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3,032,502
LUBRICANT COMPOSITIONS

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This invention relates to improvements in lubricating oils, and more particularly relates to hydrocarbon lubricating oils having improved oxidation inhibiting and corrosion inhibiting propertes.

It is known to incorporate in hydrocarbon oil compositions certain types of additives to impart to such oil compositions desired properties. Thus, for example, certain additives are employed to impart oxidation stability to the hydrocarbon oil composition, while other additives are used to impart to such oil compositions rust and/or corrosion inhibiting properties.

It is known, for example, to incorporate in hydrocarbon oils as oxidation stabilizers a small amount of an oil-soluble phenolic compound containing a tertiary aliphatic hydrocarbon radical side chain. Such compounds are suitably condensation products of low-boiling olefins and monohydric phenols and comprise tri-alkylated monohydric phenols having at least one alkyl group of at least three carbon atoms in a position ortho to the hydroxyl group. Illustrative of such compounds are tertiary butyl phenols such as 2,6-di-tertiary butyl-4-methyl phenol (often referred to as di-tertiary butyl-para-cresol), 2,4,6-tri-tertiary-butyl phenol, as well as the corresponding tertiary amyl phenols. While the various members of the defined akylated monohydric phenols are effective antioxidants for hydrocarbon oils, the 2,6-di-tertiary-butyl-4-methyl phenol is the preferred member of the class. The stabilization of liquid hydrocarbons by the herein described alkylated phenols is taught in U.S. 2,031,930, U.S. 2,202,877, 2,809,164 and others.

It is also known to incorporate in hydrocarbon oil compositions additives to impart rust and/or corrosion inhibiting properties to such compositions. Effective rust and/or corrosion inhibitors are oil-soluble or oil-insoluble unsaturated aliphatic dicarboxylic acids having at least about 10 carbon atoms in the aliphatic radical. Exmples of such acids are alkenyl succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid, etc., such as are described in U.S. 2,124,628, U.S. 2,133,734, U.S. 2,442,672, and U.S. 2,452,319.

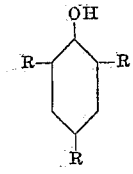
It has been found, however, that when the above described antioxidant of the phenolic compound type is used in combination with the dicarboxylic acid corrosion inhibitor in a hydrocarbon oil, the oxidation-inhibiting effectiveness of the phenolic compound is materially reduced.

It is an object of the present invention, therefore, to provide a non-corrosive hydrocarbon oil composition containing small amounts of a phenolic type antioxidant and a dicarboxylic acid corrosion inhibitor which is resistant to oxidative deterioration. Another object of the invention is to provide a hydrocarbon oil composition which is resistant to oxidative deterioration and which exhibits corrosion and/or rust inhibiting properties. Another object of this invention is to provide a method of increasing the resistance to oxidative deterioration of a hydrocarbon oil composition containing an alkylated phenolic type antioxidant in combination with an aliphatic dicarboxylic acid corrosion inhibitor. Other objects and advantages of this invention will become apparent from the following description thereof.

In accordance with the present invention, the foregoing objects can be attained by providing a hydrocarbon oil

composition comprising a major amount of a hydrocarbon oil containing in combination, from about 0.01% to about 1.0% of an oil-soluble tri-alkylated monohydric phenol as hereinafter described, from about 0.03% to about 0.1% of an oil-soluble or oil-insoluble alkenyl dicarboxylic acid having at least about 10 carbon atoms in the alkenyl radical, and from about 0.03% to about 0.1% of an aromatic amine as described hereinafter. The dicarboxylic acid and the aromatic amine are preferably present in the composition in chemically equivalent amounts.

The phenolic compound stabilizer, as above briefly described, are tri-alkylated monohydric phenols having at least one alkyl radical in a position ortho to the hydroxyl group. The alkyl radicals have up to about 10 carbon atoms and preferably from about 3 to about 8 carbon atoms. The preferred phenolic compounds are 2,4,6-tri-alkylated monohydroxy phenols having in a position ortho the hydroxyl group at least one alkyl radical of three or more carbon atoms, for example, propyl, isoproyl, butyl, secondary butyl, tertiary butyl, amyl, tertiary octyl, etc. The other alkyl radicals can be similar or different, for example, methyl, ethyl or high alkyl radicals. Such phenolic compounds have the general structure



in which R is an alkyl radical of from 1 to about 10 carbon atoms, at least one of which radical in a position ortho to the OH group contains at least three carbon atoms. Specific examples which come within the defined phenolic compounds are: 2-isopropyl-4,6-di-methyl phenol; 2-tert.-butyl-4,6-di-methyl-phenol; 2-tert.-amyl-4,6-di-methyl-phenol; 4-methyl-2,6-di-isopropyl-phenol; 4-methyl-2,6-di-tert.-butyl-phenol; 2,6-di-tert.-amyl-4-tert.-butyl-phenol; 2,6-di-tert.-butyl-4-tert. amyl-phenol; 2,4,6-tri-isopropyl-phenol; 2,4,6-tri-tert.-butyl-phenol; 2-tert.-butyl-4,6-di-tert.-amyl-phenol, etc. The preferred and most used phenolic compound is 2,6-di-tert.-butyl-4-methyl-phenol, often referred to as di-tertiary-butyl-para-cresol.

The dicarboxylic acid component of the herein described composition is an alkenyl dicarboxylic acid having at least 10 carbon atoms in the aliphatic radical. Dicarboxylic acids such as phthalic acid, malonic acid, citraconic acid, succinic acid and the like are suitable, although the preferred acid is the unsaturated aliphatic or alkenyl succinic acid. The alkenyl succinic acid can be readily prepared by the condensation of an olefin or a mixture of olefins of at least six carbon atoms and preferably ten or more carbon atoms, with maleic acid anhydride to form the alkenyl succinic acid anhydride, and then hydrating the resultant alkenyl succinic acid anhydride to liberate the free alkenyl succinic acid. A method of preparing such alkenyl succinic acids is set forth in U.S. 2,055,456, and U.S. 2,133,734. Illustrative of suitable alkenyl succinic acids are decenyl succinic acid, dodecenyl succinic acid, pentadecenyl succinic acid, octadecenyl succinic acid and the like.

As alluded to above, when the alkenyl succinic acid is used in combination with the above defined phenolic com-

pound in lubricant compositions to impart rust and/or corrosion inhibiting properties to the composition, the oxidation inhibiting property of the phenolic compound is materially reduced. However, the addition of the third essential additive results in a composition more resistant to oxidative deterioration than is provided by the phenolic antioxidant in the absence of the dicarboxylic acid corrosion inhibitor. The third essential additive, as mentioned above, is an aromatic amine. Illustrative of suitable aromatic amines are triphenyl amine, phenyl alpha naphthylamine, and an alkyl substituted diamino diphenyl alkane in which the alkyl substituent contains from 1 to about 5 carbon atoms and the alkane contains from 1 to 2 carbon atoms, i.e. methane or ethane. Examples of the latter compounds are tetraethyl diamino diphenyl methane, diisoamyldiamino diphenyl methane, tetraamyldiamino diphenyl methane, tetraamyldiamino diphenyl methane, dimethyldiamino diphenyl methane, tetramethyldiamino diphenyl ethane, etc., of which the tetramethyldiamino diphenyl methane is preferred.

The hydrocarbon oil component can be any synthetic hydrocarbon oil or natural hydrocarbon oil such as petroleum oil preferably in the viscosity range of from about 150 seconds to about 1500 seconds at 100° F. Saybolt Universal, although oils of lower or higher viscosities can be used depending upon the intended use or service of the lubricant composition. The base oil can be acid treated and/or solvent refined overhead distillates or bright stocks or blends thereof. The present invention is particularly adapted to turbine oils, and the class of industrial oils known as circulating oils, which are lubricating oils of good demulsibility and stability designed for use in open or closed forced lubrication systems, in which the lubricant is returned after each use to collection points at which contaminants such as water, dirt, etc. are separated and the oil recirculated. It is to be understood, however, that the lubricant of the present invention can be employed for uses other than those given for the purposes of illustration.

In addition to the three essential components above named, the lubricant composition can contain other additives such as a four point depressor, an anti-foam agent, an EP agent, an oiliness agent, etc.

The following examples of compositions of the present invention are given by way of illustration and are not intended to be indicative of the scope of the invention:

TABLE I

	Examples, Percent (Vol.)			
	1	2	3	4
Mineral Base Oil	99.05	99.65	99.52	99.46
Di-t-butyl-p-cresol	0.25	0.25	0.4	0.4
Dodecenyl succinic acid	0.05	0.05	0.03	.05
Tetramethyl diamino diphenyl methane	0.05	0.05		
Phenyl alpha naphthylamine			0.05	
Tri phenyl amine				0.09
Pour point depressor [1]	0.60			
Anti-foam agent [2] (p.p.m.)	1	1		

[1] Condensation product of naphthalene and a chlorinated paraffin wax, e.g. "Paraflow."
[2] Silicone polymer, e.g. Dow-Corning Fluid 200.

To determine the effectiveness of the present invention in providing hydrocarbon oil compositions which are resistant to oxidation in various compositions were subjected to the ASTM turbine oil oxidation test having ASTM Designation: D943–54. In Table II are presented data in respect to the oxidation tests.

TABLE II

Oxidation Tests

Test No.	Oil Composition	Oil Life (Hrs.)
1	Base mineral oil [a]	150
2	#1+0.4% di-t-butyl-paracresol	2,220–2,250
3	#2+0.03% dodecenyl succinic acid	1,250
4	#2+0.05% dodecenyl succinic acid	1,150
5	#3+0.027% tetramethyl diamino diphenyl methane	1,510
6	#4+0.045% tetramethyl diamino diphenyl methane	2,320
7	#3+0.046% phenyl alpha naphthylamine	1,700
8	#4+0.077% phenyl alpha naphthylamine	1,880
9	#4+0.085% triphenyl amine	1,880
10	#1+0.25% DBPC [1]+0.05% DSA [2]+0.05% MB [3]	2,700
11	#1+0.10% DBPC [1]+0.05% DSA [2]+0.05% MB [3]	1,970
12	#1+0.05% DSA+0.05% MB	860

[a] Contained 0.6% pour point depressor "Paraflow."
[1] Di-tertiary-butyl-para-cresol.
[2] Dodecenyl succinic acid.
[3] Tetramethyl diamino diphenyl methane.

The above data demonstrate the effectiveness of the present invention in providing oxidation resistant hydrocarbon oil compositions.

The corrosion and/or rust inhibiting property of the dicarboxylic acid corrosion inhibitor is not deleteriously affected by the presence of the phenolic compound and the aromatic amine. This is demonstrated by the data in Table III obtained in the ASTM rust test having ASTM Designation: D665–54.

TABLE III

Test No.	Composition	Synthetic Sea Water
1	Base mineral oil (no additives)	Severe.
2	#1+0.25% di-tert-butyl-para-cresol	Do.
3	#2+0.05% dodecenyl succinic acid	Very Slight—None.
4	#3+0.05% tetramethyl diamino diphenyl methane.	Slight—None.
5	#3+0.077% phenyl alpha naphthyl amine.	None—None.
6	#1+0.05% dodecenyl succinic acid	Moderate—Slight.
7	#6+0.045% tetramethyl diamino diphenyl methane.	Slight—Slight.
8	#6+0.077% phenyl alpha naphthyl-amine.	Very Slight—Very Slight.

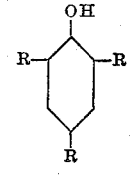
The present invention contemplates concentrates of a suitable hydrocarbon oil base containing more than 0.5% of the above defined phenolic compound, and more than 0.1% of each of the defined dicarboxylic acid and the defined aromatic amine which concentrate is capable of being blended or diluted with additional hydrocarbon oil in the proportions desired for the particular condition of use to give a finished product containing from about 0.01% to about 1.0% of said phenolic compound from about 0.03% to about 0.1% of the dicarboxylic acid and of the aromatic amine.

Percentages given herein and in the appended claims are weight percentages unless otherwise stated.

Although the present invention has been described with reference to specific preferred embodiments thereof, the invention is not to be considered as limited thereto, but includes within its scope such modifications and variations as come within the spirit of the appended claims.

We claim:

1. A lubricant composition resistant to oxidative deterioration and which has corrosion inhibiting properties comprising a major proportion of a hydrocarbon oil from about 0.01% to about 1.0% of a trialkylated phenol compound having the general structure



in which R is an alkyl radical of from 1 to about 10 carbon atoms, at least one of which radical in a position ortho to the OH group contains at least 3 carbon atoms, from about 0.3% to about 0.1% of an alkenyl dicarboxylic acid having at least 10 carbon atoms in the alkenyl group, and from about 0.03% to about 0.1% of an aromatic amine.

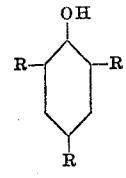
2. A lubricant composition as described in claim 1 in which the alkyl radicals ortho to the OH group contain at least 3 carbon atoms and the alkyl radical para to the OH group contain 1 to about 3 carbon atoms, the alkenyl dicarboxylic acid is an alkenyl succinic acid; and the aromatic amine is selected from the group consisting of triphenyl amine, phenyl alpha naphthylamine and an alkyl substituted diamino diphenyl alkane in which the alkyl substituent contains from 1 to 5 carbons atoms and the alkane contains from 1 to 2 carbon atoms.

3. A lubricant composition resistant to oxidative deterioration and which has corrosion inhibiting properties comprising a major proportion of a hydrocarbon oil from about 0.01% to about 1.0% 2,6-di-tertiary butyl-4-methyl phenol, from about 0.03% to about 0.1% dodecenyl succinic acid and from about 0.03% to about 0.1% phenyl alpha naphthylamine.

4. A lubricant composition resistant to oxidative deterioration and which has corrosion inhibiting properties comprising a major proportion of a hydrocarbon oil from about 0.01% to about 1.0% 2,6-di-tertiary butyl-4-methyl phenol, from about 0.03% to about 0.1% dodecenyl succinic acid and from about 0.03% to about 0.1% of an alkyl substituted diamino diphenyl alkane in which the alkyl substituent contains from 1 to 5 carbon atoms and the alkane contains 1 to 2 carbon atoms.

5. A lubricant composition resistant to oxidative deterioration and which has corrosion inhibiting properties comprising a major proportion of a hydrocarbon oil from about 0.01% to about 1.0% 2,6-di-tertiary butyl-4-methyl phenyl, from about 0.03% to about 0.1% dodecenyl succinic acid and from about 0.03% to about 0.1% tetramethyl diamino diphenyl methane.

6. An additive concentrate for lubricating oils consisting essentially of a hydrocarbon oil containing more than 0.5% of a tri-alkylated phenol compound having the general structure



in which R is an alkyl radical of from 1 to about 10 carbon atoms, at least one of which radicals in a position ortho to the OH group contains at least 3 carbon atoms, more than 0.1% of an alkenyl succinic di-carboxylic acid having at least 10 carbon atoms in the alkenyl group and more than 0.1% of an aromatic amine, said additive concentrate being capable of dilution with a hydrocarbon oil to form a lubricant composition containing a major amount of a hydrocarbon oil, from about 0.01% to about 1.0% of said phenol compound, from about 0.03% to about 0.1% of said alkenyl dicarboxylic acid and from 0.03% to about 0.1% of said aromatic amine.

7. An additive concentrate as described in claim 6 in which the phenol compound is 2,6-di-tertiary butyl-4-methyl-phenol, said alkenyl dicarboxylic acid is dodecenyl succinic acid and said aromatic amine is tetramethyl diamino diphenyl methane.

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