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LUBRICANT COMPOSITIONS

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This application is a continuation-in-part of George J. Benoit, Jr., U.S. patent application Serial No. 794,801, filed February 24, 1959, now abandoned, directed to "Dialkyl Diesters of Dibasic Acids."

This invention relates to a novel lubricant composition having as the base oil a new class of dialkyl diesters of dibasic acids. More particularly, the invention is concerned with a synthetic lubricating oil composition comprising a novel class of dialkyl diesters of alkoxy succinic acids and alkylthiosuccinic acids having superior properties.

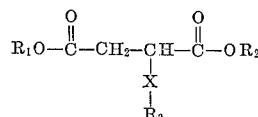
Synthetic oils are useful in a variety of applications, including the lubricants of instruments, weapons, optical equipment, gas turbines, etc. A combination of special properties is desirable in synthetic oils for these purposes. At high temperatures, they should not be excessively volatile in order to avoid the loss of the oil through evaporation to permit their circulation, and the provision of proper lubrication over wide ranges of operating conditions. It is also important that the synthetic oils remain fluid at low as well as high temperatures. Good viscosity-temperature properties are likewise desirable in synthetic oils since they should be adaptable to changes in temperature conditions without extreme variations in viscosity. Suitable synthetic oils should also be stable to oxidation, particularly at high temperatures, since undesirable residues such as tars and coke will otherwise result.

It has now been found that a superior new gas turbine lubricating oil composition is provided by the composition comprising a major proportion of a synthetic lubricating oil base of the class consisting of the dialkyl diesters of alkoxy succinates and alkylthiosuccinates in which the alkoxy and the alkylthio group contain from 1 to about 12 carbon atoms and the alkyl ester groups contain from about 4 to about 12 carbon atoms each in combination with an arylamine oxidation inhibitor and an alkylamine salt of acid alkyl esters of phosphoric acid as extreme pressure additive. Such compositions are excellent synthetic oils having special properties which make them particularly suitable as synthetic lubricants.

The novel dialkyl diesters of alkoxy succinic acids and alkylthiosuccinic acids according to the present invention, as described above, are characterized by unusually low freezing points compared to other types of dialkyl diesters of dibasic acids. This property shows that they are capable of remaining fluid and provide effective lubrication at low as well as high temperatures. The superior new esters of the invention also possess excellent viscosity-temperature characteristics as indicated by their high viscosity indexes. From the standpoint of oxidation stability, the novel dialkyl diesters of alkoxy succinic acid and alkylthiosuccinic acids according to the invention are particularly desirable since they form less tar and coke under actual operating conditions than other types of dialkyl diesters of dibasic acids.

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The superior new dialkyl diesters of alkoxy succinic acids and alkylthiosuccinic acids according to the invention have the general formula



in which R_1 and R_2 are the same or different alkyl groups containing from about 4 to about 12 carbon atoms each, R_3 is an alkyl group containing from 1 to about 12 carbon atoms and X is a member of the group consisting of oxygen and sulfur. The dialkyl diesters in which one of the alkyl groups is straight chain in structure and the other branched chain are particularly desirable since they are characterized by an excellent combination of high viscosity index and low pour point. Particularly preferred for present purposes are the dialkyl diesters of methoxy succinic acid in which one of the alkyl groups is a straight chain alkyl group of from about 6 to about 10 carbon atoms and the other alkyl group is a branched chain alkyl group of from about 6 to about 10 carbon atoms.

Examples of the superior new dialkyl diesters of alkoxy succinic acid or dialkyl diesters of alkylthiosuccinic acids according to the invention include the diisooctyl diester of isooctoxy succinic acid, the di-2-ethylhexyl diester of 2-ethylhexoxy succinic acid, the diisooctyl diester of n-butylthiosuccinic acid, and other similar compounds within the aforementioned general description. For our purposes, the n-octyl, "oxo" decyl diester of methoxy succinic acid is preferred for its outstanding combination of physical properties including high viscosity index and low pour point. The "oxo" decyl group in this case is a typical branched chain alkyl group of 10 carbon atoms derived from "oxo" decyl alcohol prepared by the "oxo" process from propylene trimer.

The dialkyl diesters of the alkoxy succinic acids according to this invention are conveniently prepared by reacting an alkali metal alcoholate in alcohol (i.e., methanol) solution with a dialkyl diester of maleic acid. The alcohol, for example, methanol, adds across the double bond of the maleate ester, for example, diethyl maleate, to give the dialkyl diester of methoxy succinic acid. This dialkyl diester is then reacted with another type of alcohol such as n-octanol in an ester interchange to give the di(n-octyl) diester of methoxy succinic acid.

The arylamine oxidation inhibitor is employed in amounts of from 0.2 to 5%, and preferably from 0.5 to 3% by weight. Suitable arylamine oxidation inhibitors include phenyl- α -naphthylamine, diphenylamine, dioctyl diphenylamine, phenothiazine and the like. Particularly suitable are the diarylamines which contain from about 10 to about 25 carbon atoms. For present purposes, phenothiazine is preferred.

The extreme pressure additive is employed in the amount of from 0.05 to 1%, and preferably of from 0.1 to 0.5% by weight. This compound is selected from the group consisting of alkylamine salts of acid alkyl esters of phosphoric acid and blends of said salts with acid alkyl esters of phosphoric acid in which the amine salt constitutes at least 25% by weight, the alkyl groups here referred to containing from 8 to 18 carbon atoms each. Suitable additives coming within this group are dodecyl-

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amine dodecyl acid phosphate, blends made up of from 25 to 95% of dodecylamine dodecyl acid phosphate and from 5 to 75% of dodecyl dihydrogen phosphate, octylamine dioctyl phosphate, di(decylamine)dodecyl phosphate, hexadecylamine dodecyl acid phosphate, octadecylamine dioctadecyl phosphate, and blends containing 2-ethylhexylamine 2-ethylhexyl acid phosphate and 2-ethylhexyl dihydrogen phosphate in equal proportions. A preferred extreme pressure additive is a blend made up of an alkylamine acid alkyl phosphate with an alkyl dihydrogen phosphate, in which blend the amine salt component is present to the extent of from 25 to 95% by weight.

The synthetic lubricating oil compositions according to the invention may also contain anti-wear additives, metal deactivators, foam inhibitors, and the like.

The anti-wear additive is present in the amount of from 0.5 to 5% and is a compound selected from the group consisting of neutral aryl phosphates and neutral alkyl aryl phosphates. Representative additives coming within this grouping are triphenyl phosphate, tricresyl phosphate, butyl diphenyl phosphate, phenyl dibutyl phosphate, benzyl dicresyl phosphate, trixylyl phosphate and diphenyl cresyl phosphate. A preferred additive of this class is tricresyl phosphate.

The metal deactivator additive, which is present in the amount of from 0.005 to 0.2%, and preferably from 0.01 to 0.1% by weight, is a compound selected from the group consisting of quinizarin, alizarin, purpuranthrene, anthrarufin, and chrysazin. The preferred additive of this class is quinizarin.

As the foam inhibitor there is employed from 0.0001 to 0.02% of a di(lower alkyl)silicone polymer such as dimethyl silicone, diethyl silicone, methylethyl silicone and methylphenyl silicone. The preferred additive of this class is dimethyl silicone.

In further illustration of the invention, reference is had to the following examples. The proportions in the examples are given on a weight basis unless otherwise specified.

EXAMPLE I

In this example, dioctyl methoxysuccinate was prepared. A sodium methylate solution in methanol was prepared by reacting 2.3 g. sodium (0.1 g. atom) with 160 g. methanol (5.0 moles). To this solution 172 g. diethyl maleate (1.0 mole) was added and the reactants heated to 50–60° C. for 4 hours. A mixture of 500 g. n-octanol and 500 ml. toluene was next added and the mixture distilled until all the toluene and lower boiling alcohols were removed. The pot temperature at this point was 195° C. It was then distilled under a vacuum of 3.4 mm. of mercury to a pot temperature of 220° C. This yielded a bottoms fraction of 263 g. which was filtered and treated with 5 g. of acetic acid. The stock so treated was distilled, topping at a pressure of 1 mm. of mercury, to a pot temperature of 100° C. and filtered. The analytical results and physical property data for this ester are given in the attached table.

EXAMPLE II

This example illustrates the preparation of di-(2-ethylhexyl) 2-ethylhexoxysuccinate.

Sodium 2-ethylhexoxide was prepared by adding 2.3 g. (0.1 g. atom) sodium to 650 g. 2-ethylhexanol (5.0 moles). One hundred seventy-two grams diethyl maleate (1.0 mole) was added to the solution of the sodium alcoholate and the mixture heated to 50–60° C. for 4 hours. Five hundred milliliters of toluene was added and the mixture subjected to distillation to a pot temperature of 200° C. Eight grams of acetic acid was next added and the mixture distilled under a pressure of 2 mm. of mercury to a pot temperature of 200° C. The bottoms was decolorized with carbon at 100° C., filtered, and topped at a pressure of 8 mm. of mercury to a pot temperature of 220° C.

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EXAMPLE III

In this example, di-n-hexyl n-hexoxysuccinate was prepared.

A solution of sodium n-hexoxide in n-hexanol was prepared as in the preceding experiments. To 512 g. of this solution containing 0.1 g. atom of sodium was added 172 g. diethyl maleate (1.0 mole). This mixture was heated to 50–60° C. for 4 hours, cooled, and 500 ml. of toluene was added. The volatile material was removed by distilling at atmospheric pressure to a pot temperature of 160° C. It was then neutralized with acetic acid, and decolorizing carbon was added. The mixture was distilled at a pressure of 5.0 mm. of mercury to a pot temperature of 235° C.; and the bottoms, weighing 373 g. was filtered.

EXAMPLE IV

This example illustrates the preparation of mixed hexyl-octyl hexoxysuccinate.

A solution of sodium hexoxide was prepared as in the preceding experiment, except that only 2.0 moles of n-hexanol was used for the 0.1 g. atom of sodium. To this solution, weighing 206 g., 172 g. of diethyl maleate (1.0 mole) was added and the temperature maintained at 50–60° C. for 4 hours. A mixture of 130 g. (1.0 mole) isooctyl alcohol, 204 g. (2.0 moles) 2-ethylbutanol, and 500 ml. of toluene was added. The mixture was distilled at atmospheric pressure to 170° C., acetic acid was added to neutralize, and carbon was added to decolorize. This was distilled finally under a vacuum of 5.0 mm. of mercury to a maximum pot temperature of 195° C. The bottoms, weighing 386 g., was filtered.

EXAMPLE V

In this example, di-"oxo" decyl methoxy-succinate was prepared.

One hundred grams of the diethyl methoxy-succinate prepared in the previous experiment was mixed with 2.7 g. sodium methylate, 300 g. "oxo" decyl alcohol, and 300 g. toluene. This mixture was distilled at atmospheric pressure to remove toluene and everything boiling below toluene. It was then neutralized with 8 g. acetic acid, and 10 g. decolorizing carbon was added. The mixture was distilled at atmospheric pressure to a pot temperature of 140° C. and then distilled under a vacuum of 1.8 mm. of mercury to a pot temperature of 200° C. The bottoms weighed 220 g.

EXAMPLE VI

In this example, mixed n-octyl "oxo" decyl methoxy-succinate was prepared.

Two hundred grams of diethyl methoxysuccinate was mixed with 234 g. n-octyl alcohol, 284 g. "oxo" decyl alcohol, 600 ml. toluene, and 10.8 g. sodium methylate. The two alcohols were present in equimolar proportions. This mixture was distilled at atmospheric pressure until all the toluene had been removed, and 32 g. acetic acid was added to neutralize. The neutralized mixture was washed three times with water and distilled at atmospheric pressure to a pot temperature of 180° C. Thirty grams decolorizing carbon was added, and it was then distilled at a pressure of 3.5 mm. of mercury to a maximum pot temperature of 212° C. The weight of the bottoms was 361 g.

EXAMPLE VII

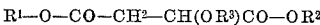
The preparation of 2-ethylhexyl, isooctyl n-butylthio-succinic acid is illustrated by this example.

Ninety-nine grams (1.1 g. mole) of n-butyl mercaptan under nitrogen was reacted with 2.3 g. sodium (0.1 g. atom) to prepare a solution of sodium n-butyl mercaptide in n-butyl mercaptan. When the reaction was complete, there was slowly added 170 g. diethyl maleate (1.0 g. mole). The mixture was held at 50–60° C. for several hours. Then there was added 325 g. 2-ethylhexanol and 325 g. isooctyl alcohol and 300 ml. toluene. The mixture was distilled to a pot temperature of 200° C. at atmos-

pheric pressure, which removed all components boiling below C₈ alcohols. The material was then given additional workings as in the above examples to give the 2-ethylhexyl, isooctyl n-butyl thiosuccinic acid.

The following table provides additional analytical data on the compositions of the above examples as well as other compositions illustrative of the invention. The physical properties of the esters are also given where appropriate. It will be noted that in some of the examples, the esters were obtained in pure form whereas in others the esters are crude products containing the esters and other unidentified materials of comparable boiling point.

Dialkyl alkoxysuccinates



Ex. No.	R ¹	R ²	R ³	Equivalent weight		Alkoxy-succinate, percent	Neut. No.	Viscosity (cs.)		Visc. Index	F.P., ° F.
				Found	Theory			100° F.	210° F.		
I	n-Octyl	n-Octyl	Methyl	190	186	55		16.83	3.963	155	+45
II	2-ethylhexyl	2-ethylhexyl	2-ethylhexyl	198	235	62		20.52	3.981	100	<-65P
III	n-Hexyl	n-Hexyl	n-Hexyl	158	193	69		9.945	2.713	125	+5
IV	Isooctyl	2-ethylbutyl	do			59		12.81	3.088	113	<-65P
V	n-Hexyl	do	do								
VI	"Oxo" decyl	"Oxo" decyl	Methyl	230	215	100	0.01	31.05	4.427	19	-40
VII	n-Octyl	do	do	208	200	100	6.7	15.52	3.52	120	-70P
VIII	2-ethylhexyl	Isooctyl	n-Butylthio	201	223	32		75.5	9.83	116	
IX	n-Octyl	"Oxo" decyl	Methyl	195	200	100	17.8	14.92	3.45	123	-80P
X	n-Octyl	do	do	202	200	100	6.6	13.44	3.17	112	-80P
XI	"Oxo" decyl	n-Octyl	do	219	200	100	0.20	22.46	4.404	120	<-65P
	n-Decyl	Isooctyl	do	202	199	100	1.0	16.51	3.866	150	+20

¹ Thio.

From the physical characteristics of the illustrative dialkyl diesters of alkoxysuccinic acids and alkylthiosuccinic acids in the above examples, it is readily seen that the compounds of the invention possess excellent viscosity-temperature properties as well as other desirable physical characteristics which make them particularly suitable as synthetic lubricants. They have unusually low freezing points compared to other types of dialkyl diesters of dibasic acids. The esters also have unusually high viscosity indexes. The dialkyl diesters of methoxysuccinic acids in which one alkyl group is straight-chain and the other branched-chain are particularly outstanding with respect to the combination of low freezing point and unusually high viscosity index.

The high temperature stability of the dialkyl diesters of alkoxysuccinic acid according to the invention was determined by heating the compounds at elevated temperatures in oxygen-containing atmosphere and noting the change, if any. In such a test, di-n-octyl n-octyloxysuccinate was heated for 48 hours at 392° F. An examination of the physical properties of the ester after heating showed essentially no change.

In further illustration of a particular embodiment of the present invention, a typical gas turbine lubricant was prepared from an illustrative ester and subjected to a modified coking test as described in government specifications Mil-L-7807c and Mil-L-2536. The test was conducted in the same manner as described in the specifications except that the temperature of the heated plate was held at 700° F. instead of 600° F. in order to make the test more severe. This gas turbine lubricant was also compared with a commercial gas turbine lubricant in the test. The composition of the experimental lubricant is as follows:

	Percent
n-Octyl "oxo" decyl methoxysuccinate	94.38
Phenothiazine	0.50
Tricresyl phosphate	5.00
Octadecylamine salt of dodecylphosphoric acid	0.10
Quinizarin	0.02
Dimethyl silicone foam inhibitor	0.002

The above oil was heated in the coking test for 8 hours at 700° F. and gave 2749 mg. of coke. A commercial gas turbine lubricant blended with the same additives but consisting of a di-2-ethylhexyl sebacate for the base fluid yields 3600 mg. of coke.

The above tests show that illustrative dialkyl diesters of alkoxysuccinic acids according to the present invention have excellent high temperature properties which make them ideally suited as base lubricants in the preparation of gas turbine lubricating oils.

I claim:

1. A gas turbine lubricating oil composition consisting essentially of a major proportion of a dialkyl diester of methoxysuccinic acid in which one of the ester-linked alkyl groups is n-octyl and the other ester-linked alkyl group is a branched chain decyl, a minor proportion of phenothiazine sufficient to inhibit oxidation, a minor proportion of tricresyl phosphate sufficient to improve wear inhibition and a minor proportion of octadecylamine salt of dodecylphosphoric acid sufficient to improve the extreme pressure characteristics.

2. A gas turbine lubricating oil composition consisting essentially of a major proportion of a dialkyl diester of methoxysuccinic acid in which one of the ester-linked alkyl groups is n-octyl and the other ester-linked alkyl group is a branched chain decyl, from 0.2 to 5% by weight of phenothiazine, from 0.5 to 5% by weight of tricresyl phosphate and from 0.05 to 1% by weight of octadecylamine salt of dodecylphosphoric acid.

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