

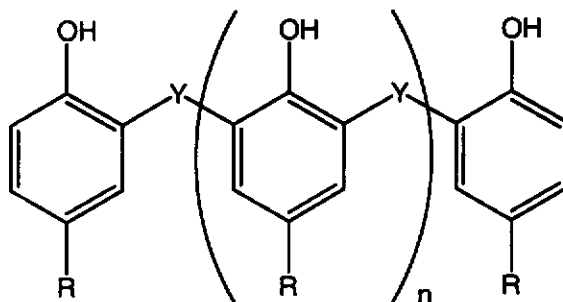
Lubricating Oil Compositions

This invention concerns lubricating oil compositions, in particular, lubricating oil compositions for use in marine diesel engines such as marine diesel cylinder engines.

Lubricating oil compositions for use in marine diesel cylinder engines are known as marine diesel cylinder lubricant ('MDCL') compositions. They are total loss lubricants and their purpose is to provide a strong oil film between the cylinder liner and the piston rings. Marine diesel cylinder lubricant compositions need to withstand high operating temperatures and pressures, such as, for example, temperatures of 300°C and above and firing pressures of 150 bar and above. If the lubricant composition breaks down under these high operating temperatures and pressures, the internal walls of the cylinder liner will be subjected to excessive adhesive wear (i.e. scuffing).

The aim of the present invention is to provide a lubricating oil composition for a marine crosshead diesel engine. A further aim of the present invention is to provide a marine diesel lubricating oil composition that exhibits good resistance to high temperatures and pressures, such as, for example, temperatures as high as 300°C and above and pressures as high as 150 bar and above, and can provide improved protection against scuffing of the cylinder liners.

In accordance with the present invention there is provided use of an oil-soluble hydrocarbyl phenol aldehyde condensate as an antiwear additive in a lubricating oil composition, the oil-soluble hydrocarbyl phenol aldehyde condensate having the following structure:



wherein n is 0 to 10, preferably 1 to 8, more preferably 2 to 6, and most preferably 3 to 5; Y is a divalent bridging group, and is preferably a hydrocarbyl group, preferably having from 1 to 4 carbon atoms; and R is a hydrocarbyl group having from 4 to 30, preferably 8 to 18, and most preferably 9 to 15 carbon atoms.

5

The inventors have surprisingly found that the use of an oil-soluble hydrocarbyl phenol aldehyde condensate in a lubricating oil composition reduces wear in a marine diesel engine. The wear is preferably adhesive wear. The marine diesel engine is preferably a marine diesel cylinder engine.

10

The hydrocarbyl phenol aldehyde condensate is preferably a hydrocarbyl phenol formaldehyde condensate. The hydrocarbyl phenol aldehyde condensate is preferably metal-free. The hydrocarbyl phenol aldehyde condensate is preferably sulphur-free.

15

The term "hydrocarbyl" as used herein means that the group concerned is primarily composed of hydrogen and carbon atoms and is bonded to the remainder of the molecule via a carbon atom, but does not exclude the presence of other atoms or groups in a proportion insufficient to detract from the substantially hydrocarbon characteristics of the group. The hydrocarbyl group is preferably composed of only hydrogen and carbon atoms. Advantageously, the hydrocarbyl group is an aliphatic group, preferably alkyl or alkylene group, especially alkyl groups, which may be linear or branched. R is preferably an alkyl or alkylene group. R is preferably branched.

25

In accordance with the present invention, there is also provided a method of improving the wear reducing properties of a lubricating oil composition, the method including the step of adding the hydrocarbyl phenol aldehyde condensate defined above to the lubricating oil composition.

30

The lubricating oil composition preferably has a TBN of greater than 55, more preferably greater than 60, even more preferably greater than 65, as determined by ASTM D2896.

The hydrocarbyl phenol aldehyde condensate preferably has a weight average molecular weight (Mw) in the range of 800 to 4500, preferably 1100 to 4200, more preferably 1300 to 4000, most preferably 1700 to 3800, as measured by MALDI-TOF (Matrix Assisted Laser Desorption Ionization- Time of Flight) Mass

5 Spectrometry.

The hydrocarbyl phenol aldehyde condensate is preferably obtainable by the condensation reaction between at least one aldehyde or ketone or reactive equivalent thereof and at least one hydrocarbyl phenol, in the presence of an acid catalyst such as, for example, an alkyl benzene sulphonic acid. The product is preferably subjected to stripping to remove any unreacted hydrocarbyl phenol, preferably to less than 5.0% by mass, more preferably to less than 3.0% by mass, even more preferably to less than 1.0% by mass, of unreacted hydrocarbyl phenol. Most preferably, the product includes less than 0.5%, such as, for
15 example, less than 0.1%, by mass of unreacted hydrocarbyl phenol.

Although a basic catalyst can be used, an acid catalyst is preferred. The acid catalyst may be selected from a wide variety of acidic compounds such as, for example, phosphoric acid, sulphuric acid, sulphonic acid, oxalic acid and
20 hydrochloric acid. The acid may also be present as a component of a solid material such as an acid treated clay. The amount of catalyst used may vary from 0.05 to 10% or more, such as for example 0.1 to 1%, by mass of the total reaction mixture.

25 In particular, the hydrocarbyl phenol aldehyde condensate is preferably branched dodecyl phenol formaldehyde condensate, such as, for example, a tetrapropenyl phenol formaldehyde condensate.

The hydrocarbyl phenol aldehyde condensate is preferably used in the lubricating oil composition in an amount ranging from 0.1 to 20 mass%, more preferably from
30 0.2 to 15 mass%, even more preferably from 0.5 to 12 mass%, and most preferably from 1 to 10 mass%, based on the mass of the lubricating oil composition.

The lubricating oil composition includes an oil of lubricating viscosity.

Oil of Lubricating Viscosity

5 The oil of lubricating viscosity (sometimes referred to as lubricating oil) may be any oil suitable for the lubrication of a marine diesel engine. The lubricating oil may suitably be an animal, a vegetable or a mineral oil. Suitably the lubricating oil is a petroleum-derived lubricating oil, such as a naphthenic base, paraffinic base or mixed base oil. Alternatively, the lubricating oil may be a synthetic lubricating
10 oil. Suitable synthetic lubricating oils include synthetic ester lubricating oils, which oils include diesters such as di-octyl adipate, di-octyl sebacate and tridecyl adipate, or polymeric hydrocarbon lubricating oils, for example liquid polyisobutene and poly-alpha olefins. Commonly, a mineral oil is employed. The lubricating oil may generally comprise greater than 60, typically greater than 70,
15 mass% of the composition, and typically have a kinematic viscosity at 100°C of from 2 to 40, for example for 3 to 15, mm^2s^{-1} and a viscosity index of from 80 to 100, for example from 90 to 95.

Another class of lubricating oils is hydrocracked oils, where the refining process
20 further breaks down the middle and heavy distillate fractions in the presence of hydrogen at high temperatures and moderate pressures. Hydrocracked oils typically have a kinematic viscosity at 100°C of from 2 to 40, for example from 3 to 15, mm^2s^{-1} and a viscosity index typically in the range of from 100 to 110, for example from 105 to 108.

25 The term 'brightstock' as used herein refers to base oils which are solvent-extracted, de-asphalted products from vacuum residuum generally having a kinematic viscosity at 100°C of from 28 to 36 mm^2s^{-1} and are typically used in a proportion of less than 30, preferably less than 20, more preferably less than 15,
30 most preferably less than 10, such as less than 5, mass%, based on the mass of the composition.

Preferably, the oil of lubricating viscosity is present in the lubricating oil composition in an amount greater than 40 mass%, more preferably greater than

50 mass%, more preferably greater than 60 mass%, and most preferably greater than 65 mass%, based on the mass of the lubricating oil composition.

Detergents

5

The lubricating oil composition preferably includes at least one metal-containing detergent. A detergent is an additive that reduces formation of piston deposits, for example high-temperature varnish and lacquer deposits, in engines; it has acid-neutralizing properties and is capable of keeping finely divided solids in suspension. It is based on metal "soaps", that is metal salts of acidic organic compounds, sometimes referred to as surfactants.

10

The detergent comprises a polar head with a long hydrophobic tail. The polar head comprises a metal salt of a surfactant. Large amounts of a metal base are included by reacting an excess of a metal compound, such as an oxide or hydroxide, with an acidic gas such as carbon dioxide to give an overbased detergent which comprises neutralized detergent as the outer layer of a metal base (e.g. carbonate) micelle.

15

The metal may be an alkali or alkaline earth metal such as, for example, sodium, potassium, lithium, calcium, barium and magnesium. Calcium is preferred.

20

The surfactant may be a salicylate, a sulphonate, a carboxylate, a phenate, a thiophosphate or a naphthenate. Metal salicylate is the preferred metal salt.

25

The detergent may be a complex/hybrid detergent prepared from a mixture of more than one metal surfactant, such as a calcium alkyl phenate and a calcium alkyl salicylate. Such a complex detergent is a hybrid material in which the surfactant groups, for example phenate and salicylate, are incorporated during the overbasing process. Examples of complex detergents are described in the art (see, for example, WO 97/46643, WO 97/46644, WO 97/46645, WO 97/46646 and WO 97/46647).

30

Surfactants for the surfactant system of the metal detergents contain at least one hydrocarbyl group, for example, as a substituent on an aromatic ring. The term "hydrocarbyl" as used herein means that the group concerned is primarily composed of hydrogen and carbon atoms and is bonded to the remainder of the molecule via a carbon atom, but does not exclude the presence of other atoms or groups in a proportion insufficient to detract from the substantially hydrocarbon characteristics of the group. Advantageously, hydrocarbyl groups in surfactants for use in accordance with the invention are aliphatic groups, preferably alkyl or alkylene groups, especially alkyl groups, which may be linear or branched. The total number of carbon atoms in the surfactants should be at least sufficient to impact the desired oil-solubility. Advantageously the alkyl groups include from 5 to 100, preferably from 9 to 30, more preferably 14 to 20, carbon atoms. Where there is more than one alkyl group, the average number of carbon atoms in all of the alkyl groups is preferably at least 9 to ensure adequate oil-solubility.

The detergents may be non-sulphurized or sulphurized, and may be chemically modified and/or contain additional substituents. Suitable sulphurizing processes are well known to those skilled in the art.

The detergents may be borated, using borating processes well known to those skilled in the art.

The detergents preferably have a TBN of 50 to 500, preferably 100 to 400, and more preferably 150 to 350.

The detergents may be used in a proportion in the range of 0.5 to 30, preferably 2 to 20, or more preferably 5 to 19, mass% based on the mass of the lubricating oil composition.

Dispersants

The lubricant composition preferably includes at least one dispersant. A dispersant is an additive for a lubricating composition whose primary function in lubricants is to accelerate neutralization of acids by the detergent system.

A noteworthy class of dispersants are "ashless", meaning a non-metallic organic material that forms substantially no ash on combustion, in contrast to metal-containing, hence ash-forming, materials. Ashless dispersants comprise a long chain hydrocarbon with a polar head, the polarity being derived from inclusion of, e.g., an O, P or N atom. The hydrocarbon is an oleophilic group that confers oil-solubility, having for example 40 to 500 carbon atoms. Thus, ashless dispersants may comprise an oil-soluble polymeric hydrocarbon backbone having functional groups that are capable of associating with particles to be dispersed.

Examples of ashless dispersants are succinimides, e.g. polyisobutene succinic anhydride; and polyamine condensation products that may be borated or unborated.

The dispersants may be used in a proportion in the range of 0 to 10.0, preferably 0.5 to 6.0, or more preferably 1.0 to 5.0, mass% based on the mass of the lubricating oil composition.

Antiwear Additives

The lubricating oil composition may include at least one further antiwear additive. Dihydrocarbyl dithiophosphate metal salts constitute a preferred class of antiwear additive. The metal in the dihydrocarbyl dithiophosphate metal may be an alkali or alkaline earth metal, or aluminium, lead, tin, molybdenum, manganese, nickel or copper. Zinc salts are preferred, preferably in the range of 0.1 to 1.5, preferably 0.5 to 1.3, mass%, based upon the total mass of the lubricating oil composition. They may be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohol or a phenol with P_2S_5 and then neutralizing the formed DDPA with a zinc

compound. For example, a dithiophosphoric acid may be made by reacting mixtures of primary and secondary alcohols. Alternatively, multiple dithiophosphoric acids can be prepared comprising both hydrocarbyl groups that are entirely secondary in character and hydrocarbyl groups that are entirely primary in character. To make the zinc salt, any basic or neutral zinc compound may be used but the oxides, hydroxides and carbonates are most generally employed. Commercial additives frequently contain an excess of zinc due to use of an excess of the basic zinc compound in the neutralization reaction.

- 10 The preferred zinc dihydrocarbyl dithiophosphates are oil-soluble salts of dihydrocarbyl dithiophosphoric acids and may be represented by the following formula:



15

where R and R¹ may be the same or different hydrocarbyl radicals containing from 1 to 18, preferably 2 to 12, carbon atoms and including radicals such as alkyl, alkenyl, aryl, arylalkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R and R¹ groups are alkyl groups of 2 to 8 carbon atoms. Thus, the radicals may, for example, be ethyl, n-propyl, l-propyl, n-butyl, l-butyl, sec-butyl, amyl, n-hexyl, l-hexyl, n-octyl, decyl, dodecyl, octadecyl, 2-ethylehexyl, phenyl, butylphenyl, cyclohexyl, methylcyclopentyl, propenyl, butenyl. In order to obtain oil-solubility, the total number of carbon atoms (i.e. in R and R¹) in the dithiophosphoric acid will generally be 5 or greater. The zinc dihydrocarbyl dithiophosphate can therefore comprise zinc dialkyl dithiophosphates.

25

The further antiwear additive may be used in a proportion in the range of 0.1 to 1.5, preferably 0.2 to 1.3, or more preferably 0.3 to 0.8, mass% based on the mass of the lubricating oil composition.

30

The lubricating oil composition may also include at least one of the following additives: an antioxidant, a pour point depressant, an antifoaming agent, a viscosity index improver, a dye, a metal deactivator, a demulsifier, or a mixture thereof.

It may be desirable, although not essential, to prepare one or more additive packages or concentrates comprising the additive or additives, which can be added simultaneously to the oil of lubricating viscosity (or base oil) to form the lubricating oil composition. Dissolution of the additive package(s) into the lubricating oil may be facilitated by solvents and by mixing accompanied with mild heating, but this is not essential. The additive package(s) will typically be formulated to contain the additive(s) in proper amounts to provide the desired concentration, and/or to carry out the intended function in the final formulation when the additive package(s) is/are combined with a predetermined amount of base lubricant. The additive package may contain active ingredients in an amount, based on the additive package, of, for example, from 2.5 to 90, preferably from 5 to 75, most preferably from 8 to 60, mass% of additives in the appropriate proportions, the remainder being base oil.

The final formulations may typically contain about 5 to 40 mass% of the additive packages(s), the remainder being base oil.

The term 'active ingredient' (a.i.) as used herein refers to the additive material that is not diluent.

The term 'oil-soluble' as used herein does not necessarily indicate that the compounds or additives are soluble in the base oil in all proportions. It does mean, however, that it is, for instance, soluble in oil to an extent sufficient to exert the intended effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular additive, if desired.

The lubricant compositions of this invention comprise defined individual (i.e. separate) components that may or may not remain the same chemically before and after mixing.

The following examples illustrate, but in no way limit, the invention.

EXAMPLES

Preparation of Hydrocarbyl Phenol Aldehyde Condensates

5

Reaction Components

	Hydrocarbyl Phenol Aldehyde Condensates			
	1158 Mw	1663 Mw	1839 Mw	3692 Mw
Dodecylphenol	2200 g	2200 g	2200 g	2200 g
Sulphonic Acid Catalyst	22 g	22 g	22 g	22 g
Paraformaldehyde	170g	209g	221g	330g
Water	550 g	550 g	550 g	550 g
Heptane	831 g	831 g	831 g	831 g

Method

10

Add the dodecylphenol, sulphonic acid catalyst, paraformaldehyde, water and heptane to a 5L baffled reactor with stirrer (200 rpm), nitrogen blanket (600ml/min), condenser, Dean and Stark trap, a temperature controlling system, and Cardice/Acetone trap vacuum system. Heat the reaction components from ambient to 80°C over 30 minutes, then heat further from 80 to 100°C over 2 hours and remove water by azeotropic distillation. Remove residual heptane and dodecyl phenol from the reaction mixture under reduced pressure at 200°C. Finally, decrease the temperature to 120°C and add an appropriate quantity of ESN 150 to produce a product with the desired polymer concentration. (Mw refers to weight average molecular weight.)

20

Lubricating Oil Compositions

The following lubricating oil compositions were prepared and tested using the HFRR test.

25

The HFRR or High Frequency Reciprocating Rig Test is a computer controlled reciprocating oscillatory friction and wear test system for the wear testing of lubricants under boundary lubrication conditions. An electromagnetic vibrator oscillates a steel ball over a small amplitude while pressing it with a load of 10N against a stationary steel disk. The lower, fixed disk is heated electrically and is fixed below the lubricant under test. The temperature is ramped from 80°C to 380°C in 15 minutes. The lubricity of the fluid is evaluated by measuring the wear scar on the steel ball in micrometres at the end of test. The lower the wear scar on the steel ball, the better the anti-wear protection of the lubricant when two metal surfaces are experiencing boundary lubrication conditions. In addition, as the temperature is ramped from 80 to 380°C, the friction coefficient does not increase as long as satisfactory oil film exists between the two metal surfaces. At a certain temperature, the friction coefficient starts increasing sharply, indicating that the oil film is breaking down and the metal surfaces are experiencing direct contact to an extent to cause the friction coefficient to start increasing with temperature. The higher the temperature at which this turning point in the friction coefficient occurs, the better the protection of the cylinder liner from adhesive wear.

High Temperature HFRR: improved wear protection

Formulation	Comparative Example 1	Comparative Example 2	Comparative Example 3	Example 1
410BN Calcium sulphonate/phenate	14.00	14.00	14.00	14.00
258BN Calcium phenate	5.00	5.00	5.00	5.00
Highly borated dispersant	3.00	3.00	3.00	3.00
Primary ZDDP	0.50	0.50	0.50	0.50
C12 branched alkyl phenol		3.00		
Sulphurised C12 branched alkyl phenol			3.00	
Phenol aldehyde condensate, Mw 1663				3.00
Base oil	77.5	74.5	74.5	74.5
Kinematic viscosity @ 100C, cSt	19.00	17.79	18.98	19.45
Base number, D2896, mgKOH/g	71.1	79.9	71.6	71.8
HFRR wear scar average, μm .	201.5	242	207	194

Formulation	Comparative Example 1	Comparative Example 4	Comparative Example 5	Example 2
410BN Calcium sulphonate/phenate	14.00	14.00	14.00	14.00
258BN Calcium phenate	5.00	5.00	5.00	5.00
Highly borated dispersant	3.00	3.00	3.00	3.00
Primary ZDDP	0.50	0.50	0.50	0.50
C12 branched alkyl phenol		8.00		
Sulphurised branched alkyl phenol			8.00	
Phenol aldehyde condensate, Mw 1863				8.00
Base oil	77.5	69.5	69.5	69.5
Kinematic viscosity @ 100C, cSt	19.00	16.85	19.20	20.54
Base number, D2896, mgKOH/g	71.1	79.0	72.4	72.6
HFRR wear scar average, μm	201.5	227.5	212.5	197.5

As shown above, examples 1 and 2 exhibit less wear in the HFRR test than comparative examples 1-5.

The following examples show the use of phenol aldehyde condensates with different weight average molecular weights (Mw):

10

Formulation	Example 3	Example 4	Example 5
410BN Calcium sulphonate/phenate detergent	17.40	17.40	17.40
Borated dispersant	3.00	3.00	3.00
Antirust agent, p-nonyl phenoxy tetra ethoxy ethanol	0.80	0.80	0.80
Phenol aldehyde condensate, Mw 1158	8.00		
Phenol aldehyde condensate, Mw 1839		8.00	
Phenol aldehyde condensate, Mw 3692			8.00
Base oil	70.80	70.80	70.80
Kinematic viscosity @ 100C, cSt	20.73	21.95	23.17
Base number, D2896, mgKOH/g	73.87	73.57	72.09
HFRR, temperature of minimum friction coefficient, $^{\circ}\text{C}$	223.3	238.5	258.3

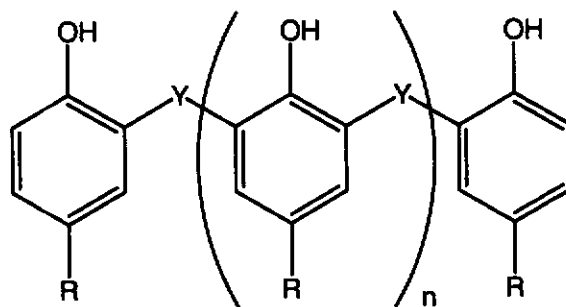
Formulation	Example 6	Example 7	Example 8
410BN Calcium sulphate/phenate detergent	17.40	17.40	17.40
Borated dispersant	3.00	3.00	3.00
Antirust agent, p-nonyl phenoxy tetra ethoxy ethanol	0.80	0.80	0.80
Phenol aldehyde condensate, Mw 1158	3.00		
Phenol aldehyde condensate, Mw 1839		3.00	
Phenol aldehyde condensate, Mw 3692			3.00
Base oil	75.8	75.8	75.8
Kinematic viscosity @ 100C, cSt	19.30	19.83	20.53
Base number, D2896, mgKOH/g	73.31	73.05	73.35
HFRR, temperature of minimum friction coefficient, °C	221.6	228.5	249.7

Formulation	Example 9	Example 10	Example 11
410BN Calcium sulphate/phenate detergent	14.00	14.00	14.00
258BN Calcium phenate	5.00	5.00	5.00
Borated dispersant	3.00	3.00	3.00
Primary ZDDP	0.50	0.50	0.50
Phenol aldehyde condensate, Mw 1158	3.00		
Phenol aldehyde condensate, Mw 1839		3.00	
Phenol aldehyde condensate, Mw 3692			3.00
Base oil	74.5	74.5	74.5
Kinematic viscosity @ 100C, cSt	19.25	19.70	20.02
Base number, D2896, mgKOH/g	72.21	71.76	72.25
HFRR, temperature of minimum friction coefficient, °C	362.8	363.1	375.1

The above tables show that as the weight average molecular weight (Mw) of the phenol aldehyde condensate increases, so does the temperature of minimum friction coefficient (°C).

CLAIMS

1. Use of an oil-soluble hydrocarbyl phenol aldehyde condensate as an antiwear additive in a lubricating oil composition, the oil-soluble hydrocarbyl phenol aldehyde condensate having the following structure:



wherein n is 0 to 10, preferably 1 to 8, more preferably 2 to 6, and most preferably 3 to 5; Y is a divalent bridging group, and is preferably a hydrocarbyl group, preferably having from 1 to 4 carbon atoms; and R is a hydrocarbyl group having from 4 to 30, preferably 8 to 18, and most preferably 9 to 15 carbon atoms.

2. The use as claimed in claim 1, wherein the lubricating oil composition is for use in a marine diesel engine.

3. The use as claimed in claims 1 or 2, wherein the hydrocarbyl phenol aldehyde condensate has a number average molecular weight (M_w) in the range of 800 to 4500, preferably 1100 to 4200, more preferably 1300 to 4000, most preferably 1700 to 3800, as measured by MALDI-TOF (Matrix Assisted Laser Desorption Ionization- Time of Flight) Mass Spectrometry.

4. The use as claimed in any one of the preceding claims, wherein the condensate includes less than 5.0% mass, more preferably less than 3.0% mass, even more preferably to less than 1.0% by mass, of unreacted hydrocarbyl phenol.

5. The use as claimed in any one of the preceding claims, wherein the hydrocarbyl phenol aldehyde condensate is obtainable by the condensation reaction between at least one aldehyde or ketone or reactive equivalent thereof and a hydrocarbyl phenol, in the presence of an acid catalyst.

6. The use as claimed in any one of the preceding claims, wherein the hydrocarbyl group in the hydrocarbyl phenol aldehyde condensate is branched.
7. The use as claimed in any one of the preceding claims, wherein the hydrocarbyl phenol aldehyde condensate is a hydrocarbyl phenol formaldehyde condensate.
8. The use as claimed in any one of the preceding claims, wherein the hydrocarbyl phenol aldehyde condensate is tetrapropenyl phenol formaldehyde condensate.
9. The use as claimed in any one of the preceding claims, wherein the lubricating oil composition includes at least one of the following additives: a detergent, a dispersant, an antioxidant, an antiwear additive, a pour point depressant, an antifoaming agent, a viscosity index improver, a dye, a metal deactivator, a demulsifier, or a mixture thereof.
10. A method of improving the wear reducing properties of a lubricating oil composition, the method including the step of adding the hydrocarbyl phenol aldehyde condensate defined in any one of claims 1-7 to the lubricating oil composition.