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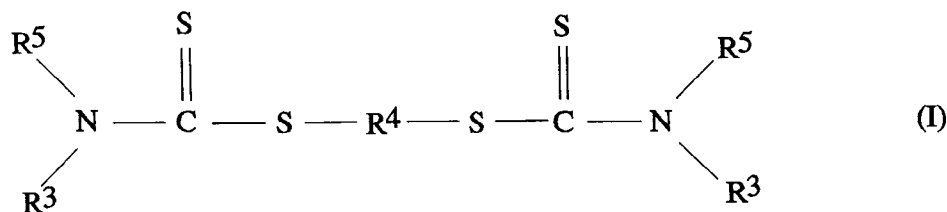
02.10.1996 Bulletin 1996/40(21) Application number: **96302164.7**(22) Date of filing: **28.03.1996**(51) Int Cl.⁶: **C10M 141/08**, C10M 141/10// (C10M141/08, 133:12,
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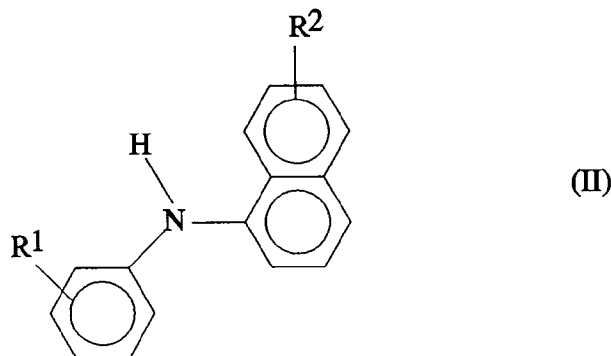
BE GB(30) Priority: **28.03.1995 US 413038**(71) Applicant: **ETHYL CORPORATION****Richmond Virginia 23217 (US)**(72) Inventor: **Iyer, Ramnath****Midlothian, Virginia 23113 (US)**(74) Representative: **Cresswell, Thomas Anthony****J.A. KEMP & CO.****14 South Square****Gray's Inn****London WC1R 5LX (GB)**(54) **Extended life rust and oxidation oils**

(57) A lubricant composition comprising a base oil, rust and oxidation inhibitors and

(a) a dithiocarbamate of formula (I)



wherein R⁴ is a hydrocarbylene group having 1 to 10 carbon atoms, the groups R⁵ are the same or different and each is hydrogen or a hydrocarbyl group having 1 to 18 carbon atoms, and the groups R³ are the same or different and each is a hydrocarbyl group having 1 to 18 carbon atoms; and

(b) an alkylphenyl- α -naphthylamine of formula (II)

wherein R¹ and R² are the same or different and each is hydrogen or C₁ to C₁₈ alkyl.

EP 0 735 128 A2

Description

BACKGROUND OF THE INVENTION

1. Field of the Invention.

This invention relates to the field of improved thermal and oxidative stability of lubricating fluids.

2. Description of the Prior Art.

Lubricating oils such as circulating oils, turbine oils, hydraulic fluids and transformer oils as well as others require good oxidation stability and good rust inhibition properties. Extended life for such fluids where desired rust and oxidation (R&O) inhibition properties are maintained for extended periods of use is demanded by industrial users and provides important economic benefit. R&O oils are widely used in turbine and compressor circulating systems. Their thermal and oxidative stability are of particular importance. In addition, R&O oils provide rust protection, corrosion protection and metal passivation. Antiwear protection is sometimes needed.

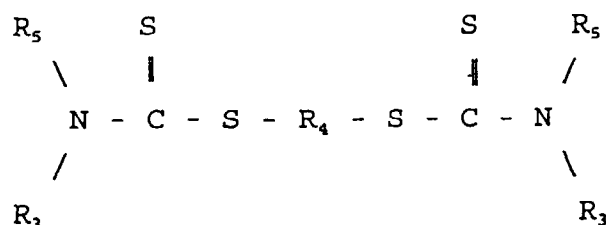
U. S. Patent 4,125,479 to Chesluk et al. discloses an oxidation inhibited lubricating oil with a combination of additives comprising methylenebis(di-n-butylthiocarbamate) and 4-methyl-2,6-ditertiary butyl phenol, said to provide enhanced oxidation inhibition. U. S. Patent 4,880,551 to Doe discloses an antioxidant composition consisting of a 1-(di(4-octylphenyl) aminomethyl)tolutriazole and at least one antioxidant selected from the group consisting essentially of methylenebis(di-n-butylthiocarbamate); 2,6-di-t-butyl-4-sec-butylphenol; 2,6-di-t-butyl-4-methylphenol and butylated phenol mixture. International PCT Publication Number WO 92/19703, published 12 November 1992, to Lubrizol Corporation discloses thermally stable lubricant and functional fluid compositions containing hydrocarbyl phosphite in combination with at least one basic alkali or alkaline earth metal salt of an acidic organic compound and a metal deactivator, the composition may additionally contain a dithiocarbamate compound for an antiwear agent. These references do not teach or suggest the combination of components claimed herein.

There is an increasing demand for inhibited oils with extended lifetimes. R&O lubricant concentrate packages typically contain phenolic, amino and other antioxidants, rust inhibitor(s), a metal deactivator, and a demulsifying agent. They may include additional components such as an antiwear agent depending on the final performance properties desired. The principle function of the antioxidants is the inhibition of oxidative degradation of R&O oils that are obtained by blending the R&O lubricant concentrate package in a particular basestock oil of choice. Basestock oils have varying degrees of thermal and oxidative stability.

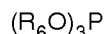
This invention will serve to improve the thermal and oxidative properties of even those basestock oils that are known to have less than satisfactory stability. The current invention relates to the use of certain components, that contribute directly to prolonging the life of R&O oils.

SUMMARY OF THE INVENTION

In a rust and oxidation (R&O) inhibited lubricant composition comprising a base oil and rust and oxidation inhibitors, the invention is directed to the improvement wherein said lubricant composition comprises (a) a dithiocarbamate compound represented by the formula



wherein R_4 is a hydrocarbylene group having 1 to 10 carbon atoms, each R_5 is a hydrogen or a hydrocarbyl group having 1 to 18 carbon atoms, and each R_3 is a hydrocarbyl group having 1 to 18 carbon atoms; and (b) an alkylphenyl- α -naphthylamine. The lubricant composition further optionally comprises (c) a hydrocarbyl phosphite represented by the formula



where each R_6 is independently C_1 to C_{18} alkyl, C_2 to C_{18} alkenyl, or C_6 to C_{18} aryl. Each component (a) and (b), or (a), (b) and (c) is present in an amount sufficient to provide improved inhibition of oxidation to the R&O lubricant com-

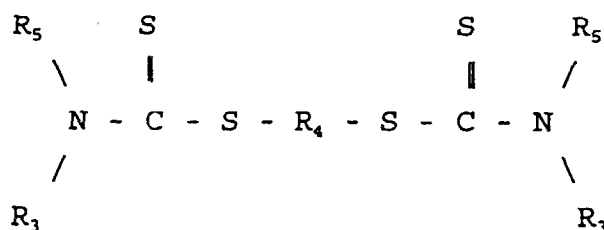
position.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The additive combinations of this invention may be used in any lubricating oil where oxidation inhibition is required. This may include circulating oils used in compressor and turbine circulating systems, transformer oils, engine oils and other oils which are subjected to conditions where oxidation is a problem. It has been found that a dithiocarbamate compound in combination with an alkylphenyl- α -naphthylamine, in effective amounts, and that combination in further combination with an effective amount of hydrocarbyl phosphite, provide important and unexpected enhancement of thermal and oxidation stability, with resulting improvement in the life of the R&O oil.

The additive combinations of this invention can be incorporated in a wide variety of lubricants and functional fluids in effective amounts to provide suitable active ingredient concentrations. The base oils useful herein can be hydrocarbon oils of suitable viscosities; synthetic oils such as hydrogenated polyolefin oils; poly- α -olefin oligomers (such as hydrogenated poly-1-decene); alkyl esters of dicarboxylic acids; complex esters of dicarboxylic acid, polyglycol and alcohol; alkyl esters of carbonic or phosphoric acids; polysilicones; fluorohydrocarbon oils; and mixtures of mineral, natural and/or synthetic oils in any proportion, etc. The term "base oil" for this disclosure includes all the foregoing and mixtures thereof.

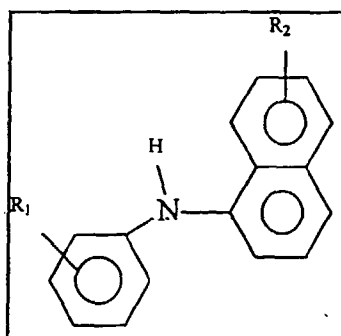
The dithiocarbamate compound to be included in the combination of the invention is represented by the formula



wherein R_4 is a hydrocarbylene group having 1 to 10 carbon atoms, preferably 1 to 4 carbon atoms. Preferably, R_4 is an alkylene group, most preferably a methylene or ethylene group. Each R_5 is a hydrogen or a hydrocarbyl group having 1 to 18 carbon atoms, preferably 2 to 10, more preferably 2 to 6. Each R_3 is a hydrocarbyl group having 1 to 18 carbon atoms, preferably 2 to 10, more preferably 2 to 6. A commercially available dithiocarbamate compound appropriate for use in the invention is VANLUBE[®] 7723, methylenebis(di-n-butylthiocarbamate).

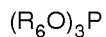
Beyond a certain level, the dithiocarbamate compound may start hurting or interfering with relevant bench tests other than R&O tests. Higher levels of dithiocarbamate compound may result in deterioration of thermal stability, causing undesired sludge in thermal stability tests. Also rust problems may occur at higher dithiocarbamate compound levels, which may result in failure of specified rust tests. An effective amount of dithiocarbamate compound is up to 1.0 weight percent of the finished lubricant composition, for example 0.01 to 1.0 weight percent, 0.02 to 0.5 preferred, 0.03-0.2 most preferred.

The alkylphenyl- α -naphthylamine for use in the invention is represented by the formula



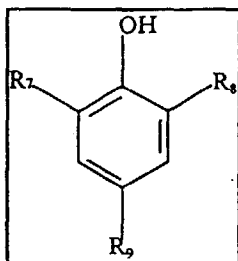
wherein R_1 and R_2 are independently hydrogen or C_1 to C_{18} alkyl. For purposes herein, "alkylphenyl- α -naphthylamine" includes phenyl- α -naphthylamine (PANA), where both R_1 and R_2 are hydrogen. An effective amount of alkylphenyl- α -naphthylamine for use in the invention is up to 0.15 weight percent of the finished lubricant composition, for example 0.025 to 0.15 weight percent, 0.03 to 0.125 weight percent preferred.

The hydrocarbyl phosphite compound for use in the invention is represented by the formula:



where each R_6 is independently C_1 to C_{18} alkyl, C_2 to C_{18} alkenyl, or C_6 to C_{18} aryl. In preferred compounds, each R_6 is independently C_3 to C_{12} alkyl or C_6 to C_{18} aryl. In most preferred compounds, R_6 is C_6 to C_{18} aryl, including triphenylphosphite, tricresylphosphite, trionylphenylphosphite (C_{15}), tridodecylphenylphosphite, and mixtures thereof. An effective amount of the hydrocarbyl phosphite compound for use in the invention is up to 0.075 weight percent of the finished lubricant composition, for example 0.005 to 0.075 weight percent, 0.01 to 0.06 preferred.

R&O oils will typically contain a conventional quantity of one or more antioxidants in order to protect the composition from premature degradation in the presence of air, especially at elevated temperatures. Typical antioxidants include various alkylated phenols, hindered phenols and phenol derivatives such as t-butyl hydroquinone, butylated hydroxyanisole, polybutylated bisphenol A, butylated hydroxy toluene, alkylated hydroquinone, 2,5-ditertaryl hydroquinone; 2,6-ditert-butyl-para-cresol; 2,2'-methylenebis(6-tert-butyl-p-cresol); 1,5-naphthalenediol; 4,4'-thiobis(t-tert-butyl-m-cresol); p,p'-biphenol; 4,4'-butylidenebis(6-tert-butyl-m-cresol); 4-methoxy-2,6-di-tert-butylphenol; and the like; also amino antioxidants such as aldehyde amines, ketone amines, ketone-diarylamines, alkylated diphenylamines, phenylenediamines, and the phenolic amines; secondary aromatic amine antioxidants, sulfurized phenolic antioxidants, oil-soluble copper compounds, phosphorus-containing antioxidants, and the like as well as mixtures of antioxidants. Phenolic antioxidants are known and may be represented by the general formula:



where R_7 is hydrogen or an alkyl group with 1 to 4 carbons, R_8 is an alkyl group with 1 to 4 carbons or a benzylic group, and R_9 is hydrogen, an alkyl group with 1 to 6 carbons, or an alkoxy group with 1 to 6 carbons. In one example of a phenolic antioxidant for use with the invention, R_7 is hydrogen, R_8 is an alkyl group with 1 to 4 carbons, and R_9 is an alkyl group with 1 to 6 carbons; most preferably both R_8 and R_9 are t-butyl. In a second example R_9 is hydrogen, R_7 is an alkyl group with 1 to 4 carbons, and R_8 is an alkyl group with 1 to 4 carbons; most preferably both R_7 and R_8 are t-butyl.

The R&O oil compositions useful herein will also typically comprise a rust inhibitor and a metal deactivator. These are commonly selected from alkenyl succinic acid esters and from triazoles and triazole derivatives, known for these purposes.

It is also useful to this invention to employ in the lubricant compositions and additive concentrates a suitable quantity of a corrosion inhibitor. This may be a single compound or a mixture of compounds having the property of inhibiting corrosion of metallic surfaces. One type of such additives are inhibitors of copper corrosion. Such compounds include thiazoles, triazoles and thiadiazoles. Examples of such compounds include benzotriazole, tolyltriazole, octyltriazole, decyltriazole, dodecyltriazole, 2-mercaptobenzothiazole, 2, 5-dimercapto-1, 3, 4-thiadiazole, 2-mercapto-5-hydrocarbylthio-1,3,4-thiadiazoles, 2-mercapto-5-hydrocarbyldithio-1, 3, 4-thiadiazoles, 2, 5-bis(hydrocarbylthio)-1, 3, 4-thiadiazoles, and 2, 5-(bis)hydrocarbyldithio, 1, 3, 4-thiadiazoles. The preferred compounds are the 1, 3, 4-thiadiazoles, a number of which are available as articles of commerce. Such compounds are generally synthesized from hydrazine and carbon disulfide by known procedures. See for example U.S. Pat. Nos. 2,765,289; 2,749, 311; 2,760,933; 2,850,453; 2,910,439; 3,663,561; 3,862,798; and 3,840,549. Other types of corrosion inhibitors are known and suitable for use in the compositions of this invention. Suitable corrosion inhibitors include ether amines; acid phosphates; amines; polyethoxylated compounds such as ethoxylated amines, ethoxylated and/or propoxylated phenols, and ethoxylated alcohols; imidazolines; and the like. Materials of these types are well known to those skilled in the art and a number of such materials are available as articles of commerce.

The lubricating composition of the present invention may further contain other additives such as extreme pressure agents and/or antiwear agents.

The additives of the present invention can be incorporated into a lubricating oil in any convenient way. The compounds, or mixtures thereof, can be added directly to the oil at the desired level or by adding concentrates of the additive to the oil. Accordingly, the additive compounds can be blended with a suitable oil soluble solvent such as mineral spirits and/or base oil to form a concentrate and then the concentrate may be blended with lubricating oil to obtain a final formulation. A complete R&O lubricant concentrate package can be prepared containing antioxidants, rust inhibitor, metal, deactivator, demulsifier, additional desired components as well as the components of the invention,

i.e. the dithiocarbamate compound and the alkylphenyl- α -naphthylamine compound; or the dithiocarbamate compound, the alkylphenyl- α -naphthylamine compound, and the hydrocarbyl phosphite. The components are present in the lubricant concentrate package at a level sufficient to provide an effective level in the finished composition to provide the enhanced oxidation inhibition properties.

EXAMPLES

The following tests were performed to demonstrate the advantages of the invention:

(a) The American Society for Testing and Materials (ASTM) provides a Standard Test Method for Oxidation Characteristics of Inhibited Mineral Oils (ASTM D943-81(Reapproved 1991)). The D943 test method was developed for, and is used to evaluate the oxidation stability of inhibited steam turbine oils and other oils containing R&O inhibitors in the presence of oxygen, water, and copper and iron metals at an elevated temperature and is considered of value in the industry in estimating the oxidation stability of lubricants, especially those that are prone to water contamination.

(b) ASTM D-2272-85(Reapproved 1991), Standard Test Method for Oxidation Stability of Steam Turbine Oils by Rotating Bomb, (RBOT) utilizes an oxygen-pressured bomb to evaluate the oxidation stability of new and in service turbine oils having the same composition (base stock and additives) in the presence of water and a copper catalyst coil at 150°C.

(c) The Cincinnati Milacron Thermal Stability Test procedure "A" (CM "A") is intended to check the thermal stability of a designated oil sample by immersing copper and iron rods into an oil sample, heating in an oil bath or oven (135-138° C) for one week (168 hours), and determining the weight of resulting residue or "sludge".

HiTec 575® Ashless Rust & Oxidation Inhibitor is a lubricant additive concentrate package commercially available from Ethyl Corporation. This is fully formulated for high-performance, turbine-quality hydraulic fluids. It provides extended oxidation life, excellent rust control, demulsibility and filterability, and is compatible with other additives commonly used in hydraulic fluids. HiTec 575 lubricant additive represents a typical R&O package and has been used in the studies reported herein to demonstrate the improved oxidation properties obtained with the present invention. Texaco ISO 46 basestock oil was used in preparing the formulation of the examples below. In Example 1, HiTec 575 lubricant additive was blended with the basestock oil at its recommended dosage, 0.80 weight percent. HiTec 575 lubricant additive contains PANA in an amount that provides 0.10 weight percent to the blended lubricant composition at this recommended dosage. For Examples 2 through 6 below, the PANA was removed from the HiTec 575 lubricant additive. The HiTec 575 lubricant additive without PANA was blended with the Texaco ISO 46 basestock oil at 0.80 weight percent dosage, and the dithiocarbamate compound and triphenylphosphite were added in the amounts indicated. For Examples 7 through 14, commercially available HiTec 575 lubricant additive was blended with the basestock at 0.80 weight percent dosage, and the dithiocarbamate compound and triphenylphosphite were added in the amounts indicated. A commercially available dithiocarbamate compound, VANLUBE® 7723, methylenebis(di-n-butylthiocarbamate), was used in the Examples in the amounts indicated. Table I below provides the composition of Examples 1-11 and the results of D943 and RBOT testing and CM "A" Sludge testing. The composition and the results of RBOT testing for Examples 12-14 are also provided in Table I.

TABLE I

Example	PANA wt %	DITHIOCARBAM. wt %	TPP wt %	RBOT minutes	CM "A" SLUDGE mg/100ml	D943 hours
1	0.10	-	-	745	14.00	2644
2	-	-	-	708	14.03	2634
3	-	0.025	-	765	9.92	2756
4	-	0.025	0.025	775	19.5	2523
5	-	0.050	-	805	12.25	2922
6	-	0.050	0.025	826	20.08	2526
7	0.10	0.025	0.025	945	23.05	2724

TABLE I (continued)

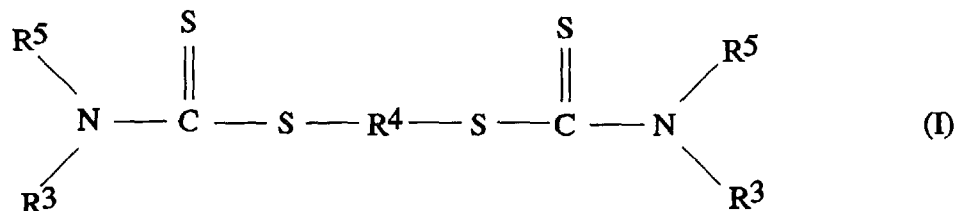
Example	PANA wt %	DITHIOCARBAM. wt %	TPP wt %	RBOT minutes	CM "A" SLUDGE mg/100ml	D943 hours
8	0.10	0.050	0.025	1048	22.10	3852
9	0.10	0.050	0.050	986	25.40	3684
10	0.10	0.100	0.025	1130	19.75	> 3700*
11	0.10	0.100	0.050	1195	29.03	3850
12	0.10	0.05	-	942		
13	0.10	0.10	-	1080		
14	0.10	0.20	-	1335		

* Test still running at time of filing

Claims

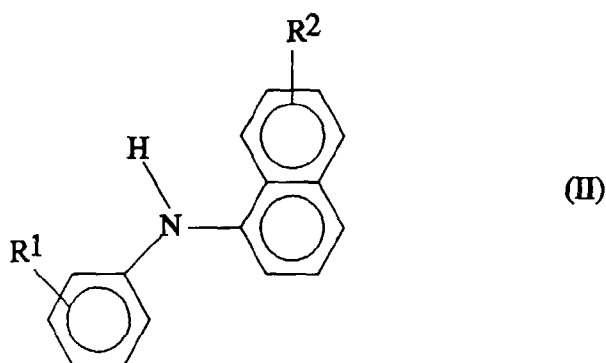
1. A lubricant composition comprising a base oil, rust and oxidation inhibitors and

(a) a dithiocarbamate of formula (I)



wherein R^4 is a hydrocarbylene group having 1 to 10 carbon atoms, the groups R^5 are the same or different and each is hydrogen or a hydrocarbyl group having 1 to 18 carbon atoms, and the groups R^3 are the same or different and each is a hydrocarbyl group having 1 to 18 carbon atoms; and

(b) an alkylphenyl- α -naphthylamine of formula (II)



wherein R^1 and R^2 are the same or different and each is hydrogen or C_1 to C_{18} alkyl.

2. A composition according to claim 1 wherein in the dithiocarbamate compound (a), R^4 is an alkylene group having 1 to 4 carbon atoms, each R^5 is hydrogen or a hydrocarbyl group having 2 to 10 carbon atoms, and each hydrocarbyl group R^3 has 2 to 10 carbon atoms.

3. A composition according to claim 2 wherein both groups R^5 are hydrogen and each group R^3 has 2 to 6 carbon atoms.

4. A composition according to claim 1 wherein the dithiocarbamate compound (a) is methylenebis(di-n-butylthiocarbamate).

5. A composition according to any one of claims 1 to 4 additionally comprising (c) a hydrocarbyl phosphite of formula (III)



where the groups R^6 are the same or different and each is C_1 to C_{18} alkyl, C_1 to C_{18} alkenyl, or C_6 to C_{18} aryl.

6. A composition according to claim 5 wherein each R^6 is independently C_3 to C_{12} alkyl or C_6 to C_{18} aryl.

7. A composition according to claim 6 wherein the hydrocarbyl phosphite compound (c) is triphenylphosphite or tricresylphosphite.

8. A composition according to any one of claims 1 to 7 comprising from 0.01 to 1.0 weight percent of the dithiocarbamate (a) and from 0.025 to 0.15 weight percent of the alkylphenyl- α -naphthylamine (b).

9. A composition according to any one of claims 5 to 7 comprising from 0.01 to 1.0 weight percent of the dithiocarbamate (a); from 0.025 to 0.15 weight percent of the alkylphenyl- α -naphthylamine (b); and from 0.005 to 0.075 weight percent of the hydrocarbyl phosphite (c).

10. A composition according to claim 9 wherein the dithiocarbamate (a) is present in an amount of 0.02 to 0.5 weight percent, the alkylphenyl- α -naphthylamine (b) is present in an amount of 0.03 to 0.125 weight percent, and the hydrocarbyl phosphite (c) is present in an amount of 0.01 to 0.06 weight percent.

11. Use of

- (a) a dithiocarbamate of formula (I) as defined in claim 1 and
(b) an alkylphenyl- α -naphthylamine of formula (II) as defined in claim 1

and optionally (c) a hydrocarbyl phosphite of formula (III) as defined in claim 5 for improving the inhibition of oxidation of a lubricant composition containing rust and oxidation inhibitors.

12. A lubricant additive concentrate for formulation of rust and oxidation inhibited lubricant compositions comprising a base oil and rust and oxidation inhibitors, the lubricant additive concentrate comprising

- (a) a dithiocarbamate of formula (I) as defined in claim 1
(b) an alkylphenyl- α -naphthylamine of formula (II) as defined in claim 1

and optionally (c) a hydrocarbyl phosphite of formula (III) as defined in claim 5, components (a), (b) and, optionally (c) being present in an amount sufficient to provide improved inhibition of oxidation to the rust and oxidation inhibited lubricant composition.