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NON-ASH CONTAINING LUBRICATING OIL COMPOSITIONS

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This invention relates to improved lubricating oil compositions possessing multifunctional properties. More particularly the invention relates to mineral lubricating oils useful in the lubrication of engines operating over wide temperature ranges and under extreme pressures and other adverse conditions.

It is known that lubricating oils containing certain metallic salts or soaps such as metal sulfonates possess good dispersing and detergent properties. Such lubricants, however, tend to form metallic deposits in engine parts which interfere with the effective operation of the engine. As a result, recent trends in this field have been to the use of non-ash forming basic and essentially neutral nitrogen-containing dispersants of high molecular weight such as copolymers of polymerizable amines or amides with long-chain acrylate esters and available commercially under the trade names of LOA–564 or 565, Acryloid 315X, 917 or 966 or certain rather high molecular weight amines, amides and/or imines derivatives of high molecular weight alkenyl maleic anhydride or the like. These non-ash forming nitrogen-containing compounds are excellent detergents but under extreme pressure conditions exhibit a lack of stability and wear inhibiting properties and are non-resistant in combating sludge and corrosion. Attempts to overcome the deficiencies of these polymeric detergent materials either by modifying the polymers or using auxiliary additives has met with little success. In most cases the auxiliary additives which appear to be promising stabilizers and wear inhibitors are metal-containing compounds such as metal sulfonates or metal carboxylates and these are to be avoided for reasons stated. Also these materials tend to complex and form sludge.

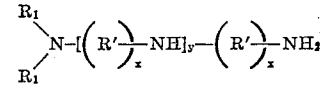
It is an object of the present invention to provide an improved non-ash forming lubricating oil composition. It is another object of the invention to provide an improved detergent lubricant possessing good stability and antiwear properties. Still another object of the invention is to provide a corrosion and sludge resistant non-ash containing or forming lubricating oil composition. Other objects will become apparent during the following description of the invention.

Now in accordance with the present invention, it has been found that stability, as well as sludge, wear and corrosion inhibiting properties can be imparted to lubricating oils by incorporating thereon small amounts of each of certain non-ash forming nitrogen-containing detergents selected from the group consisting of (I) (A) an oil-soluble amino-imide of a long-chain monosubstituted polymeric hydrocarbyl succinic anhydride and (B) full or partial amino-amides or polyamine salts of long-chain monosubstituted polymeric hydrocarbyl succinic anhydride and (II) oil-soluble bisphenols. To this additive combination of (I) and (II) can be incorporated (III) partial or full esters of organic phosphates, phosphites, phosphonates, phosphonites and their thio derivatives. In compounds of (I) by long-chain hydrocarbyl is meant an olefinic polymer straight or branch chain and derived from olefins of from 2 to 8 carbon atoms such as ethylene, propylene, 1-butene, isobutene, 1-hexene, styrenes, and copolymers thereof, from 20 to 500 carbon atoms and a molecular weight of 300 to 5000, preferably from 800 to 1500.

It is surprising to find that the bisphenols which will be hereinbelow fully described, and which are known for their antioxidant properties should in combination with the detergents of this invention impart to them properties not exhibited by the bisphenols when used along or when also aided by he presence of esters of phosphorus as described.

The olefinic polymer present as an oil-solubilizing substituent and detergent aid of the nitrogen-containing compounds of the present invention may be prepared by any known means provided it is within the molecular weight range indicated above. Examples of such polymers include polyethylene, polypropylene, polybutene, polyisobutylene, copolymer of ethylene/propylene, copolymer of ethylene/isobutylene, copolymer of ethylene/α-methylstyrene and the like. Monoalkylation of maleic anhydride with the above type olefinic polymers may also be made by conventional means known in the art, preferably in the absence of a catalyst and at temperatures ranging from about 300° F. to 600° F., preferably between 350° F. and 450° F. The mole ratio of the polyolefin to maleic anhydride may vary from 1:1 to 1:10, preferably from 1:1 to 1:5 respectively.

The amines used to form the compounds of (I) (A) namely the succinimides of the compounds or (I) (B), namely the full or partial amides or amine salts of the monosubstituted polymeric hydrocarbyl succinic anhydride can be represented by the formula



where the R_1's can be hydrogen or the same or different C_{1-6} alkyl and/or aryl radicals and R' is an alkylene radical of from 1 to 8, preferably 1 to 4 carbon atoms. Examples of such amines are alkylene polyamines such as ethylene diamine, diethylene triamine, triethylene tetramine, 1-methyl ethylene diamine, 1-ethyl ethylene diamine, propylene diamine, butylene diamine, trimethyl trimethylene diamine, tetramethylene diamine, diaminopentane or pentamethylene diamine, diaminohexane, hexamethylene diamine, heptamethylene diamine, diamino-octane, decamethylene diamine, and the higher homologues up to 18 carbon atoms, phenylene diamine, the alkylated phenylene diamines having nuclear substituents such as methyl, ethyl, propyl, butyl, etc., naphthalene diamine, and the alkylated naphthalene diamines; N,N'-dimethyl ethylene diamine, N,N'-(diethylethylene) diamine, N,N'-(dipropyl)ethylene diamine, N,N'-(2-hydroxypropyl)ethylene diamine, N,N'-(diethylpropylene) diamine, N,N'-(dipropyl)propylene diamine, N,N'-(dimethyl)butylene diamine, N,N'-(diethyl)butylene diamine; penta-(1-methylpropylene)hexamine; tetrabutylenepentamine; hexa-(1,1-dimethylethylene)heptamine; di-(1-methylbutylene)triamine; pentaamylenehexamine; tri-(1,2,2 - trimethylethylene)tetramine; di-(1 - methylamylene)triamine; tetra-(1,3 - dimethylpropylene)pentamine; penta-(1,5-dimethylamylene)hexamine; di-(1 - methyl-4-ethylbutylene)triamine; penta-(1,2-dimethyl-1-isopropylethylene)hexamine; tetraoctylenepentamine and the like.

The polyalkylenepolyamines can be prepared by several methods well known to the art. One well accepted method comprises reacting ammonia with an alkyl, or substituted alkyl, dihalide. For example, tetraethylenepentamine has been prepared by reacting ammonia with ethylene bromide. The preferred polyamines are the ethylene amines such as ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, N-dimethyl aminopropylamine, N-dimethylaminobutylamine, N-diethylaminopropylamine, methylpropylaminoamylamine.

In forming the second stage of the reaction using the

polyamines control of the mole ratio of the monopolyolefinic succinic anhydride and polyamine and the reaction temperature is important to obtaining desired end products of the (I) (A) or (I) (B) type. The mole ratio of the polyamine to the anhydride compound can vary from 0.1:1 to 1:1 respectively. The reaction temperature for formation of compounds (I) (A), the succinimides may vary from 220° F. to 500° F., preferably from 300° F. to 450° F. and in the formation of the compounds (I) (B) as described above the temperature may vary from room temperature to about 300° F., preferably from 100° F. to 300° F.

The invention is illustrated by the following examples in which the percentages are by weight.

EXAMPLE I (TYPE (A) COMPOUND)

250 gms. of polyisobutylene having a molecular weight of 615 and bromine number of 21 was heated to 212° F. and 30 gms. of maleic anhydride was added slowly over a period of 30 minutes. The reactants were heated to 390° F. to 400° F. and maintained at this temperature for four hours and then heated to 440° F. and maintained at this temperature for 16 hours. On cooling, the reactants were dissolved in 1.5 liters of petroleum spirit (60–80° C. B. P.) and filtered. 19 gms. of tetraethylene pentamine was added to the petroleum spirit solution. The petroleum spirit was distilled off and replaced by 1 liter of toluene which was also distilled off to azeotropically remove water, and the residue was heated to 390° F. to 400° F. and maintained at this temperature for three hours.

EXAMPLE II

A mixture of 1000 gms. (1 mole) of a polybutene having a molecular weight of about 1000 and 98 gms. (1 mole) of maleic anhydride was heated at 410° F. in a nitrogen atmosphere with agitation for a period of 24 hours. The reaction mixture was cooled to 150° F. and 700 cc. of hexane added; after which the mixture was filtered under vacuum. After vacuum distillation to remove the hexane from the filtrate, the product was maintained at 350° F. at an absolute pressure of 10 mm. Hg for one hour to remove traces of maleic anhydride. The crude polybutenyl succinic anhydride thus prepared had a saponification number of 79.

EXAMPLE IIA.—PREPARATION OF TETRAETHYLENEPENTAMINE DERIVATIVE OF THE POLYBUTENYL SUCCINIC ANHYDRIDE OF EXAMPLE II HEREINABOVE (TYPE (A) COMPOUND)

A mixture of 84 gms. (0.45 mol) of tetraethylene pentamine and 702 gms. (0.45 mol.) of the polybutenyl succinic anhydride of Example II hereinabove, was blended with agitation at 125° F. in a nitrogen atmosphere. The temperature was increased to 400° F. during a period of one hour, after which the absolute pressure was reduced to about 200 mm. Hg during a period of 30 minutes to facilitate the removal of water. The reaction mixture was then allowed to reach room temperature at this reduced pressure. The reaction product contained 5.1% nitrogen (theory=5.4%). Infra-red analysis showed that the reaction product was an imide containing a polybutene side chain.

EXAMPLE III (TYPE (A) COMPOUND)

A mixture of 21.3 gms. (0.21 mole) of dimethylaminopropylamine and 150 gms. (0.09 mol.) of the polybutenyl succinic anhydride of Example II hereinabove, was blended with agitation in a nitrogen atmosphere, and the mixture was heated at 500° F. for a period of one hour, after which the absolute pressure was reduced to about 200 mm. Hg at this temperature during a period of 30 minutes to facilitate the removal of water and excess amine. The reaction mixture was then allowed to reach room temperature at this reduced pressure. The reaction product contained 1.7% nitrogen (theory=1.8%). The identity of the N-dimethylaminopropylalkenyl succinimide was established by means of infra-red spectroscopy.

EXAMPLE IV (TYPE (B) COMPOUND)

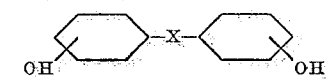
Polyisobutylene succinic anhydride was prepared by reacting a polyisobutylene (M.W. 850) and succinic anhydride at around 400° F. as in Example I. About 500 gms. of polyisobutylene succinic anhydride thus formed was admixed with 50 gms. of diethylene triamine in toluene at ambient temperature. The amine was added in increments and the temperature controlled so as not to rise above about 120° F. The reaction proceeded for 15 to 30 minutes after which the solvent was removed and the end product, a semi-amide of the above reactants, had a nitrogen-content of 1.6%.

Other examples of additives of the present invention include:

1 Olefin-Succinic Anhydride	2 Amine	3 Mole Ratio	4 Temp., °F.	Type of End Product
V. Polyisobutylene (M.W. 850)-succinic anhydride.	Diethylamine propylamine.	1/1	420	(A) Imide.
VI. Polyisobutylene (M.W. 850)-succinic anhydride.	Tetraethylene pentamine.	1.5/1	120	(B) Semi-amide.
VII. Polyethylene/isobutylene (M.W. 1,000)-succinic anhydride.	Dimethylamine propylamine.	1/1	450	(A) Imide.
VIII. Polyethylene/α-methylstyrene (M.W. 800)-succinic anhydride.	Tetraethylene pentamine.	1/1	450	Do.
IX. Polyisobutylene (M.W. 1,000)-succinic anhydride.	Tetraethylene	1/1	120	(B) Amine salt of polyisosuccinic anhydride.

The above described non-ash forming detergents such as monopolyalkylene succinimides according to the invention may be incorporated into lubricating oils in amounts between 0.1% and 10% by weight, preferably between 0.25% and 5% by weight, based on the weight of the oil.

The other essential additives are (II) alkylated bis-phenols which are used in the lubricating oil compositions according to the invention and are preferably alkyl derivatives of bis-phenols having the formula:



wherein X stands for —S—, —S—S—, Se, —S—CH_2—, —CH_2—S—CH_2—, —CHR—, —CR_2—, —$(CH_2)_m$—, —NH—, —O—, and wherein R stands for methyl or ethyl and *m* stands for an integer from 1 to 3. The preferred alkylated bis-phenols are those having a sulfur bridge or a methylene bridge.

The alkylated bis-phenols may contain from 1 to 8 alkyl groups, but preferably they contain from 2 to 6 alkyl groups. Alkylated bis-phenols having 4 alkyl groups are particularly preferred. Each of the alkyl groups may contain from 1 to 10 carbon atoms, preferably 2 to 6

carbon atoms and especially 4 carbon atoms. Furthermore, the alkyl groups contained by any particular bis-phenol may be the same or different and may also be primary, secondary or tertiary alkyl groups. Bis-phenols containing at least one tertiary alkyl group are particularly preferred.

As examples of the alkylated bis-phenols which may be used according to the invention there are mentioned

bis(3-ethyl-4-hydroxyphenyl)disulfide,
bis(3-methyl-4-propyl-5-hydroxyphenyl)disulfide,
bis(2-isopropyl-3-butyl-5-hydroxyphenyl)selenide,
2:2'-diethyl-3-tertiary butyl-4''4'-dihydroxy diphenyl selenide,
bis 1.2(2:6-di-tertiary butyl-4-hydroxyphenyl)thiaethane,
bis 1.2(2:5-di-isopropyl-3-hydroxyphenyl)thiaethane,
bis(3:5-di-tertiary butyl-4-hydroxyphenyl)sulfide,
2:4-di-isobutyl-3-hydroxybenzyl-2':4'-dipropyl-3'-hydroxybenzyl sulfide,
bis 1.2(3-octyl-5-tertiary butyl-4-hydroxyphenyl)ethane,
bis 1.1(2:6-di-isopropyl-4-hydroxyphenyl)ethane,
1.2-bis(2:4-di-tertiary pentyl-3-hydroxyphenyl)propane,
bis 2.2(4:5-di-tertiary butyl-2-hydroxyphenyl)propane,
bis(2-tertiary butyl-5-isopentyl-4-hydroxyphenyl)amine,
bis(3:5-dibutyl-4-hydroxyphenyl)ether,
bis(2:6-dipropyl-4-hydroxyphenyl)ether.

Examples of alkylated bis-phenols having a sulfur bridge are bis(2:5-dipentyl-4-hydroxyphenyl)sulfide,
bis(2:5-dihexyl-3-hydroxyphenyl)sulfide,
bis(2-methyl-5-tertiary butyl-4-hydroxyphenyl)sulfide,
bis(2-methyl-5-tertiary butyl-6-hydroxyphenyl)sulfide and particularly bis(3-tertiary butyl-5-methyl-2-hydroxyphenyl)sulfide.

Examples of alkylated bis-phenols having a methylene bridge are bis(2:3-di-tertiary butyl-4-hydroxyphenyl) methane,
bis(2:5-di-tertiary butyl-4-hydroxyphenyl)methane,
bis(2:6-di-tertiary butyl-4-hydroxyphenyl)methane,
bis(3:5-di-tertiary octyl-4-hydroxyphenyl)methane,
bis(3-tertiary butyl-5-tertiary octyl-4-hydroxyphenyl) methane, and especially
bis(3:5-di-tertiary butyl-4-hydroxyphenyl)methane.

The alkylated bis-phenol may be prepared by any of the methods known in the art of bis-phenol manufacture, for example, by selecting the appropriate alkylated phenols as starting materials and condensing them together by any of the established methods.

The bis-phenols may be used in amounts of from 0.1% to 5%, preferably from 0.5% to 1% by weight.

The lubricating oil compositions according to the invention may be further improved by addition of small amounts of a third additive which are (III) metal-free organic phosphorus-containing compounds such as alkyl, cycloalkyl, alkaryl, aralkyl, and aryl phosphites, phosphates, phosphonates, and their thio-derivatives, such as C_{3-18} alkyl phosphites, e.g. di- and tributyl, octyl, lauryl, stearyl, cyclohexyl, benzyl, cresyl, phenyl phosphites or phosphates, as well as their thio-derivatives: P_2S_5-terpene reaction product, P_2S_5-pine oil reaction product and metal salts thereof such as sodium, potassium, calcium, or barium salts of P_2S_5-terpene reaction product; dibutyl methanephosphonate, dibutyl trichloromethanephosphonate, dibutyl monochloromethanephosphonate, dibutyl chlorobenzenephosphonate, dibutyl monochloromethanephosphonate, dibutyl chlorobenzenephosphonate and the like. The esters of pentavalent phosphorus acids such as diphenyl, dicresyl, triphenyl, tricresyl, trilauryl and tristearyl phosphate, P_2S_5-terpene reaction products and mixtures thereof are preferred.

The phosphorus compounds may be used in amounts of from 0.01% to 5%, preferably from 0.1% to 1% by weight.

Lubricating oils which can be used as base oils for the lubricating oil compositions according to the invention include a wide variety of lubricating oils, such as naphthenic base, paraffin bases, and mixing base lubricating oils, other hydrocarbon lubricants, e.g. lubricating oils derived from coal products, and synthetic oils, e.g., alkylene polymers (such as polymers of propylene, butylene, etc., and the mixtures thereof), alkylene oxide-type polymers (e.g. alkylene oxide polymers prepared by polymerizing the alkylene oxide, e.g. propylene oxide, etc., in the presence of water or alcohols, e.g. ethyl alcohol), dicarboxylic acid esters (e.g. those which are prepared by esterifying such dicarboxylic acids as adipic acid, azelaic acid, suberic acid, sebacic acid, succinic acid, fumaric acid, maleic acid, etc., with alcohols, such as butyl alcohol, hexyl alcohol, 2-ethylhexyl alcohol, dodecyl alcohol, etc.) liquid esters of acids of phosphorus, alkyl benzenes, polyphenyls (e.g. biphenyls and terphenyls), alkyl biphenyl ethers, polymers of silicon (e.g. tetraethyl silicate), tetra-isopropyl silicates, tetra (4-methyl-2-tetraethyl) silicate, hexyl (4-methyl-2-pentoxy) disiloxane, poly(methyl) siloxane, and poly(methylphenyl) siloxane.

The above base oils may be used individually or in combinations thereof, wherever miscible or wherever made so by the use of mutual solvents.

The following non-ash lubricating compositions are representative of the invention.

	Percent
Composition A.	
Example I additive	2
Bis(3,5-ditert-butyl-4-hydroxyphenyl) methane	0.75
Mineral lubricating oil (SAE 20)	Balance
Composition B:	
Example II additive	2
Bis(3,5-ditert-butyl-4-hydroxyphenyl) methane	0.75
Mineral lubricating oil (SAE 20)	Balance
Composition C:	
Example III additive	2
Bis(3,5-ditert-butyl-4-hydroxyphenyl) methane	0.75
Mineral lubricating oil (SAE 20)	Balance
Composition D:	
Example IV additive	2
Bis(3,5-ditert-butyl-4-hydroxyphenyl) methane	0.75
Mineral lubricating oil (SAE 20W–30)	Balance
Composition E:	
Example I additive	2
Bis(3,5-ditert-butyl-4-hydroxyphenyl) methane	0.75
Tricresylphosphate	0.5
Mineral lubricating oil (SAE 20)	Balance
Composition F:	
Example IV additive	2
Bis(3,5-ditert-butyl-4-hydroxyphenyl) methane	0.75
Tricresylphosphate	0.5
Mineral lubricating oil (SAE 20)	Balance
Composition G:	
Example IV additive	1
Bis(3,5-ditert-butyl-4-hydroxyphenyl) methane	0.75
Tricresylphosphate	0.5
Mineral lubricating oil (SAE 20)	Balance
Composition H:	
Example VIII	3
Bis(3,5-ditert-butyl-4-hydroxyphenyl) methane	0.75
Tricresylphosphate	0.80
Dicresyl	0.04
Mineral lubricating oil (SAE 10W–30)	Balance

Tests

Hot-plate test.—A plate 12 inches long and 2.5 inches wide is provided with troughs along its width at top and

bottom for the distribution and collection of oil. The plate is heated to and maintained at a temperature of 270° C. and 500 gms. of lubricating oil is circulated over the plate for six hours maintaining a flow rate of approximately 6.5 mls. per minute. After the test the deposits are scraped from the plate, and washed into a sintered glass filter with petroleum ether. After thorough washing with petroleum ether (boiling range 60° C. to 80° C.). the deposit is dried at 100° C. and weighed after cooling.

This hot-plate test was carried out on a variety of lubricating oil compositions based on an SAE 20 lubricating oil, and the results are tabulated below.

TABLE I.—HOT-PLATE TEST

Base Oil	Additive	Deposit wt. in M gms.
SAE 20	2% Example I additive	198.4
SAE 20	¾% Bis(3,5-ditert-butyl-4-hydroxyphenyl)-methane.	182.0
SAE 20	¾% Bis(3,5-ditert-butyl-4-hydroxyphenyl)-methane plus ¾% tricresylphosphate.	125
SAE 20	Composition A	31.4
SAE 20	Composition E	3.8
SAE 20	Composition F	14.4

Engine test.—A BMC Series B gasoline engine is bench test run over 34 of the following 4-hour cycles.

Period.	Duration	Speed, r.p.m.	B. hp.
1	1 hour	2,000	5
2	15 mins.	3,800	17.5
3	1 hour	600	Idling
4	15 mins.	3,800	17.5
5	1 hour	600	Idling
6	30 mins.	Shut-down with forced cooling	

(Each 4-hour cycle is approximately equivalent to 56 road miles.) The jacket temperature of the engine is controlled at 45° C. and the coolant flow to the sump jacket is controlled so that the sump temperature is 60° C. during period 1 of the cycle.

The engine is charged with 6½ pints of test oil and is checked at the end of every 6th cycle, and, if necessary, more test oil is added to bring the oil level back to the initial setting. No oil check or addition is made at the end of the 30th cycle.

After the 34 4-hour cycles an examination is made of the rocker cover, timing cover and side covers sump. A visual rating from 0 to 10 is made, 10 being perfectly clean and 0 being completely covered by sludge, over ⅛ inch thick.

Various lubricating oils, including a lubricating oil according to the invention were tested by this procedure and the results are given in Table II.

TABLE II.—ENGINE TEST

Base Oil	Additives	Over All Cover	Sump Wall	Sump Sludge
SAE 20	None	3.1	6.6	5
SAE 20	Composition E	8.0	7.9	8

Other additives may also be incorporated into the lubricating composition according to the invention, for example antiscuffing agents, anti-foaming agents, e.g. silicone polymers; viscosity index improvers, for example polymeric acrylic esters; extreme pressure additive, for example dibenzyl disulfide; rust inhibitors, for example sorbitanmonooleates or butyl stearate, oiliness agents, for example acidless tallow, oleic acid and the like.

I claim as my invention:

1. A lubricating composition consisting essentially of a major amount of lubricating oil and from about 0.1% to about 10% by weight of (I) an oil-soluble succinimide of a mono-(C_{20-300} olefinic hydrocarbyl)succinic anhydride and a poly(C_{1-6} alkylene)polyamine having at least 2 amino groups in the molecule, (II) from about 0.1% to about 5% by weight of bis(dialkyl hydroxy phenyl)methane and (III) from about 0.01% to about 5% by weight of tri(monoaryl)phosphate.

2. A lubricating oil composition consisting essentially of a major amount of mineral lubricating oil and from about 0.25% to about 5% by weight of (I) an oil-soluble succinimide of mono-(polyisobutylene) succinic anhydride and tetraethylene pentamine, the polyisobutylene radical having a molecular weight of from 500 to 3000, (II) from about 0.5% to about 1% of bis(dialkylhydroxyphenyl)methane and (III) from about 0.01% to about 5% by weight of tricresyl phosphate.

3. A lubricating oil composition consisting essentially of a major amount of mineral lubricating oil and from about 0.25% to about 5% by weight of (I) an oil-soluble succinimide of mono-(polyisobutylene) succinic anhydride and tetraethylene pentamine, the polyisobutylene radical having a molecular weight of from 500 to 3000, (II) from about 0.5% to about 1% of bis (3,5-ditert-butyl-4-hydroxyphenyl)methane and (III) from about 0.01% to about 5% by weight of tricresyl phosphate.

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