rate that is completely unsatisfactory for a usable oil.

DSC Oxidation Test

The DSC 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 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.

Black Sludge Deposit (BSD) Test

This test is used to evaluate the ability of marine lubricants to cope with unstable—unburned asphaltenes in the residual fuel oil. The test measures the tendency of lubricants to cause deposits on a test strip, by applying oxidative thermal strain on a mixture of heavy fuel oil and lubricant. A sample of a marine lubricant oil composition was mixed with a specific amount of marine residual fuel to form test mixtures. The test mixture is pumped during the test as a thin film over a metal test strip, which is controlled at test temperature (200° C.) for a period of time (12 hours). The test oil-fuel mixture is recycled into the sample vessel. After the test, the test strip is cooled and then washed and dried. The test plates are then weighed. In this manner, the weight of the deposit remaining on the test plates was measured and recorded as the change in weight of the test plate.

Examples 1-4, and Comparative Example A

Examples 1-4 and Comparative Example A were prepared and evaluated using the Komatsu Hot Tube (KHT) test, which is a measure of high temperature detergency, and the Differential Scanning Calorimeter (DSC) test which is used to evaluate thin film oxidation stability of test oils.

Comparative Example A: A 5BN, SAE 30 viscosity grade fully formulated marine cylinder lubricating oil composition was prepared comprising majority amount of Group I base oil (mixture of XOM Core 150N and XOM Core 600N, having kinematic viscosities of about 5.14 and 11.8 cSt @ 100°C, respectively), a high overbased calcium sulfonate detergent, a low overbased calcium sulfonate detergent, medium overbased calcium sulfurized phenate detergent, aminic anti-oxidant, foam inhibitor, and about 2.5 wt. % ethylene carbonated post-treated bis-succinimide dispersant derived from 2300 MW PIB.

Example 1: The cylinder lubricant of Comparative Example A was duplicated except that Example 1 further contained about 1.0 wt. % of a Mannich reaction product (a reaction product of a polyisobutyl- substituted phenol prepared with a 1,000 number average molecular weight polyisobutylene having greater than 70 wt. % methylvinylidene isomer, sodium glycine, and formaldehyde, having about 45 wt. % diluent oil).

Example 2: The cylinder lubricant of Comparative Example A was duplicated except that Example 2 further contained about 5.0 wt. % of a Mannich reaction product

(a reaction product of a polyisobutyl- substituted phenol prepared with a 1,000 number average molecular weight polyisobutylene having greater than 70 wt. % methylvinylidene isomer, sodium glycine, and formaldehyde, having about 45 wt. % diluent oil).

Example 3: A 15BN, SAE 50 viscosity grade fully formulated marine cylinder lubricating oil composition was prepared comprising majority amount of Group I base oil, mixture of XOM Core 150N (1.71 mass%), XOM Core 2500BS (24.64 mass%) and XOM Core 600N (41.21 mass%), a high overbased calcium sulfonate detergent, a low overbased calcium sulfonate detergent, a medium overbased calcium sulfurized phenate detergent, aminic anti-oxidant, foam inhibitor, about 0.19 wt. % ethylene carbonated post-treated bis-succinimide dispersant derived from 2300 MW PIB and about 5.0 wt. % of a Mannich reaction product (a reaction product of a polyisobutyl- substituted phenol prepared with a 1,000 number average molecular weight polyisobutylene having greater than 70 wt. % methylvinylidene isomer, sodium glycine, and formaldehyde, having about 45 wt. % diluent oil).

Example 4: A 25BN, SAE 50 viscosity grade fully formulated marine cylinder lubricating oil composition was prepared comprising majority amount of Group I base oil, mixture of XOM Core 150N (1.83 mass%), XOM Core 2500BS (23.15 mass%) and XOM Core 600N (40.35 mass%), a high overbased calcium sulfonate detergent, a low overbased calcium sulfonate detergent, a medium overbased calcium sulfurized phenate detergent, aminic anti-oxidant, foam inhibitor, about 0.19 wt. % ethylene carbonated post-treated bis-succinimide dispersant derived from 2300 MW PIB and about 5.0 wt. % of a Mannich reaction product (a reaction product of a polyisobutyl- substituted

phenol prepared with a 1,000 number average molecular weight polyisobutylene having greater than 70 wt. % methylvinylidene isomer, sodium glycine, and formaldehyde, having about 45 wt. % diluent oil).

The results of the KHT test and DSC Oxidation Test for the MCL compositions of Comparative Example A and Examples 1-4 of the invention are set forth in Table 1 below.

Table 1

	Comp Ex A	Example 1	Example 2	Example 3	Example 4
KHT @ 280°C, rating	3.5	3.5	8.5	-	-
KHT @ 310°C, rating	Blocked	0.0	0.0	9.5	9.5
KHT @ 320°C, rating	-	-	-	8.5	8.5
DSC, min	23.96	-	27.03	26.45	33.93

As is evident from the results illustrated in Table 1, the marine cylinder lubricating oil compositions containing a Mannich reaction product of a polyisobutyl-substituted phenol prepared with a 1,000 number average molecular weight polyisobutylene having greater than 70 wt. % methylvinylidene isomer, sodium glycine, and formaldehyde exhibited surprisingly better thin film oxidation stability of the test oil, as is evident by the overall higher oxidation induction time, relative to the

comparative example which does not contain the Mannich reaction product. In addition, the marine cylinder lubricating oil compositions containing a Mannich reaction product of a polyisobutyl- substituted phenol prepared with a 1,000 number average molecular weight polyisobutylene having greater than 70 wt. % methylvinylidene isomer, sodium glycine, and formaldehyde exhibited surprisingly better detergency and oxidative stability properties at elevated temperatures, as is evident by their overall higher ratings, over the comparative example.

Examples 5-6, and Comparative Example B

Examples 5-6 and Comparative Example B were prepared and evaluated using the Komatsu Hot Tube (KHT) test, which is a measure of high temperature detergency, and the Differential Scanning Calorimeter (DSC) test which is used to evaluate thin film oxidation stability of test oils.

Comparative Example B: A 30 BN, SAE 50 viscosity grade fully formulated marine cylinder lubricating oil composition was prepared comprising majority amount of Group I base oil (mixture of XOM Core 150N and ESSO Core 2500BS brightstock, having kinematic viscosities of about 5.14 and 31.3 cSt @ 100°C, respectively), a high overbased calcium sulfonate detergent, a medium overbased calcium sulfurized phenate detergent, a medium overbased carboxylate detergent which is a calcium salt of an alkylsubstituted hydroxyaromatic carboxylic acid, a foam inhibitor, and about 2.5 wt. % ethylene carbonated post-treated bis-succinimide dispersant derived from 2300 MW PIB.

Example 5: The cylinder lubricant of Comparative Example B was duplicated except that Example 5 further contained about 1.0 wt. % of a Mannich reaction product

(a reaction product of a polyisobutyl- substituted phenol prepared with a 1,000 number average molecular weight polyisobutylene having greater than 70 wt. % methylvinylidene isomer, sodium glycine, and formaldehyde, having about 45 wt. % diluent oil).

Example 6: The cylinder lubricant of Comparative Example B was duplicated except that Example 6 further contained about 5.0 wt. % of a Mannich reaction product (a reaction product of a polyisobutyl- substituted phenol prepared with a 1,000 number average molecular weight polyisobutylene having greater than 70 wt. % methylvinylidene isomer, sodium glycine, and formaldehyde, having about 45 wt. % diluent oil).

The results of the KHT test and DSC Oxidation Test for the MCL compositions of Comparative Example B and Examples 5 and 6 of the invention are set forth in Table 2 below.

Table 2

	Comp Ex B	Example 5	Example 6
KHT @ 310°C, rating	9.0	9.0	9.0
KHT @ 320°C, rating	9.0	9.0	9.0
KHT @ 325°C, rating	8.5	8.5	9.0
DSC, min	31.35	-	32.26

As is evident from the results illustrated in Table 2, the marine cylinder lubricating oil compositions containing a Mannich reaction product of a polyisobutyl-substituted phenol prepared with a 1,000 number average molecular weight polyisobutylene having greater than 70 wt. % methylvinylidene isomer, sodium glycine, and formaldehyde exhibited surprisingly better thin film oxidation stability of the test oil, as is evident by the overall higher oxidation induction time, relative to the comparative example which does not contain the Mannich reaction product. In addition, the marine cylinder lubricating oil compositions containing a Mannich reaction product of a polyisobutyl-substituted phenol prepared with a 1,000 number average molecular weight polyisobutylene having greater than 70 wt. % methylvinylidene isomer, sodium glycine, and formaldehyde exhibited surprisingly better detergency and oxidative stability properties at the elevated temperature, as is evident by the overall higher

ratings, over the comparative example at a temperature of 325°C. This demonstrates the test oils improved detergency performance at the higher temperature.

Example 7: A 30 BN fully formulated trunk piston lubricating oil composition was prepared comprising majority amount of Group I base oil, a high overbased calcium carboxylate detergent which is a calcium salt of an alkylsubstituted hydroxyaromatic carboxylic acid, a medium overbased calcium carboxylate detergent which is a calcium salt of an alkylsubstituted hydroxyaromatic carboxylic acid, a secondary zinc dithiophosphate, an aminic antioxidant, foam inhibitor, and about 5.0 wt. % of a Mannich reaction product (a reaction product of a polyisobutyl- substituted phenol prepared with a 1,000 number average molecular weight polyisobutylene having greater than 70 wt. % methylvinylidene isomer, sodium glycine, and formaldehyde, having about 45 wt. % diluent oil).

Example 8: A 15 BN fully formulated trunk piston lubricating oil composition was prepared comprising majority amount of Group I base oil, a high overbased calcium carboxylate detergent which is a calcium salt of an alkylsubstituted hydroxyaromatic carboxylic acid, a medium overbased calcium carboxylate detergent, a secondary zinc dithiophosphate, an aminic antioxidant, foam inhibitor, and about 5.0 wt. % of a Mannich reaction product (a reaction product of a polyisobutyl- substituted phenol prepared with a 1,000 number average molecular weight polyisobutylene having greater than 70 wt. % methylvinylidene isomer, sodium glycine, and formaldehyde, having about 45 wt. % diluent oil).

Examples 7-8

Examples 7 and 8 were prepared and evaluated using the Komatsu Hot Tube (KHT) test, which is a measure of high temperature detergency, and Black Sludge

Deposit (BSD) test which is used to evaluate detergency of the oils. The results are set forth in Table 3 below.

Table 3

	Example 7	Example 8
KHT @ 310°C, rating	8.5	8.5
BSD, mg deposits	1.1	1.7

As is evident from the results illustrated in Table 3, the marine trunk piston lubricating oil compositions containing a Mannich reaction product of a polyisobutyl-substituted phenol prepared with a 1,000 number average molecular weight polyisobutylene having greater than 70 wt. % methylvinylidene isomer, sodium glycine, and formaldehyde exhibited good detergency performance as demonstrated in both the KHT and BSD tests.

For the avoidance of doubt, the present application is directed to the subject-matter described in the following numbered paragraphs:

1. A marine diesel lubricating oil composition comprising:
 - (a) a major amount of an oil of lubricating viscosity; and
 - (b) about 0.1 wt. % to about 10 wt. % actives, based on the total weight of the lubricating oil composition, of at least one Mannich reaction product prepared by the condensation of a polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl group is derived from polyisobutene containing at least about 70 wt. %

methylvinyldiene isomer and has a number average molecular weight of from about 400 to about 2500, an aldehyde, an amino acid or ester derivative thereof, and an alkali metal base;

wherein the lubricating oil composition has a BN of 5 to 200 mg KOH/g, and further wherein the marine diesel lubricating oil composition is a monograde lubricating oil composition meeting the specifications for SAE J300 revised January 2015 requirements for a SAE 20, SAE 30, SAE 40, SAE 50 or SAE 60 monograde lubricating oil.

2. The marine diesel lubricating oil composition according to numbered paragraph 1, wherein the BN is between 5 to 150 mg KOH/g, between 5 to 100 mg KOH/g, between 5 to 75 mg KOH/g, between 5 to 70 mg KOH/g, between 5 to 60 mg KOH/g, between 5 to 50 mg KOH/g, between 5 to 40 mg KOH/g, between 5 to 35 mg KOH/g, between 5 to 30 mg KOH/g, between 5 to 25 mg KOH/g, between 5 to 20 mg KOH/g, or between 5 to 15 mg KOH/g.

3. The marine diesel lubricating oil composition according to numbered paragraph 1, wherein (b) includes about 0.5 wt. % to about 10 wt. % actives, about 1 wt. % to about 10 wt. % actives, about 2 wt. % to about 8 wt. % actives, about 2 wt. % to about 6 wt. % actives, or about 2.5 wt. % to about 5.5 wt. % actives, based on the total weight of the lubricating oil composition, of the at least one Mannich reaction product.

4. The marine diesel lubricating oil composition according to numbered paragraph 1 further including a detergent selected from sulfonates, phenates, naphthenates, carboxylates, salicylates, or any combination thereof.

5. A marine trunk piston engine oil lubricating oil composition comprising:

- (a) a major amount of an oil of lubricating viscosity; and
- (b) about 0.1 wt. % to about 10 wt. % actives, based on the total weight of the marine trunk piston engine lubricating oil composition, of at least one Mannich reaction product prepared by the condensation of a polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl group is derived from polyisobutene containing at least about 70 wt. % methylvinylidene isomer and has a number average molecular weight of from about 400 to about 2500, an aldehyde, an amino acid or ester derivative thereof, and an alkali metal base;

wherein the marine trunk piston engine lubricating oil composition has a TBN of 10 to 80 mg KOH/g, and further wherein the marine trunk piston engine oil lubricating oil composition is a monograde lubricating oil composition meeting the specifications for SAE J300 revised January 2015 requirements for a SAE 30, or SAE 40 monograde lubricating oil.

6. The marine trunk piston engine oil lubricating oil composition according to numbered paragraph 5, wherein the BN is between 10 to 75 mg KOH/g, between 10 to 70 mg KOH/g, between 10 to 65 mg KOH/g, between 10 to 60 mg KOH/g, between 10 to 55 mg KOH/g, between 10 to 50 mg KOH/g, between 10 to 45 mg KOH/g, between

10 to 40 mg KOH/g, between 10 to 35 mg KOH/g, between 10 to 30 mg KOH/g, between 10 to 25 mg KOH/g, between 10 to 20 mg KOH/g, or between 10 to 15 mg KOH/g.

7. The marine trunk piston engine oil lubricating oil composition according to numbered paragraph 5, wherein (b) includes about 0.5 wt. % to about 10 wt. % actives, about 1 wt. % to about 10 wt. % actives, about 2 wt. % to about 8 wt. % actives, about 2 wt. % to about 6 wt. % actives, or about 2.5 wt. % to about 5.5 wt. % actives, based on the total weight of the lubricating oil composition, of the at least one Mannich reaction product.

8. The marine trunk piston engine oil lubricating oil composition according to numbered paragraph 5 further including a detergent selected from sulfonates, phenates, naphthenates, carboxylates, salicylates, or any combination thereof.

9. A marine system lubricating oil composition comprising:

- (a) a major amount of an oil of lubricating viscosity; and
- (b) about 0.1 wt. % to about 10 wt. % actives, based on the total weight of the marine system lubricating oil composition, of at least one Mannich reaction product prepared by the condensation of a polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl group is derived from polyisobutene containing at least about 70 wt. % methylvinylidene isomer and has a number average

molecular weight of from about 400 to about 2500, an aldehyde, an amino acid or ester derivative thereof, and an alkali metal base;

wherein the marine system oil lubricating oil composition has a TBN of 5 to 40 mg KOH/g, and further wherein the marine system oil lubricating oil composition is a monograde lubricating oil composition meeting the specifications for SAE J300 revised January 2015 requirements for a SAE 20, SAE 30 or SAE 40 monograde lubricating oil.

10. The marine system lubricating oil composition according to numbered paragraph 9, wherein (b) includes about 0.5 wt. % to about 10 wt. % actives, about 1 wt. % to about 10 wt. % actives, about 2 wt. % to about 8 wt. % actives, about 2 wt. % to about 6 wt. % actives, or about 2.5 wt. % to about 5.5 wt. % actives, based on the total weight of the lubricating oil composition, of the at least one Mannich reaction product.

11. The marine system lubricating oil composition according to numbered paragraph 9 further including a detergent selected from sulfonates, phenates, naphthenates, carboxylates, salicylates, or any combination thereof.

12. A marine diesel cylinder lubricating oil composition comprising:

- (a) a major amount of an oil of lubricating viscosity; and
- (b) about 0.1 wt. % to about 10 wt. % actives, based on the total weight of the marine diesel cylinder lubricating oil composition, of at least one Mannich reaction product prepared by the condensation of a

polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl group is derived from polyisobutene containing at least about 70 wt. % methylvinylidene isomer and has a number average molecular weight of from about 400 to about 2500, an aldehyde, an amino acid or ester derivative thereof, and an alkali metal base;

wherein the marine diesel cylinder lubricating oil composition has a TBN of 5 to 200 mg KOH/g, and further wherein the marine diesel cylinder lubricating oil composition is a monograde lubricating oil composition meeting the specifications for SAE J300 revised January 2015 requirements for a SAE 30, SAE 40, SAE 50 or SAE 60 monograde lubricating oil.

13. The marine diesel cylinder lubricating oil composition according to numbered paragraph 12, wherein the BN is between 5 to 150 mg KOH/g, between 5 to 100 mg KOH/g, between 5 to 75 mg KOH/g, between 5 to 70 mg KOH/g, between 5 to 60 mg KOH/g, between 5 to 50 mg KOH/g, between 5 to 40 mg KOH/g, between 5 to 35 mg KOH/g, between 5 to 30 mg KOH/g, between 5 to 25 mg KOH/g, between 5 to 20 mg KOH/g, or between 5 to 15 mg KOH/g.

14. The marine diesel cylinder lubricating oil composition according to numbered paragraph further including a detergent selected from sulfonates, phenates, naphthenates, carboxylates, salicylates or any combination thereof.

15. The marine diesel cylinder lubricating oil composition according to numbered paragraph 12, wherein (b) includes about 0.5 wt. % to about 10 wt. % actives,

about 1 wt. % to about 10 wt. % actives, about 2 wt. % to about 8 wt. % actives, about 2 wt. % to about 6 wt. % actives, or about 2.5 wt. % to about 5.5 wt. % actives, based on the total weight of the lubricating oil composition, of the at least one Mannich reaction product.

16. A marine diesel cylinder lubricating oil composition comprising:

- (a) a major amount of an oil of lubricating viscosity; and
- (b) about 0.1 wt. % to about 10 wt. % actives, based on the total weight of the marine diesel cylinder lubricating oil composition, of at least one Mannich reaction product prepared by the condensation of a polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl group is derived from polyisobutene containing at least about 70 wt. % methylvinylidene isomer and has a number average molecular weight of from about 400 to about 2500, an aldehyde, an amino acid or ester derivative thereof, and an alkali metal base;

wherein the marine diesel cylinder lubricating oil composition has a TBN of 5 to 40 mg KOH/g, and further wherein the marine diesel cylinder lubricating oil composition is a monograde lubricating oil composition meeting the specifications for SAE J300 revised January 2015 requirements for a SAE 30, SAE 40, SAE 50 or SAE 60 monograde lubricating oil.

17. The marine diesel cylinder lubricating oil composition according to numbered paragraph 16, wherein (b) includes about 0.5 wt. % to about 10 wt. % actives, about 1 wt. % to about 10 wt. % actives, about 2 wt. % to about 8 wt. % actives, about

2 wt. % to about 6 wt. % actives, or about 2.5 wt. % to about 5.5 wt. % actives, based on the total weight of the lubricating oil composition, of the at least one Mannich reaction product.

18. The marine diesel cylinder lubricating oil composition according to numbered paragraph 16, further including a detergent selected from sulfonates, phenates, naphthenates, carboxylates, salicylates or any combination thereof.

WHAT IS CLAIMED IS:

1. A marine diesel lubricating oil composition comprising:

- (a) a major amount of an oil of lubricating viscosity; and
- (b) 0.1 wt. % to 10 wt. % actives, based on the total weight of the lubricating oil composition, of at least one Mannich reaction product prepared by the condensation of a polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl group is derived from polyisobutene containing at least 70 wt. % methylvinylidene isomer and has a number average molecular weight of from 400 to 2500, an aldehyde, an amino acid or ester derivative thereof, and an alkali metal base;

wherein the lubricating oil composition has a Base Number (BN) of 5 to 200 mg KOH/g, and further wherein the marine diesel lubricating oil composition is a monograde lubricating oil composition meeting the specifications for SAE J300 revised January 2015 requirements for a SAE 20, SAE 30, SAE 40, SAE 50 or SAE 60 monograde lubricating oil.

2. The marine diesel lubricating oil composition according to claim 1, wherein the BN is between 5 to 150 mg KOH/g, between 5 to 100 mg KOH/g, between 5 to 75 mg KOH/g, between 5 to 70 mg KOH/g, between 5 to 60 mg KOH/g, between 5 to 50 mg KOH/g, between 5 to 40 mg KOH/g, between 5 to 35 mg KOH/g, between 5 to 30 mg KOH/g, between 5 to 25 mg KOH/g, between 5 to 20 mg KOH/g, or between 5 to 15 mg KOH/g.

3. The marine diesel lubricating oil composition according to claim 1 or claim 2, wherein (b) includes 0.5 wt. % to 10 wt. % actives, 1 wt. % to 10 wt. % actives, 2 wt. % to 8

wt. % actives, 2 wt. % to 6 wt. % actives, or 2.5 wt. % to 5.5 wt. % actives, based on the total weight of the lubricating oil composition, of the at least one Mannich reaction product.

4. The marine diesel lubricating oil composition according to any one of the preceding claims, further including a detergent selected from sulfonates, phenates, naphthenates, carboxylates, salicylates, or any combination thereof.

5. A marine trunk piston engine oil lubricating oil composition comprising:

- (a) a major amount of an oil of lubricating viscosity; and
- (b) 0.1 wt. % to 10 wt. % actives, based on the total weight of the marine trunk piston engine lubricating oil composition, of at least one Mannich reaction product prepared by the condensation of a polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl group is derived from polyisobutene containing at least 70 wt. % methylvinylidene isomer and has a number average molecular weight of from 400 to 2500, an aldehyde, an amino acid or ester derivative thereof, and an alkali metal base;

wherein the marine trunk piston engine lubricating oil composition has a Total Base Number (TBN) of 10 to 80 mg KOH/g, and further wherein the marine trunk piston engine oil lubricating oil composition is a monograde lubricating oil composition meeting the specifications for SAE J300 revised January 2015 requirements for a SAE 30, or SAE 40 monograde lubricating oil.

6. The marine trunk piston engine oil lubricating oil composition according to claim 5, wherein the BN is between 10 to 75 mg KOH/g, between 10 to 70 mg KOH/g, between 10

to 65 mg KOH/g, between 10 to 60 mg KOH/g, between 10 to 55 mg KOH/g, between 10 to 50 mg KOH/g, between 10 to 45 mg KOH/g, between 10 to 40 mg KOH/g, between 10 to 35 mg KOH/g, between 10 to 30 mg KOH/g, between 10 to 25 mg KOH/g, between 10 to 20 mg KOH/g, or between 10 to 15 mg KOH/g.

7. The marine trunk piston engine oil lubricating oil composition according to claim 5 or claim 6, wherein (b) includes 0.5 wt. % to 10 wt. % actives, 1 wt. % to 10 wt. % actives, 2 wt. % to 8 wt. % actives, 2 wt. % to 6 wt. % actives, or 2.5 wt. % to 5.5 wt. % actives, based on the total weight of the lubricating oil composition, of the at least one Mannich reaction product.

8. The marine trunk piston engine oil lubricating oil composition according to any one of claims 5-7, further including a detergent selected from sulfonates, phenates, naphthenates, carboxylates, salicylates, or any combination thereof.

9. A marine system lubricating oil composition comprising:

- (a) a major amount of an oil of lubricating viscosity; and
- (b) 0.1 wt. % to 10 wt. % actives, based on the total weight of the marine system lubricating oil composition, of at least one Mannich reaction product prepared by the condensation of a polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl group is derived from polyisobutene containing at least 70 wt. % methylvinylidene isomer and has a number average molecular weight of from 400 to 2500, an aldehyde, an amino acid or ester derivative thereof, and an alkali metal base;

wherein the marine system oil lubricating oil composition has a TBN of 5 to 40 mg KOH/g, and further wherein the marine system oil lubricating oil composition is a monograde lubricating oil composition meeting the specifications for SAE J300 revised January 2015 requirements for a SAE 20, SAE 30 or SAE 40 monograde lubricating oil.

10. The marine system lubricating oil composition according to claim 9, wherein (b) includes 0.5 wt. % to 10 wt. % actives, 1 wt. % to 10 wt. % actives, 2 wt. % to 8 wt. % actives, 2 wt. % to 6 wt. % actives, or 2.5 wt. % to 5.5 wt. % actives, based on the total weight of the lubricating oil composition, of the at least one Mannich reaction product.

11. The marine system lubricating oil composition according to claim 9 or claim 10, further including a detergent selected from sulfonates, phenates, naphthenates, carboxylates, salicylates, or any combination thereof.

12. A marine diesel cylinder lubricating oil composition comprising:

- (a) a major amount of an oil of lubricating viscosity; and
- (b) 0.1 wt. % to 10 wt. % actives, based on the total weight of the marine diesel cylinder lubricating oil composition, of at least one Mannich reaction product prepared by the condensation of a polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl group is derived from polyisobutene containing at least 70 wt. % methylvinylidene isomer and has a number average molecular weight of from 400 to 2500, an aldehyde, an amino acid or ester derivative thereof, and an alkali metal base;

wherein the marine diesel cylinder lubricating oil composition has a TBN of 5 to 200 mg KOH/g, and further wherein the marine diesel cylinder lubricating oil composition

is a monograde lubricating oil composition meeting the specifications for SAE J300 revised January 2015 requirements for a SAE 30, SAE 40, SAE 50 or SAE 60 monograde lubricating oil.

13. The marine diesel cylinder lubricating oil composition according to claim 12, wherein the BN is between 5 to 150 mg KOH/g, between 5 to 100 mg KOH/g, between 5 to 75 mg KOH/g, between 5 to 70 mg KOH/g, between 5 to 60 mg KOH/g, between 5 to 50 mg KOH/g, between 5 to 40 mg KOH/g, between 5 to 35 mg KOH/g, between 5 to 30 mg KOH/g, between 5 to 25 mg KOH/g, between 5 to 20 mg KOH/g, or between 5 to 15 mg KOH/g.

14. The marine diesel cylinder lubricating oil composition according to claim 12 or claim 13, further including a detergent selected from sulfonates, phenates, naphthenates, carboxylates, salicylates or any combination thereof.

15. The marine diesel cylinder lubricating oil composition according to any one of claims 12-14, wherein (b) includes 0.5 wt. % to 10 wt. % actives, 1 wt. % to 10 wt. % actives, 2 wt. % to 8 wt. % actives, 2 wt. % to 6 wt. % actives, or 2.5 wt. % to 5.5 wt. % actives, based on the total weight of the lubricating oil composition, of the at least one Mannich reaction product.

16. A marine diesel cylinder lubricating oil composition comprising:

- (a) a major amount of an oil of lubricating viscosity; and
- (b) 0.1 wt. % to 10 wt. % actives, based on the total weight of the marine diesel cylinder lubricating oil composition, of at least one Mannich reaction

product prepared by the condensation of a polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl group is derived from polyisobutene containing at least 70 wt. % methylvinylidene isomer and has a number average molecular weight of from 400 to 2500, an aldehyde, an amino acid or ester derivative thereof, and an alkali metal base;

wherein the marine diesel cylinder lubricating oil composition has a TBN of 5 to 40 mg KOH/g, and further wherein the marine diesel cylinder lubricating oil composition is a monograde lubricating oil composition meeting the specifications for SAE J300 revised January 2015 requirements for a SAE 30, SAE 40, SAE 50 or SAE 60 monograde lubricating oil.

17. The marine diesel cylinder lubricating oil composition according to claim 16, wherein (b) includes 0.5 wt. % to 10 wt. % actives, 1 wt. % to 10 wt. % actives, 2 wt. % to 8 wt. % actives, 2 wt. % to 6 wt. % actives, or 2.5 wt. % to 5.5 wt. % actives, based on the total weight of the lubricating oil composition, of the at least one Mannich reaction product.

18. The marine diesel cylinder lubricating oil composition according to claim 16 or claim 17, further including a detergent selected from sulfonates, phenates, naphthenates, carboxylates, salicylates or any combination thereof.