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LUBRICATING COMPOSITIONS

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U.S. Cl. 252—33.6 7 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to an additive which when added to not only a synthetic ester lubricant but also a mineral, animal or vegetable lubricating oil confers load carrying properties, and which is non-corrosive, does not have deleterious effects on silicone rubbers, and is hydrolytically stable. Such a lubricant composition comprises a major proportion by weight of a lubricating oil, a minor proportion by weight of an amine salt of a halogen substituted carboxylic acid wherein there is at least one halogen atom in the alpha position, and a minor proportion by weight of an antioxidant. Preferably such lubricant compositions also contain a minor proportion by weight of a corrosion inhibitor.

This invention relates to lubricating compositions having a load carrying additive.

Proposed specifications for 5 cs. lubricants for aviation gas turbine engines such as the Ministry of Defence specification DERD 2497, or the U.S. Navy specification XAS 2354 call for load-carrying demands for synthetic ester lubricants which are usually beyond the capacity of the base oil itself. In order to meet these demands load-carrying additives have to be used. Many previously suggested load-carrying additives are corrosive, or have deleterious effects upon silicone rubbers, or are hydrolytically unstable, and therefore such additives usually make the lubricant unsuitable for general aviation use.

We have now discovered an additive which when added to not only a synthetic ester lubricant but also a mineral, animal or vegetable lubricating oil confers load carrying properties, and which does not result in a lubricant having the above-mentioned disadvantages.

According to this invention a lubricant composition comprises a major proportion by weight of a lubricating oil, a minor proportion by weight of an amine salt of a halogen substituted carboxylic acid wherein there is at least one halogen atom in the alpha position, and a minor proportion by weight of an antioxidant. Preferably such lubricant compositions also contain a minor proportion by weight of a corrosion inhibitor.

The lubricating oil can be any mineral, animal, fish, vegetable or synthetic oil, for example, petroleum oil fractions ranging from naphthas to spindle oil to SAE 30, 40 or 50 lubricating oil grades, castor oil, animal or fish oils or oxidized mineral oil, e.g. palm oil, lard oil, tallow oil, arachis oil or sperm oil.

The preferred lubricating oil is a synthetic ester and suitable diesters include diesters of the general formula

ROOCR'COOR and RCOOR'OOCR

where R represents a C_6 to C_{12} alkyl group, while R_1 represents a C_4 to C_{10} saturated aliphatic hydrocarbon group or an ether-interrupted saturated aliphatic hydrocarbon group. The above types of esters may be prepared from alcohols and dicarboxylic acids or glycols and monocarboxylic acids or glycols and monocarboxylic acids.

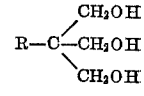
Another suitable class of ester lubricant are the polyesters which are prepared by reacting polyhydric alcohols e.g. those having 2 to 12 hydroxyl groups per molecule and 2 to 40 carbon atoms per molecule, such as trimethylolpropane, pentaerythritol and di-pentraerythritol with mono-carboxylic acids such as butyric acid, caproic acid, caprylic acid and pelargonic acid to give the corresponding tri- or tetraesters.

The complex esters which may be used as base oils are formed by esterification reactions between a dicarboxylic acid, a glycol and an alcohol and/or a monocarboxylic acid. These esters may be represented by the following formulae:

$$R_4COO—R_3—(OOCR_2COO—R_3)_n—OOCR_4$$
$$R_1—OOCR_2COO—(R_3—OOCR_2COO)_n—R_1$$
$$R_1—(OOCR_2COO—R_3)_nOOCR_4$$

wherein R_1 represents alkyl radicals derived from a monohydric alcohol, R_2 represents hydrocarbon radicals derived from a dicarboxylic acid, e.g. alkanedioic acids, R_3 represents divalent hydrocarbon or hydrocarbon-oxy radicals such as $—CH_2(CH_2)_n—$, or $—CH_2CH_2(OCH_2CH_2)_n—$, or $CH_2CH(CH_3)\ (OCH_2CH(CH_3))_n—$, derived from an alkylene glycol or polyalkyleneglycol, while R_4 represents the alkyl group derived from a monocarboxylic acid. "n" in the complex ester molecule which is an integer will usually range from 1 to 6 depending upon the product viscosity desired which is controlled by the relative molar ratio of the glycol or polyglycol to the dicarboxylic acid. In preparing the complex ester, there will always be some simple ester formed, i.e. n=0, but this will generally be a minor portion. In general these complex esters will have a total of between 15 and 80, e.g. between 20 and 65 carbon atoms per molecule.

Particularly suitable lubricants are esters of polyhydric alcohols having the formulae



where R is a $—CH_2OH$ group or an alkyl group, e.g. an alkyl group containing 1 to 6 carbon atoms. Thus, suitable esters of this type are the neopentyl polyol esters of trimethylol ethane, trimethylol propane, trimethylol butane and of pentaerythritol or di-pentaerythritol.

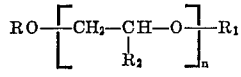
The preferred acids used to esterify trimethylol propane are the C_4 to C_{12} monocarboxylic acids. Particularly preferred are the C_7–C_{10} esters, e.g. C_8 (caprylic) and C_9 (pelargonic) acid esters. Mixtures of these C_7–C_{12} acids may be used. When such an acid mixture is used, it is preferred that the mixture average between C_8 and C_9. Although more difficult to form, it is even more preferred that one methylol group be esterified with a neo-heptanoic acid, e.g. 2,2-dimethylpentanoic acid, and the remaining methylol groups esterified with non-hindered acids, e.g. pelargonic acid. This particular ester is substantially as thermally stable as the completely hindered ester but has superior volatility and low temperature characteristics.

The preferred acids used to esterify pentaerythritol are the C_4–C_{10} monocarboxylic acids with the more preferred esters being those of C_5 to C_9 acids, e.g. n-valeric, isovaleric, 2-ethyl butyric, caproic, n-heptylic, n-octanoic or 2-ethyl hexoic acids or a mixture of C_5 to C_9 acids.

Blends of diesters with minor proportions of one or more thickening agents may also be used as lubricants. Thus one may use blends containing up to 50% by volume of one or more water insoluble polyoxyalkylene glycols, for example, polyethylene or polypropylene glycol, or mixed oxyethylene/oxypropylene glycol.

Formulations suitable for gas turbine lubrication include from 65 to 90 vol. percent of one or more diesters of azelaic or sebacic acid and a C_6–C_{16} branched chain alcohol, particularly of 2-ethyl hexanol, or "Oxo" alcohols consisting predominantly of C_8, C_9 or C_{10} alcohols, or of mixtures of such alcohols, and 35 to 10% of poly-

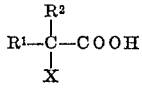
oxyalkylene glycol ether represented by the general formula:



wherein R_1, R and R_2 are hydrogen or C_1–C_{12} alkyl groups and wherein not more than two such groups are hydrogen, and n is an integer greater than 1. Particularly useful compounds are poly-oxypropylene glycol mono-ethers and the corresponding diethers.

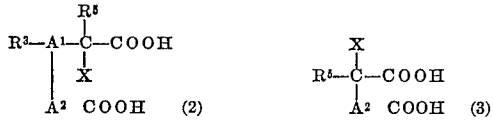
The thermal stability of such diester/polyoxyalkylene glycol ethers may be improved if a small proportion of a complex ester derived from three or more carboxylic acids or alcohols, at least two of which are difunctional acids or alcohols is incorporated. Such complex esters may be glycol- or dicarboxylic acid centered, the molecule being terminated with a mono-hydroxy or monocarboxylic acid compound. A particularly preferred complex ester of this type is derived from polyethylene glycol of molecular weight 200, 2 molecules of sebacic or azelaic acid, and 2 molecules of a C_6–C_{10} branched chain aliphatic monohydric alcohol, particularly 2-ethyl hexanol.

The amine salt of a halogen-substituted carboxylic acid is derived from a carboxylic acid substituted by halogen atoms at least one of which halogen atoms is in the alpha position. Suitable monocarboxylic acids include those of the general formula:



(1)

where R^1 and R^2 are hydrogen atoms, halogen atoms, or hydrogen- and carbon-containing groups or hydrogen-, carbon-, and halogen-containing groups and X is a halogen atom. Suitable dicarboxylic acids include those of the formula:



(2) (3)

where A^1 and A^2 are hydrogen- and carbon-containing groups, or hydrogen-, carbon- and halogen-containing groups, R^3 and R^5 are hydrogen atoms, halogen atoms, hydrogen- and carbon-containing groups, or hydrogen-, carbon- and halogen-containing groups and X is a halogen atom. In the case of dicarboxylic acids it is preferable if there are halogen atoms in both alpha positions.

The monocarboxylic acids must contain at least two carbon atoms and preferably 2 to 20 carbon atoms per molecule. The dicarboxylic acids must contain at least three carbon atoms, and preferably 3 to 25 carbon atoms per molecule. It is preferred that the carboxylic acid be saturated rather than unsaturated.

The halogen substituent is preferably chlorine, although fluorine, bromine and iodine could equally well be present. It is preferred that there be at least three halogen atoms per molecule. When there are more than one halogen atom per molecule it is desirable that the halogen atoms be as close to the carboxylic group as possible, e.g. three α-halogen atoms in the case of a halogenated acetic acid, and two α-halogen atoms in the case of longer chain monocarboxylic acids and four α-halogen atoms in the case of di-carboxylic acids.

The halogenated acids are preferably aliphatic acids but they can be aralkyl carboxylic acids where there is at least one halogen atom in the alpha position. Other halogen atoms are preferably in the alkyl portion of the molecule, but some or even all of the other halogen atoms can be substituted in the aryl, e.g. benzene, ring.

Suitable examples of halogenated carboxylic acids include monochloro acetic acid, dibromo acetic acid, difluoro acetic acid, trichloracetic acid, trifluoro acetic acid, α-chlor propionic acid; α-iodo propionic acid; α,β-dichloro propionic acids; α,α-dibromo propionic acid; α,α,γ-trichloro butyric acid; α,α-dibromo caproic acid; α,β,β-trichloro nonanoic acid; chloromalonic acid; dibromo malonic acid; α,α-dichloro glutonic acid; α,α,α-trifluoro glutonic acid; α,α-dibromo suberic acid; α,α,β,β-tetraiodo suberic acid; and α,α-dichloro phenyl acetic acid.

The amine salt of the halogenated carboxylic acid may be derived from a primary, secondary, tertiary, or quaternary amines. Suitable primary amines include primary alkyl amines, especially those wherein the alkyl group contains 2 to 20 carbon atoms, e.g. propyl amine, n-butyl amine, n-hexyl amine, a dodecyl amine, a tetradecyl-amine or eicosylamine, or branched chain primary amine analogues, e.g. Primene 81–R (a t-alkyl primary amine C_{12}–C_{14}). Although aliphatic primary amines are preferred, aromatic amines, e.g. aryl amines, such as aniline, or aralkylamines, such as benzylamine, could be used.

Suitable secondary amines include secondary alkyl amines, especially those wherein each alkyl group has 2 to 15 carbon atoms, e.g. di ethylamine; a di propylamine; a dihexyl amine; octyl, nonyl amine, or a didodecylamine. Although aliphatic secondary amines are preferred, aromatic amines, e.g. aryl amines such as diphenyl amine or methyl aniline, or aralkylamines such as dibenzylamine may be used.

Suitable tertiary amines include tertiary alkyl amines, especially wherein each alkyl group contains 2 to 12 carbon atoms. Thus examples of tertiary alkyl amines are triethyl amine; tri-n-propyl amine; tri-n-butylamine; a trihexyl amine; heptyl, dioctyl amine; or a tridecyl amine. Aliphatic tertiary amines are preferred, but aromatic amines, e.g. aryl amines such as dimethyl aniline, or triphenyl amine, or aralkylamines such as tribenzyl amine may be used.

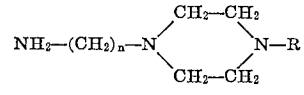
As an alternative polyamines may be used such as those of the formula

$$NH_2(CH_2)_n—(NH(CH_2)_n)_m—NH_2$$

where n is an integer and m is zero or an integer of from 1 to 10. Thus one may use hexylene diamine, diethyl-amine-triamine, tetraethylene pentamine, dipropylene triamine, octaethylene nonamine, and tetra-propylenepent-amine.

Alternatively one can use N-hydrocarbyl or N,N'-dihydrocarbyl substituted ethylene or propylene diamines where the hydrocarbyl groups have at least 3 carbon atoms, e.g. 3-laurylamino - 1 - butyl amine or N,N'-didodecyl-1,3-propylene diamine.

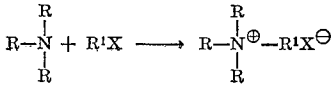
Other polyamino compounds that may be used include the N-aminoalkylpiperazines of the formula



wherein n is a number of 1 to 3, and R is hydrogen or an amino alkyl radical containing 1 to 3 carbon atoms. Thus, one may use N-(2-aminoethyl) piperazine; N-(2-amino-isopropyl) piperazine; or N,N'-di-(2-amino ethyl) piperazine.

To prepare the desired amine salt the halogenated acid and thhe amine are mixed together in substantially stoichiometric proportions (one mole of amine per mole of monocarboxylic acid, two moles of amine per mole of dicarboxylic acid etc.) and the reaction mixture is preferably heated.

In a preferred embodiment of the invention, the amine salt of the halogenated carboxylic acid is a quaternary ammonium salt. Such salts are conveniently prepared by heating a tertiary amine with an alkyl halide to form the quaternary ammonium halide, i.e.

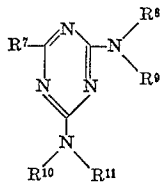


The halide thus produced is mixed with a solution of silver oxide in water and the reaction mixture is agitated. Silver halide is precipitated and a solution containing quaternary ammonium cations and hydroxide anions is obtained. This solution is then reacted with the halogenated carboxylic acid whence the desired quaternary ammonium salt of the halogenated acid is obtained. Thus for example if tri-n-butyl amine is reacted with n-butyl chloride, tetra-n-butyl ammonium chloride is obtained. This is reacted with silver oxide in water and tetra-n-butyl ammonium hydroxide is obtained which on reaction with trichloroacetic acid results in the production of tetra-n-butyl ammonium tri-chloro acetate.

The other component of the lubricant composition is an antioxidant. Many antioxidants for synthetic lubricants are known and these includue diarylamines and thiodiaryl amines. Suitable diarylamines include diphenyl amine; phenyl-α-naphthylamine; phenyl-β-naphthylamine; α,α-dinaphthyl amine; β,β-dinaphthylamine; or α,β-dinaphthylamine. Also suitable antioxidants are diarylamines wherein one or both of the aryl groups are alkylated, e.g. with alkyl groups containing 1 to 10 carbon atoms, such as the diethyl diphenylamines; dioctyldiphenyl amines, methyl phenyl - α - naphthylamines; phenyl-β (butylnaphthyl) amine; di(4-methyl phenyl) amine or phenyl (3-propyl phenyl) amine.

Suitable thiodiarylamines include phenothiazine, the alkylated phenothiazines, phenyl thio-α-naphthyl amine; phenyl thio-β-naphthylamine; α,α - thio dinaphthylamine; β,β-thio dinaphthylamine; phenyl thio-α (methyl naphthyl) amine; thio-di (ethyl phenyl) amine; (butyl phenyl) thio phenyl amine.

Other suitable antioxidants include s-triazines of the formula



where R^8, R^9, R^{10}, R^{11}, are hydrogen, C_1 to C_{20} hydrocarbyl or pyridyl, and R^7 is C_1 to C_8 hydrocarbyl, C_1 to C_{20} hydrocarbylamine, pyridyl or pyridylamine. If desired mixtures of antioxidants may be present in the lubricant composition of the invention.

The lubricant compositions of this invention may also incorporate one or more corrosion inhibitors. A particularly suitable corrosion inhibitor is sebacoc acid, although other dicarboxylic acids such as adipic acid may be used. Alternatively, the corrosion inhibitor may be a metal deactivator such as quinizarin, alizarin, anthrarufin, azoles (for example imidazole, benzotriazole, naphthotriazole) or alkyl gallates (for example, C_1 to C_{20} alkyl gallates such as propyl gallate).

Other additives which may be incorporated in the lubricant composition of the invention are foam inhibtors e.g. a silicone polymer such as dimethyl silicone, or methyl phenyl silicone. In addition if desired a further antiwear additive or extreme pressure additive may be incorporated, e.g. neutral alkyl phosphates, or neutral alkyl aryl phosphates.

The amount of the load-carryng additive, i.e. the amine salt of the halogen-substituted carboxylic acid is preferably between 0.01 and 10.0%, e.g. between 0.1 and 5.0% by weight based on the total weight of the lubricant composition. The amount of anti-oxidant or mixture of antioxidants should preferably be between 0.01 and 10.0%, e.g. between 0.1 and 5% by weight based on the total weight of the lubricant composition.

When used the amount of corrosion inhibitor based on the total weight of the lubricant composition is preferably between 0.001 to 2.0%, e.g. 0.01 to 1.0% by weight. When used the amount of foam inhibitor based on the total weight of the lubricant composition is preferably 0.0001 to 0.05% by weight.

EXAMPLE

A lubricant was prepared by adding to a synthetic ester lubricant prepared by esterifying commercial pentaerythritol (90 wt. percent pentaerythritol plus 10 wt. percent of dipentaerythritol) with a mixture of C_5 to C_9 carboxylic acids, 0.1% of tetra-n-butyl ammonium trichloroacetate, 1.6% of bis(p-octyl phenyl) amine, 0.4% of phenothiazine, and 0.02% of sebacic acid, the percentages being based on the total weight of the lubricant.

The IAE Gear Machine Load Pentagon OCS Test and Silicone Elastomer Compatibility Tests were carried out with the following results:

	Base oil alone	Base oil plus 0.1% TBTA	Specification
IAE gear machine load (at 110° C./6,000 r.p.m.) percent.	70	110	100.
Pentagon OCS test (at 425° F./72 hr.) weight change mg./cm.²:			
Fe		−0.01	
Al		−0.02	
Ag		−0.03	
Mg		Nil	
Cu		−0.43	
Silicone elastomer compatibility by Rolls-Royce method 1009 (at 175° C./192 hours):			
½ hr. swell		9.6	No shrinkage.
48 hr. swell		6.1	Do.

What is claimed is:

1. A lubricating oil composition consisting essentially of a major proportion of a lubricating oil, a minor load-carrying amount of a quaternary ammonium salt of trichloroacetic acid, and a minor oxidation inhibiting amount of an antioxidant selected from the group consisting of diarylamines, thiodiarylamines, triazines, and mixtures thereof, the quaternary ammonium portion of said salt having alkyl groups of from 2 to 12 carbon atoms.

2. A composition according to claim 1 in which the lubricating oil is a synthetic ester.

3. A composition according to claim 2 wherein the ester is a polyester of a monocarboxylic acid and a polyol containing 2 to 12 hydroxyl groups per molecule and 2 to 40 carbon atoms per molecule.

4. A composition according to claim 3 in which the polyol is pentaerythritol and the monocarboxylic acid contains 4 to 10 carbon atoms per molecule.

5. A composition according to claim 1 wherein said antioxidant is phenothiazine.

6. A composition according to claim 1 which also contains a corrosion inhibitor.

7. A composition as defined by claim 1 wherein the quaternary ammonium salt is tetra-n-butyl ammonium trichloro-acetate.

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