

MARINE ENGINE LUBRICATION

FIELD OF THE INVENTION

This invention relates to a method for improving asphaltene dispersancy in a trunk piston marine engine.

This invention also relates to use of a detergent system for improving asphaltene dispersancy in a trunk piston marine engine.

This invention also relates to the use of a detergent system comprising a combination of hydroxybenzoates in a trunk piston marine engine lubricating composition for a medium-speed four-stroke compression-ignited (diesel) marine engine to improve the asphaltene dispersancy performance of the composition.

BACKGROUND OF THE INVENTION

Marine trunk piston engines generally use Heavy Fuel Oil ('HFO') for offshore running. Heavy Fuel Oil is the heaviest fraction of petroleum distillate and comprises a complex mixture of molecules including up to 15% of asphaltenes, defined as the fraction of petroleum distillate that is insoluble in an excess of aliphatic hydrocarbon (e.g. heptane) but that is soluble in aromatic solvents (e.g. toluene). Asphaltenes can enter the engine lubricant as contaminants either via the cylinder or the fuel pumps and injectors, and asphaltene precipitation can then occur, manifested in 'black paint' or 'black sludge' in the engine. The presence of such carbonaceous deposits on a piston surface can act as an insulating layer which can result in the formation of cracks that then propagate through the piston. If a crack travels through the piston, hot combustion gases can enter the crankcase, possibly resulting in a crankcase explosion.

It is therefore highly desirable that trunk piston engine oils ('TPEO's) prevent or inhibit asphaltene precipitation.

EP-B-1992 678 describes trunk piston engine oils that contain combinations of overbased alkylsalicylic acid calcium salts for improving wear properties. No mention is made of asphaltene dispersancy.

It is now found that, by using certain hydroxybenzoate combinations in a TPEO, it is possible to achieve improved asphaltene dispersancy properties.

SUMMARY OF THE INVENTION

A first aspect of the invention is a method for improving asphaltene dispersancy in a trunk piston marine engine, the method comprising lubricating the engine with a lubricating oil composition comprising a detergent system that includes (i) an overbased alkyl-substituted hydroxybenzoate calcium salt of TBN less than 250, which alkyl group has 20-28 carbon atoms, and (ii) an overbased alkyl-substituted hydroxybenzoate calcium salt of TBN less than 250, which alkyl group has 14-18 carbon atoms; the wt% Ca ratio of (ii) to (i) being greater than one.

A second aspect of the invention is the use of a detergent system that includes (i) an overbased alkyl-substituted hydroxybenzoate calcium salt of TBN less than 250, which alkyl group has 20-28 carbon atoms, in a trunk piston marine lubricating oil composition for a medium-speed compression-ignited marine engine during operation of the engine, where the detergent system further comprises (ii) an overbased alkyl-substituted hydroxybenzoate calcium salt of TBN less than 250, which alkyl group has 14-18 carbon atoms, the wt% Ca ratio of (ii) to (i) being greater than one, said use being to improve the asphaltene dispersancy performance of the composition.

A third aspect of the invention is the use of a detergent system that includes (i) an overbased alkyl-substituted hydroxybenzoate calcium salt of TBN less than 250, which alkyl group has 20-28 carbon atoms, in a trunk piston marine lubricating oil composition for a medium-speed compression-ignited marine engine during operation of the engine, fueled by a heavy fuel oil, and its lubrication by the composition, where the detergent system further comprises (ii) an overbased alkyl-substituted hydroxybenzoate calcium salt of TBN less than 250, which alkyl group has 14-18

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carbon atoms, the wt% Ca ratio of (ii) to (i) being greater than one, said use being to improve the asphaltene dispersancy performance of the composition in comparison with that of analogous operation using a detergent system whose wt% Ca ratio is one or less and/or where (ii) has a TBN of 250 or greater.

In this specification, the following words and expressions, if and when used, have the meanings ascribed below:

“active ingredients” or “(a.i.)” refers to additive material that is not diluent or solvent;

“comprising” or any cognate word specifies the presence of stated features, steps, or integers or components, but does not preclude the presence or addition of one or more other features, steps, integers, components or groups thereof; the expressions “consists of” or “consists essentially of” or cognates may be embraced within “comprises” or cognates, wherein “consists essentially of” permits inclusion of substances not materially affecting the characteristics of the composition to which it applies;

“major amount” means 50 mass % or more of a composition, preferably 40 mass % or more of a composition, more preferably 30 mass % or more of a composition;

“minor amount” means less than 50 mass % of a composition, preferably less than 40 mass % of a composition, more preferably less than 30 mass % of a composition;

“TBN” means total base number as measured by ASTM D2896.

Furthermore in this specification, if and when used:

“calcium content” is as measured by ASTM 4951;

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“phosphorus content” is as measured by ASTM D5185;

“sulphated ash content” is as measured by ASTM D874;

“sulphur content” is as measured by ASTM D2622;

“KV100” means kinematic viscosity at 100°C as measured by ASTM D445.

Also, it will be understood that various components used, essential as well as optimal and customary, may react under conditions of formulation, storage or use and that the invention also provides the product obtainable or obtained as a result of any such reaction.

Further, it is understood that any upper and lower quantity, range and ratio limits set forth herein may be independently combined.

DETAILED DESCRIPTION OF THE INVENTION

The features of the invention will now be discussed in more detail below.

OIL OF LUBRICATING VISCOSITY

The trunk piston marine lubricating oil composition of the invention comprises a major amount of an oil of lubricating viscosity. That may range in viscosity from light distillate mineral oils to heavy lubricating oils. Such oil may be referred to as base oil. Generally, the viscosity of the oil ranges from 2 to 40 mm²/sec, as measured at 100°C. The oil may be a natural or a synthetic oil.

Natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil); liquid petroleum oils and hydrotreated, solvent-treated or acid-treated mineral oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale may also be used.

Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymers of olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes)); alkybenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulphides and derivative, analogues and homologues thereof.

Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic lubricating oils. These may be exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide, and the alkyl and aryl ethers of polyoxyalkylene polymers (e.g., methyl-polyiso-propylene glycol ether having a molecular weight of 1000 or diphenyl ether of poly-ethylene glycol having a molecular weight of 1000 to 1500); and mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C₃-C₈ fatty acid esters and C₁₃ oxo acid diester of tetraethylene glycol.

Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Specific examples of such esters includes 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, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

Esters useful as synthetic oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

Silicon-based oils such as polyalkyl-, polyaryl-, polyalkoxy- or polyaryloxysilicone oils and silicate oils comprise another useful class of synthetic oils; such oils include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl)silicate, tetra-(4-methyl-2-ethylhexyl)silicate, tetra-(p-tert-butyl-phenyl)silicate, hexa-(4-methyl-2-ethylhexyl)disiloxane, poly(methyl)siloxanes and poly(methylphenyl)siloxanes. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

Unrefined, refined and re-refined oils can be used in lubricants of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations; petroleum oil obtained directly from distillation; or ester oil obtained directly from esterification and used without further treatment, are unrefined oils. Refined oils are similar to unrefined oils except that the oil is further treated in one or more purification steps to improve one or more properties. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration and percolation, are known to those skilled in the art. Re-refined oils are obtained by processes similar to those used to provide refined oils but begin with oil that has already been used in service. Such re-refined oils are also known as reclaimed or reprocessed oils and are often subjected to additional processing using techniques for removing spent additives and oil breakdown products.

The American Petroleum Institute (API) publication "Engine Oil Licensing and Certification System", Industry Services Department, Fourteenth Edition, December 1996, Addendum 1, December 1998 categorizes base stocks as follows:

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- a) Group I base stocks contain less than 90 percent saturates and/or greater than 0.03 percent sulphur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table E-1.
- b) Group II base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulphur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table E-1.
- c) Group III base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulphur and have a viscosity index greater than or equal to 120 using the test methods specified in Table E-1.
- d) Group IV base stocks are polyalphaolefins (PAO).
- e) Group V base stocks include all other base stocks not included in Group I, II, III, or IV.

Analytical Methods for Base Stock are tabulated below (Table E-1):

PROPERTY	TEST METHOD
Saturates	ASTM D 2007
Viscosity Index	ASTM D 2270
Sulphur	ASTM D 2622
	ASTM D 4294
	ASTM D 4927
	ASTM D 3120

By way of example, the present invention embraces Group II, Group III and Group IV basestocks and also basestocks derived from hydrocarbons synthesised by the Fischer-Tropsch process. In the Fischer-Tropsch process, synthesis gas containing carbon monoxide and hydrogen (or 'syngas') is first generated and then converted to hydrocarbons using a Fischer-Tropsch catalyst. These hydrocarbons typically require

further processing in order to be useful as a base oil. For example, they may, by methods known in the art, be hydroisomerized; hydrocracked and hydroisomerized; dewaxed; or hydroisomerized and dewaxed. The syngas may, for example, be made from gas such as natural gas or other gaseous hydrocarbons by steam reforming, when the resulting basestock may be referred to as gas-to-liquid ("GTL") base oil; or from gasification of biomass, when the resulting basestock may be referred to as biomass-to-liquid ("BTL" or "BMTL") base oil; or from gasification of coal, when the resulting basestock may be referred to as coal-to-liquid ("CTL") base oil.

Preferably, the oil of lubricating viscosity in this invention contains 50 mass % or more of a basestock containing 50 mass % or more of a basestock containing greater than or equal to 90 % saturates and less than or equal to 0.03 % sulphur or a mixture thereof. Preferably, it contains 60, such as 70, 80 or 90, mass % or more of the defined basestock or a mixture thereof. The oil of lubricating viscosity may be substantially all of the defined basestock or a mixture thereof.

Most preferably, the oil of lubricating viscosity in this invention contains 50 mass % or more of a basestock containing 50 mass % or more of a basestock containing less than 90% saturates and greater than 0.03 % sulphur or a mixture thereof. Preferably, it contains 60, such as 70, 80 or 90, mass % or more of the defined basestock or a mixture thereof. The oil of lubricating viscosity may be substantially all of the defined basestock or a mixture thereof.

The composition may have a TBN in the range of 20-60, preferably 25-55.

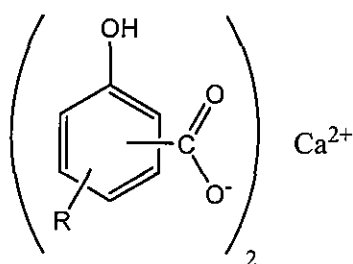
DETERGENT SYSTEM

A metal detergent is an additive based on so-called metal "soaps", that is metal salts of acidic organic compounds, sometimes referred to as surfactants. They generally comprise a polar head with a long hydrophobic tail. Overbased metal detergents, which comprise neutralized metal detergents as the outer layer of a metal base (e.g. carbonate) micelle, may be provided by including large amounts of metal

base by reacting an excess of a metal base, such as an oxide or hydroxide, with an acidic gas such as carbon dioxide.

In the present invention, detergents (i) and (ii) of the invention are overbased alkyl-substituted hydroxybenzoate calcium salts, preferably alkyl-substituted salicylate calcium salts.

A salicylate detergent of such a system typically has the structure shown:



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

In (i), R has 20-28, preferably 20-24, carbon atoms. In (ii), R has 14-18 carbon atoms. Each of (i) and (ii) may be mixtures.

Salicylic acids are typically prepared by the carboxylation, by the Kolbe-Schmitt process, of phenoxides, and in that case, will generally be obtained (normally in a diluent) in admixture with uncarboxylated phenol. Salicylic acids may be non-sulphurized or sulphurized, and may be chemically modified and/or contain additional substituents. Processes for sulphurizing an alkyl salicylic acid are well known to those skilled in the art and are described, for example, in US 2007/0027057.

The term "overbased" is generally used to describe metal detergents in which the ratio of the number of equivalents of the metal moiety to the number of equivalents of the acid moiety is greater than one. The term 'low-based' is used to

describe metal detergents in which the equivalent ratio of metal moiety to acid moiety is greater than 1, and up to about 2.

The basicity of the detergents may be expressed as a total base number (TBN). A total base number is the amount of acid needed to neutralize all of the basicity of the overbased material. The TBN may be measured using ASTM standard D2896 or an equivalent procedure. The detergents, as stated, each have a TBN of below 250; for example the TBN is in the range of 60 to 250, preferably 150 to 250.

The wt % Ca ratio of (ii) to (i) is as stated greater than one, for example in the range of 1 to 50, preferably 1 to 3.

The treat rate of the detergent system contained in the lubricating oil composition may for example be in the range of 1 to 25, preferably 2 to 20, more preferably 5 to 18, mass %.

CO-ADDITIVES

The lubricating oil composition of the invention may comprise further additives, different from and additional to the detergent system. Such additional additives may, for example include ashless dispersants, other metal detergents, anti-wear agents such as zinc dihydrocarbyl dithiophosphates, anti-oxidants and demulsifiers. In some cases, an ashless dispersant need not be provided.

It may be desirable, although not essential, to prepare one or more additive packages or concentrates comprising the additives, whereby the detergent system can be added simultaneously to the 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 oil. Thus, the detergent system, in accordance with the

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present invention, may be admixed with small amounts of base oil or other compatible solvents together with other desirable additives to form additive packages containing 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 as a trunk piston engine oil may typically contain 30, preferably 10 to 28, more preferably 12 to 24, mass % of the additive package(s), the remainder being base oil.

The present invention is illustrated by but in no way limited to the following examples.

EXAMPLES

COMPONENTS

The following components were used:

Detergent (ii):

A: a calcium alkylsalicylate detergent of TBN 225 and whose alkyl group has 14-18 carbon atoms.

B: a calcium alkylsalicylate detergent of TBN 350 whose alkyl group has 14-18 carbon atoms.

C: a calcium alkylsalicylate detergent of TBN 64 and whose alkyl group has 14-18 carbon atoms.

Detergent (i): a calcium alkylsalicylate detergent of TBN 223 whose alkyl group has 20-24 carbon atoms

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Base oil I: solvent-extracted API Group I base oil

HFO: a heavy fuel oil (ISO-F-RMK 380)

LUBRICANTS

Selections of the above components were blended to give a range of trunk piston marine engine lubricants. Some of the lubricants are examples of the invention; others are reference examples for comparison purposes. The compositions of the lubricants tested are shown in the tables below under the “Results” heading. Each lubricant had a TBN of about 40. Each lubricant also contained the same amount of HFO.

TESTING**Light Scattering**

Test lubricants were evaluated for asphaltene dispersancy using light scattering according to the Focused Beam Reflectance Method (“FBRM”), which predicts asphaltene agglomeration and hence ‘black sludge’ formation.

The FBRM test method was disclosed at the 7th International Symposium on Marine Engineering, Tokyo, 24th - 28th October 2005, and was published in ‘The Benefits of Salicylate Detergents in TPEO Applications with a Variety of Base Stocks’, in the Conference Proceedings. Further details were disclosed at the CIMAC Congress, Vienna, 21st -24th May 2007 and published in “Meeting the Challenge of New Base Fluids for the Lubrication of Medium Speed Marine Engines – An Additive Approach” in the Congress Proceedings. In the latter paper it is disclosed that by using the FBRM method it is possible to obtain quantitative results for asphaltene dispersancy that predict performance for lubricant systems based on base stocks containing greater than or less than 90% saturates, and greater than or less than

0.03% sulphur. The predictions of relative performance obtained from FBRM were confirmed by engine tests in marine diesel engines.

The FBRM probe contains fibre optic cables through which laser light travels to reach the probe tip. At the tip, an optic focuses the laser light to a small spot. The optic is rotated so that the focussed beam scans a circular path between the window of the probe and the sample. As particles flow past the window, they intersect the scanning path, giving backscattered light from the individual particles.

The scanning laser beam travels much faster than the particles; this means that the particles are effectively stationary. As the focussed beam reaches one edge of the particle the amount of backscattered light increases; the amount will decrease when the focussed beam reaches the other edge of the particle.

The instrument measures the time of the increased backscatter. The time period of backscatter from one particle is multiplied by the scan speed and the result is a distance or chord length. A chord length is a straight line between any two points on the edge of a particle. This is represented as a chord length distribution, a graph of numbers of chord lengths (particles) measured as a function of the chord length dimensions in microns. As the measurements are performed in real time, the statistics of a distribution can be calculated and tracked. FBRM typically measures tens of thousands of chords per second, resulting in a robust number-by-chord length distribution. The method gives an absolute measure of the particle size distribution of the asphaltene particles.

The Focused beam Reflectance Probe (FBRM), model Lasentec D600L, was supplied by Mettler Toledo, Leicester, UK. The instrument was used in a configuration to give a particle size resolution of 1 μm to 1mm. Data from FBRM can be presented in several ways. Studies have suggested that the average counts per second can be used as a quantitative determination of asphaltene dispersancy. This value is a function of both the average size and level of agglomerate. In this application, the average count rate (over the entire size range) was monitored using a measurement time of 1 second per sample.

The test lubricant formulations were heated to 60°C and stirred at 400rpm; when the temperature reached 60°C the FBRM probe was inserted into the sample. An aliquot of heavy fuel oil (10% w/w) was introduced into the lubricant formulation under stirring using a four-blade stirrer (at 400 rpm). A value for the average counts per second was taken when the count rate had reached an equilibrium value (typically after 30 minutes).

RESULTS

Light Scattering

The results of the FBRM tests are summarized in TABLE 1 below, where lower particle count indicates better performance.

Example 1 is an example of the invention and Examples A-F are comparison examples.

RESULTS

Example	C ₁₄₋₁₈ alkyl salicylate (225) (ii) A	C ₁₄₋₁₈ alkyl salicylate (350) (ii) B	C ₁₄₋₁₈ alkyl salicylate (64) (ii) C	C ₂₀₋₂₄ alkyl salicylate (223) (i)	Ca ratio (ii) to (i)	Lasentec Count
1	10.00	-	-	7.90	1.28	40.1
A	-	8.40	-	5.00	2.65	377.7
B	-	6.00	-	8.50	1.11	333.8
C	-	3.00	-	13.00	0.36	700.2
D	-	-	-	17.94	-	243.4
E	5.00	8.30	-	-	-	1037.6
F	-	9.80	10.00	-	-	187.8

Numbers in parentheses after the salicylate are TBN's.

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As shown above, the lowest Lasentec count is achieved by the use of Example 1 which falls within the invention. (Lower particle count indicates better performance.)

CLAIMS

1. A method for improving asphaltene dispersancy in a trunk piston marine engine, the method comprising lubricating the engine with a lubricating oil composition comprising a detergent system that includes (i) an overbased alkyl-substituted hydroxybenzoate calcium salt of TBN less than 250, which alkyl group has 20-28 carbon atoms, and (ii) an overbased alkyl-substituted hydroxybenzoate calcium salt of TBN less than 250, which alkyl group has 14-18 carbon atoms; the wt% Ca ratio of (ii) to (i) being greater than one.
2. The method of claim 1, where the hydroxybenzoates, (i) and (ii), are each salicylates.
3. The method of claims 1 or 2, where the alkyl group(s) of (i) has 20-24 carbon atoms.
4. The method of any claims 1-3, where the composition has a TBN in the range of 20-60, preferably 25-55.
5. The method of any one of claims 1-4, where the wt% Ca ratio is in the range 1 to 50, preferably 1 to 3.
6. The method of any one of claims 1-5, where the composition comprises an oil of a lubricating viscosity, in a major amount, containing 50 mass% or more of a basestock containing less than 90% saturates and/or greater than 0.03 percent sulphur.
7. The method of any one of claims 1-5, where the composition comprises an oil of a lubricating viscosity, in a major amount, containing 50 mass% or more of a basestock containing greater than or equal to 90% saturates and less than or equal to 0.03% sulphur.

8. The use of a detergent system that includes (i) an overbased alkyl-substituted hydroxybenzoate calcium salt of TBN less than 250, which alkyl group has 20-28 carbon atoms, in a trunk piston marine lubricating oil composition for a medium-speed compression-ignited marine engine during operation of the engine, where the detergent system further comprises (ii) an overbased alkyl-substituted hydroxybenzoate calcium salt of TBN less than 250, which alkyl group has 14-18 carbon atoms, the wt% Ca ratio of (ii) to (i) being greater than one, said use being to improve the asphaltene dispersancy performance of the composition.
9. The use of a detergent system that includes (i) an overbased alkyl-substituted hydroxybenzoate calcium salt of TBN less than 250, which alkyl group has 20-28 carbon atoms, in a trunk piston marine lubricating oil composition for a medium-speed compression-ignited marine engine during operation of the engine, fueled by a heavy fuel oil, and its lubrication by the composition, where the detergent system further comprises (ii) an overbased alkyl-substituted hydroxybenzoate calcium salt of TBN less than 250, which alkyl group has 14-18 carbon atoms, the wt% Ca ratio of (ii) to (i) being greater than one, said use being to improve the asphaltene dispersancy performance of the composition in comparison with that of analogous operation using a detergent system whose wt% Ca ratio is one or less and/or where (ii) has a TBN of 250 or greater.