PATENT SPECIFICATION

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713,423

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COMPLETE SPECIFICATION

Improvements in or relating to Lubricating Compositions

We, C. C. WAKEFIELD & COMPANY, LIMITED, a British Company, of 46, Grosvenor Street, London, W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention consists in improvements in or relating to lubricating compositions.

It is well known that castor oil, while possessing excellent lubricating properties, possesses the serious disadvantage of being prone to fairly rapid oxidation by atmospheric oxygen, leading to what is known as "drying," namely the hardening of the oil to form a solid resinous product or a sticky gum.

The rate of oxidation of fatty oils depends on the types of fatty acids present and particularly on their degree of unsaturation. The principal constituents of castor oil are the glycerides of ricinoleic acid, a hydroxy-substituted unsaturated fatty acid containing one ~~ethylene~~ linkage. The oxidation which takes place is almost certainly accompanied by a polymerisation process in which the unsaturated molecules take part. The rate of oxidation and gum formation will, of course, depend on the temperature to which the oil is subjected and the presence of oxidation catalysts.

The invention relates not only to castor oil but to the esters of ricinoleic acid, e.g., the simple esters of monohydric alcohols and the polyhydric alcohol esters, to lubricants consisting of mixtures of castor oil and mineral oil (comprising a major proportion of castor oil) and to the so-called castor-base greases containing a major proportion of castor oil. These compounds together with castor oil are hereinafter referred to as oils or compositions of the kind described.

It is one particular object of this invention to provide lubricating compositions suitable for use in internal combustion engines and for the lubrication of bearings, gears, etc. in which castor oil is the major ingredient. It is known to employ castor oil or mixtures of castor oil with minor amounts of mineral oil as lubricants in a variety of applications and especially in the lubrication of motor car and motor cycle engines where high speeds and severe operating conditions obtain. The excellent lubricating properties and high load-carrying capacity of such lubricants are well known, but they suffer from the serious disadvantage of gum formation due to oxidation and polymerisation. Furthermore the free acid normally present to some extent in castor oil and the acidic products produced on oxidation are liable to cause corrosion of composite metal (e.g. copper-lead) bearings under operating conditions.

It is accordingly an object of this invention to provide lubricants consisting of castor oil or mixtures of castor oil and mineral oil in which the castor oil is present in a major proportion, which lubricants have substantially increased resistance to oxidation and gum-formation under operating conditions and which are also relatively non-corrosive to composite metal bearings.

Other practical uses of this invention will be obvious to those who are familiar with the industrial uses of castor oil. Thus castor oil and blends of castor and

mineral oil are used extensively for the lubrication of automotive and industrial gears. In such instances the question of corrosion does not arise, but resistance to gum formation is of great importance.

It is already known to inhibit the oxidation of fatty oils by the addition of various organic compounds of which the phenols (especially the polyhydric phenols) and the aromatic amines are examples.

Such compounds, however, suffer from the disadvantage that their effect is only of comparatively short duration.

It is also known to use amine anti-oxidants and organic tin compounds with mineral lubricating oils.

British Patent Specification No. 675,301, as open to inspection, discloses a grease comprising a mixture of castor oil and mineral oil with a tin soap aerogel and an amine anti-oxidant which may include phenyl-alpha or -beta-naphthylamine, alpha-alpha, beta-beta, or alpha-beta di-naphthylamine. British Patent Specification No. 578,723 discloses the addition of phenyl alphanaphtylamine together with a detergent, which may be a tin salt of a phenol (including a substituted phenol), an alcohol or a thio alcohol in a lubricating oil which may be castor oil.

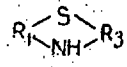
We have found that very much more effective resistance to oxidation and gum-formation can be obtained in the case of castor oil by the addition of a mixture of (a) an organic compound of tin or antimony and (b) an aromatic or heterocyclic secondary mono- or poly-amine containing at least three cyclic nuclei, at least two of which nuclei are aromatic nuclei attached directly to the nitrogen atom.

According to the present invention there is provided a lubricating composition consisting of an oil or composition of the kind described which contains (a) from 0.05 to 2.0 per cent by weight of an organic compound of tin or antimony and (b) from 0.1 to 5.0 per cent. by weight of an aromatic or heterocyclic-secondary mono- or poly-amine containing at least three cyclic nuclei at least two of which nuclei are aromatic nuclei attached directly to the nitrogen atom.

Typical formulae representative of the types of amines suitable for use in accordance with the present invention are:

$$R_1\text{-NH-}R_2$$

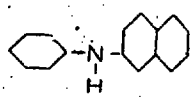
$$R_1\text{-NH-}R_3\text{-NH-}R_4$$



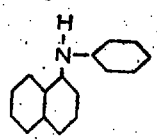
where R_1, R_3 and R_4 are the same or different and are aromatic radicals, and R_2 is a polycyclic nucleus containing at least one aromatic ring having at least ten carbon atoms. Any or all of these radicals may be further substituted by alkyl, aryl, hydroxyl or amine groups, although the preferred substituents are hydrocarbon radicals only.

Specific examples of amines which may be employed are

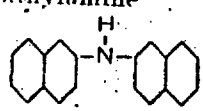
N-Phenyl-β-naphthylamine



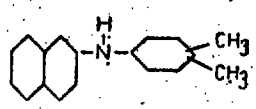
N-Phenyl-α-naphthylamine



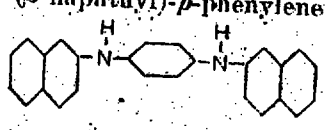
ββ-Dinaphthylamine



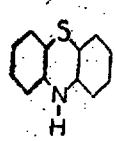
N-Xylyl-β-naphthylamines



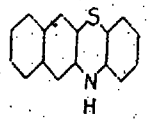
NN'-Di (β-naphthyl)-p-phenylene diamine



Phenthiazine
(Thiodiphenylamine)



Thio-phenyl-β-naphthylamine
(2.3 benzphenthiazine)

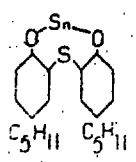


We have found surprisingly that only amines of the type described are effective for the purpose of the present invention,

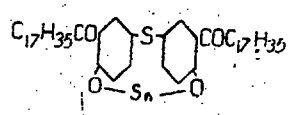
such closely related amines as α- and β-naphthylamine and diphenylamine being virtually without antioxidant effect.

The organic compounds of tin or antimony to be employed in conjunction with the amines already described are derivatives of divalent (stannous) tin or of antimony and may be the tin or antimony salts or soaps of organic carboxylic acids, organic sulphonic acids, organic dithiophosphoric acids, or the tin or antimony derivatives of phenols, phenol thioethers, or mercaptans.

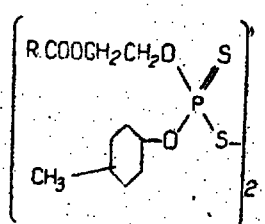
Specific examples of appropriate organic compounds of tin are tin laurate, tin oleate, tin naphthenate, tin petroleum sulphonate, the tin derivative of *p*-tertiary amyl phenol thioether



the tin derivative of *o*-stearyl phenol thioether



and the tin salt of ethylene glycol mononaphthenate cresyl dithiophosphate



(where R.COOH = naphthenic acid).

It will be understood that the compounds selected must be soluble in the particular oil in the proportion in which they are to be employed.

We have found that whereas in oils or compositions of the kind described, the tin compounds do not themselves possess any appreciable antioxidant or gum-inhibiting properties, they cooperate with the aromatic amines of the type described to give inhibition of oxidation over a period of time considerably longer than could be obtained by the use of the amines themselves in comparable proportions. In this respect the petroleum sulphonates of tin and antimony are particularly effective.

The aromatic amines used in this invention are employed in amounts ranging from 0.1 to 5.0 per cent. by weight and preferably between 0.5 and 2.0 per cent. by weight depending on the particular material to be inhibited, and the conditions under which it is to be employed, while the tin or antimony compounds are employed in amounts varying between 0.05 and 2.0 per cent. by weight and preferably between 0.1 and 1.0 per cent. by weight. In general the best results are obtained when the amount of tin or antimony compound present does not exceed the amount of amine by weight and preferably the amount of amine employed is at least double the amount of tin or antimony compound.

In certain applications, notably the lubrication of internal combustion engines fitted with composite metal (e.g. copper-lead) bearings, the inhibition of the corrosion of said bearings at elevated temperatures becomes of importance.

We have found that whereas the combinations of additives already described possess excellent anti-oxidant properties they are not effective in retarding bearing corrosion appreciably.

By the addition of a third additive (c) however, not in itself effective to any great extent in reducing such corrosion produced by fatty acids and acidic oxidation products of castor oil, we have found surprisingly that a very substantial reduction in corrosion can be effected.

The additives falling within class (c) which may be employed where necessary in conjunction with the additives of classes (a) and (b), comprise the neutral organic phosphite esters of hydroxy-substituted aromatic thioethers and disulphides. Examples of phosphite esters are described in British Patent No. 574,445.

Specific examples of such phosphite esters are di-(3-carbomethoxy-4-hydroxy phenyl) thioether cresyl phosphite, and the phosphite ester of *t*-butyl cresol thioether. These materials may be employed in amounts ranging from about 0.2 to about 5.0 per cent. by weight and preferably from 0.5 to 2.0 per cent. by weight.

If desired, further additives may be present in the compositions of this invention. Thus it may be desirable in certain instances to add viscosity index improvers, foam inhibitors, detergents, or ferrous metal corrosion inhibitors.

In particular we have found that certain additional benefits may accrue from the use in conjunction with the three

types of additives already described of the reaction products of aldehydes or ketones with basic water-soluble primary or secondary amines, a number of which compounds are described in British Patent No. 588,864.

We have found, for example that the addition of di-morpholinyl phenyl methane to a castor oil-mineral blend containing additives of types (a), (b) and (c) improved both its resistance to oxidation and its anti-corrosive properties. Advantage may accrue from the employment in certain instances of an antioxidant additive effective at high temperatures, along with the additives of the present invention. Such an antioxidant might be, for example, the metal salt of an organic dithiophosphoric acid or the metal derivative of an alkylated phenol thioether (other than the respective tin and antimony compounds).

Lubricating oil compositions typical of those falling within the scope of the present invention are:—

(The percentages in the following examples and tables are all percentages by weight).

(1) Firsts Castor Oil + 0.5% N-Phenyl-β-naphthylamine + 0.2% Tin petroleum sulphonate

(2) 90% Acidless castor oil
10% Mineral lubricating oil of viscosity 500" Redwood at 140° F.
+ 1.0% N-Phenyl-β-naphthylamine
+ 0.2% Tin petroleum sulphonate

(3) 87.5% Firsts castor oil
12.5% Mineral lubricating oil of viscosity 44" Redwood at 140° F.
+ 1.0% N-Phenyl-β-naphthylamine
0.2% Tin petroleum sulphonate
2.0% Di (3-carbomethoxy-4-hydroxyphenyl) thioether cresyl phosphite
0.2% Dimorpholinyl phenyl methane

By "tin petroleum sulphonate" is meant the tin salt of the oil-soluble petroleum sulphonic acids commonly known as "mahogany acids."

The following series of tests was carried out to determine the effectiveness of the compositions of the present invention:—

A. Gumming Tests at 120° C

One drop of the oil was placed in the centre of a watchglass and heated at 120° C. in an oven for a prolonged period. At intervals the watch glasses were withdrawn, allowed to cool and the liquid examined for signs of tackiness or gum formation.

The majority of the test results quoted were the mean of two or more such tests.

Table 1. Tests in this table serve to illustrate the surprising advantage of the use of the combination of two additives of the present invention over that of either additive used separately.

A blend of 90% Acidless castor oil
10% Mineral lubricating oil of viscosity 500" Redwood at 140° F. (Oil A).

was used as a basis for experimentation.

TABLE 1

Test No.	Additives: Amine	Additives: Tin or Antimony Compound	Approximate time (hours) to: Incidence of tackiness	Approximate time (hours) to: Gum formation
1	None	None	18	33
2	None	Tin petroleum sulphonate (0.2%)	18	23
3	N-phenyl-β-naphthylamine (1%)	None	110	125
4	" " (0.5%)	"	80	90
5	" " (1%)	Tin petroleum sulphonate (0.2%)	320	440
6	" " (0.5%)	" (0.2%)	157	190
7	" " (1.0%)	" (1.0%)	156	200
8	" " (0.5%)	Antimony petroleum sulphonate (0.2%)	160	180
9	N-phenyl-α-naphthylamine (1.0%)	None	115	135
10	" " (1.0%)	Tin petroleum sulphonate (0.2%)	160	185

Table 2. Tests in this table illustrate the range of tin and antimony compounds which may be employed in conjunction with a typical amine.

A blend of (90% Acidless castor oil, and 10% Mineral lubricating oil of viscosity 500" Redwood at 140° F. Oil A) + N-phenyl-β-naphthylamine (PBN) was employed throughout.

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TABLE 2

Test No.	Amount of PBN present	Metal compound added	Approximate time (hours) to Incidence of tackiness	Approximate time (hours) to Gum formation
1	1.0%	None	100	125
2	„	Tin petroleum sulphonate (0.2%)	320	440
3	„	Tin naphthenate (0.2%)	170	185
4	„	Tin oleate (0.2%)	125	145
5	„	Tin derivative of *p*-tertiary amyl phenol thioether (0.2%)	165	180
6	0.5%	None	80	90
7	„	Tin petroleum sulphonate (0.2%)	157	190
8	„	Tin laurate (0.2%)	120	130
9	„	Tin derivative of *o*-stearyl phenol thioether (0.2%)	130	155
10	„	Tin salt of ethylene glycol mono-naphthenate cresyl dithiophosphate (0.2%)	115	125
11	„	Antimony petroleum sulphonate (0.2%)	160	180
12	„	Antimony naphthenate (0.2%)	120	135

While, therefore, benefit accrued from the use of a wide variety of tin and antimony compounds, the petroleum sulphonates were outstandingly effective.

Table 3. Tests in this table illustrate the types of amines which may be employed in carrying out the present invention, in addition to those already cited in Table 1. The same blend was used as in Table 1 and Table 2.

TABLE 3

Test No.	Amine	Tin petroleum sulphonate present	Approximate time (hours) to: Incidence of tackiness	Approximate time (hours) to: Gum formation
1	ββ-Dinaphthylamine (0.5%)	0.2%	180	200
2	N-xylyl-β-naphthylamine (0.5%)	0.2%	145	160
3	Phenthiazine (0.5%)	0.2%	205	220
4	2.3 benzphenthiazine (0.5%)	0.2%	205	225
5	NN¹-diphenylbenzidine (saturated solution, less than 0.5%)	0.2%	over 320	—
6	NN¹di(β-naphthyl)-p-phenylene diamine (0.5%)	0.2%	320	345
7	β-naphthylamine (0.5%)	0.2%	less than 60	85
8	Diphenylamine (0.5%)	0.2%	40	65
9	Triphenylamine (1.0%)	0.2%	18	28

The last three results are quoted for comparative purposes to illustrate the relative ineffectiveness of certain amines closely related to those of the present invention.

Table 4. Tests in this table illustrate the range of ricinoleic acid derivatives which may be inhibited against gum formation by the additives of the present invention, and also the use of supplementary additives.

TABLE 4

Test No.	Material inhibited	Inhibitors added	Approximate time (hours) to: Incidence of tackiness	Gum formation
1	Firsts Castor Oil	None	21	28
2	" " "	1% N-phenyl-β-naphthylamine 0.2% Tin petroleum sulphonate 2.0% Di(3-carbomethoxy-4-hydroxy-phenyl) thioether cresyl ~~phosphate~~ phosphite 0.2% Dimorpholinyl phenyl methane	400	440
3	90% Acidless castor oil 10% Mineral oil A	None	18	33
4	" "	1% N-phenyl-β-naphthylamine 0.2% Tin petroleum sulphonate 2% Di(3-carbomethoxy-4-hydroxyphenyl) cresyl phosphite	230	250
5	" "	As No. 4 with the addition of 0.2% dimorpholinyl phenyl methane	250	275
6	Butyl ricinoleate	None	54	—
7	" "	1% N-phenyl-β-naphthylamine	235	285
8	" "	As No. 7 with the addition of 0.2% Tin petroleum sulphonate	255	—
9	Glyceryl diricinoleate	None	20	40
10	" "	1% N-phenyl-α-naphthylamine 0.2% Tin petroleum sulphonate	120	175

B. CORROSION TESTS.

The method of test employed was that described in British Patent No. 623,591 (test 4, on page 15).

The following test results illustrate the effectiveness of the hydroxyaryl thioether phosphites in conjunction with the other additives of the present invention, in inhibiting corrosion of lead at elevated temperatures.

TABLE 5

Test No.	Oil	Additives	Lead specimen weight loss (cumulative) mgs. after: hrs. 2	4	6	12
1	90% Acidless castor oil 10% Mineral oil A	None	58	153	—	—
2	,,	0.5% N-phenyl-β-naphthylamine 0.3% Tin petroleum sulphonate	264	371	—	—
3	90% Acidless caster oil 10% Mineral oil A	1.0% N-phenyl-β-naphthylamine 0.2% Tin petroleum sulphonate 2.0% Di(3-carbomethoxy-4-hydroxyphenyl) thioether cresyl phosphite 0.2% Dimorpholinyl phenyl methane	4	37	81	204
4	,,	1.0% N-phenyl-β-naphthylamine 0.2% Tin petroleum sulphonate 2.0% Tertiary butyl cresyl thioether phosphite	6	102	263	—
5	,,	1.0% N-phenyl-β-naphthylamine 0.2% Tin petroleum sulphonate 1.0% Di(3-carbomethoxy-4-hydroxyphenyl) thioether cresyl phosphite 1.0% Zinc di(α-methyl iso-amyl) dithiophosphate	13	25	42	135

C. ENGINE TESTS.

Tests were carried out in a standard H—2 type Lauson engine under the following conditions:

Jacket temperature	210° ± 2° F.
Oil sump temperature	280° ± 2° F.
Test duration	60 hours

The following test results illustrate the effectiveness of certain of the compositions used in the present invention as lubricants for internal combustion engines operating under severe conditions:—

TABLE 6

Test No.	Lubricant	Piston Lacquer rating. (CRC. visual rating)	Bearing weight loss mgs.	Used Oil Analysis: Per cent visc. inc.	Used Oil Analysis: Acidity (mgs. KOH per gm.)
1	87.5% Acidless castor oil 12.5% Mineral oil B	7.8	513	285	5.2
2	No. 1 + 1% N-phenyl-β-naphthylamine 0.2% Tin petroleum sulphonate 2% Di(3-carbomethoxy-4-hydroxyphenyl) thioether cresyl phosphite 0.2% Dimorpholinyl phenyl methane	8.2 (mean figures — 2 tests)	68	156	5.0
3	87.5% Firsts castor oil 12.5% Mineral oil B	8.5	509	442	5.9
4	No. 3 + the same additives employed in test No. 2	8.3 (mean figures — 2 tests)	103	175	6.5

In tests 1 and 3 there was a very heavy build-up of soft black gum on the neck of the inlet valve. In tests 2 and 4 the amount of deposit on the inlet valve was extremely light.

Oil B was a mineral lubricating oil of viscosity 44" Redwood at 140° F.

The method of rating piston cleanliness was that adopted by the Co-ordinating Research Council (C.R.C.) in which a perfectly clean piston is given a rating of 10 and a perfectly black piston a rating of zero.

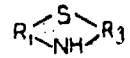
What we claim is:—

1. A lubricating composition consisting of an oil or composition of the kind described which contains (a) from 0.05 to 2.0 per cent. by weight of an organic compound of tin or antimony and (b) from 0.1 to 5.0 per cent. by weight of an aromatic or heterocyclic secondary mono- or poly-amine containing at least three cyclic nuclei at least two of which nuclei are aromatic nuclei attached directly to the nitrogen atom.

2. A lubricating composition as claimed in claim 1 in which the types of amines are:

$$R_1\text{-NH-}R_2$$

$$R_1\text{-NH-}R_3\text{-NH-}R_4$$



where R_1, R_3 and R_4 are the same or different and are aromatic radicals, and R_2 is a polycyclic nucleus containing at least one aromatic ring having at least ten carbon atoms.

3. A lubricating composition as claimed in claim 1 or in claim 2 in which constituent (a) is tin petroleum sulphonate or antimony petroleum sulphonate.

4. A lubricating composition for use in internal combustion engines as claimed in claims 1 to 3 in which a third additive is used comprising the neutral organic phosphite esters of hydroxy-substituted aromatic thioethers and disulphides.

5. A lubricating composition as claimed in claim 4 in which a fourth additive is used consisting of the reaction product of an aldehyde or ketone with a basic water-soluble primary or

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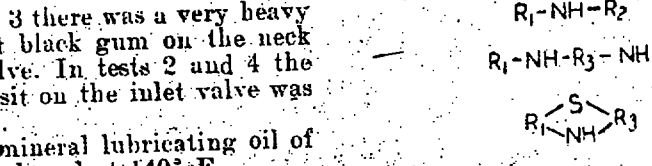
What we claim is:—

1. A lubricating composition consisting of an oil or composition of the kind described which contains (a) from 0.05 to 2.0 per cent. by weight of an organic compound of tin or antimony and (b) from 0.1 to 5.0 per cent. by weight of an aromatic or heterocyclic secondary mono- or poly-amine containing at least three cyclic nuclei at least two of which nuclei are aromatic nuclei attached directly to the nitrogen atom.

2. A lubricating composition as claimed in claim 1 in which the types of amines are:



where R_1, R_3 and R_4 are the same or different and are aromatic radicals, and R_2 is a polycyclic nucleus containing at least one aromatic ring having at least ten carbon atoms.

3. A lubricating composition as claimed in claim 1 or in claim 2 in which constituent (a) is tin petroleum sulphonate or antimony petroleum sulphonate.

4. A lubricating composition for use in internal combustion engines as claimed in claims 1 to 3 in which a third additive is used comprising the neutral organic phosphite esters of hydroxy-substituted aromatic thioethers and disulphides.

5. A lubricating composition as claimed in claim 4 in which a fourth additive is used consisting of the reaction product of an aldehyde or ketone with a basic water-soluble primary or

* C L M S *

secondary amine.

6. A lubricating composition as claimed in claim 4 or claim 5 in which there is also present an antioxidant effective at high temperatures, e.g. a metal salt of an organic dithiophosphoric acid or a metal derivative of an alkylated phenol thioether (other than the respective tin and antimony compounds).

7. Lubricating compositions substantially as described in the foregoing examples.

BOULT, WADE & TENNANT,
111 & 112, Hatton Garden,
London, E.C.1,
Chartered Patent Agents.

PROVISIONAL SPECIFICATION

Improvements in or relating to Lubricating Compositions

We, C. C. WAKEFIELD & COMPANY, LIMITED, a British Company, of 46, Grosvenor Street, London, W.1, do hereby declare this invention to be described in the following statement:—

This invention consists in improvements in or relating to lubricating compositions.

Castor oil and like compounds are prone to varying degrees of oxidation by atmospheric oxygen which may lead to what is known as "drying," namely the hardening of the oil to form solid resinous products or to form sticky gums or to produce objectional acidic bodies.

The rate of oxidation of such an oil depends on the types of fatty acids present, and particularly on their degree of unsaturation. Oils possessing a high proportion of acids having one or more double bonds are very readily oxidised. This oxidation is almost certainly accompanied by a polymerisation process in which the unsaturated molecules take part. Fatty oils are divided arbitrarily into three classes, viz. drying oils, semi-drying oils, and non-drying oils, according to their rate of drying or hardening at ordinary temperatures. These terms are only relative because all fatty oils are prone to oxidation especially at higher temperatures and especially in the presence of materials such as metals which act as catalysts. This invention relates to the treatment of castor oil and related materials, e.g. esters of monohydric alcohols.

It is one particular object of this invention to provide lubricating compositions suitable for use in internal combustion engines and for the lubrication of bearings, gears, etc., in which castor oil is the major ingredient. It is known to employ castor oil or mixtures of castor oil with minor amounts of mineral oil as lubricants in a variety of applications and especially in the lubrication of motor car and motor cycle engines where high speeds and severe operating conditions obtain. The excellent lubricating properties and high load-carrying capacity of such lubricants are well known, but they suffer from the serious disadvantage of gum formation due to oxidation and polymerisation. Furthermore the free acid normally present to some extent in castor oil and the acidic products produced on oxidation are liable to cause corrosion of composite metal (e.g. copper-lead) bearings under operating conditions.

It is accordingly an object of this invention to provide lubricants consisting of castor oil or mixtures of castor oil and mineral oil in which the castor oil is present in a major proportion, which lubricants have substantially increased resistance to oxidation and gum-formation under operating conditions and which are also relatively non-corrosive to composite metal bearings.

It is already known to inhibit the oxidation of fatty oils by the addition of various organic compounds of which the phenols (especially the polyhydric phenols) and the aromatic amines are examples.

Such compounds, however, suffer from the disadvantage that their effect is only of comparatively short duration.

We have found that very much more effective resistance to oxidation and gum-formation can be obtained in the case of castor oil by the addition of a mixture of (a) an organic compound of tin or antimony and (b) an aromatic or heterocyclic secondary or tertiary amine containing at least three cyclic nuclei, at least two of which nuclei are aromatic nuclei.

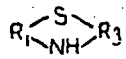
This invention in its broadest aspect therefore consist of a method of treating an oil of the kind described to inhibit oxidation and gumming which consists in adding to the oil (a) a very small proportion of an organic compound of tin or antimony and (b) a very small proportion of an aromatic or heterocyclic secondary or tertiary amine containing at least three cyclic nuclei at least two of which

nuclei are aromatic nuclei.

Typical formulae representative of the types of amines suitable for use in accordance with the present invention are:

$$R_1-NH-R_2$$

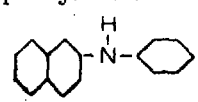
$$R_1-NH-R_3-NH-R_4$$



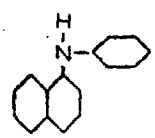
where R_1, R_3 and R_4 are the same or different and are aromatic radicals, and R_2 is a condensed aromatic nucleus having at least eight carbon atoms. Any or all of these radicals may be further substituted by alkyl, aryl, hydroxyl or amine groups.

Specific examples of amines which may be employed are:

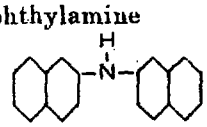
Phenyl-β-naphthylamine



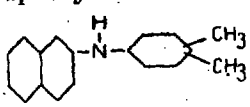
Phenyl-α-naphthylamine



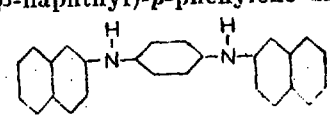
ββ-Dinaphthylamine



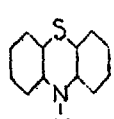
Xylyl-β-naphthylamine



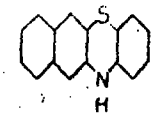
p-Di (β-naphthyl)-p-phenylene diamine



Phenothiazine



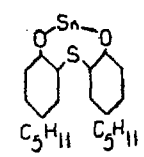
Thio-phenyl-β-naphthylamine (benzonaphthothiazine)



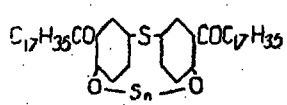
We have found surprisingly that only amines of the type described are effective for the purpose of the present invention, such closely related amines as α- and β-naphthylamine and diphenylamine being virtually without antioxidant effect.

The organic compounds of tin or antimony to be employed in conjunction with the amines already described are preferably derivatives of divalent (stannous) tin or of antimony and may be the tin or antimony salts or soaps of organic carboxylic acids, organic sulphonic acids, organic dithiophosphoric acids, or the tin or antimony derivatives of phenols, phenol thioethers, mercaptons, etc.

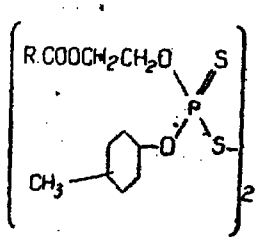
Specific examples of appropriate organic compounds of tin are tin laurate, tin oleate, tin naphthenate, tin petroleum sulphonate, tin derivative of p-tertiary amyl phenol thioether



tin derivative of o-stearyl phenol thioether



tin salt of ethylene glycol mononaphthenate cresyl dithiophosphate



(where R.COOH = naphthenic acid)

It will be understood that the compounds selected must be soluble in the particular oil in the proportions in which they are to be employed.

We have found that whereas the tin compounds do not themselves possess any appreciable antioxidant or gum-inhibiting properties, they cooperate with the aromatic amines of the type described to give inhibition of oxidation over a period of time considerably longer than could be obtained by the use of the amines themselves in comparable proportions.

The aromatic amines used in this invention may be employed in amounts ranging from about 0.1 to about 5.0 per cent. depending on the particular oil to be inhibited, while the tin or antimony compounds may be employed in amounts varying between about 0.05 and 2.0 per cent. and preferably between 0.1 and 1.0 per cent. In general the best results are obtained when the amount of tin compound present does not exceed the amount of amine by weight.

In certain applications, notably the lubrication of internal combustion engines fitted with composite metal (e.g. copper-lead) bearings, the inhibition of the corrosion of said bearings at elevated temperatures becomes of importance.

We have found that whereas the combinations of additives already described possess excellent anti-oxidant properties they are not effective in retarding bearing corrosion appreciably.

By the addition of a third additive (c) however, not in itself effective to any great extent in reducing such corrosion produced by fatty acids and acidic oxidation products of castor oil, we have found surprisingly that a very substantial reduction in corrosion can be effected.

The additives falling within class (c) which may be employed where necessary in conjunction with the additives of classes (a) and (b) comprise the neutral organic phosphite and thiophosphite esters, such as the simple trialkyl, triaryl and trialkaryl phosphites and thiophosphites and the phosphite esters of hydroxy-substituted aromatic thioethers and disulphides. Examples of these latter types of phosphite esters are described in British Patent No. 574,445.

Specific examples of such phosphite or thiophosphite esters are tri-*n*-butyl phosphite, triphenyl phosphite, tri-*p*-tertiary amyl phenyl) phosphite, tricresyl thiophosphite, di (3-carbomethoxy-4-hydroxy phenyl) thioether cresyl phosphite, phosphite esters of *t*-butyl cresol thioether, etc. These materials may be employed in amounts ranging from about 0.2 to about 5.0 per cent., and preferably from 0.5 to 2.0 per cent.

If desired, further additives may be present in the compositions of this invention. Thus it may be desirable in certain instances to add viscosity index improvers, foam inhibitors, detergents, ferrous metal corrosion inhibitors, etc.

In particular we have found that certain additional benefits may accrue from the use in conjunction with the three types of additives already described of the reaction products of aldehydes or ketones with basic water-soluble primary or secondary amines, a number of which compounds are described in British Patent No. 588,864.

We have found, for example that the addition of di morpholinyl phenyl methane to a castor-mineral oil blend containing additives of types (a), (b) and (c) improved both its resistance to oxidation and its anti-corrosive properties.

Lubricating oil compositions typical of those falling within the scope of the present invention are:—

(1) Firsts Castor Oil + 0.5% Phenyl-*β*-naphthylamine
0.2% Tin petroleum sulphonate

(2) 90% Acidless castor oil
10% Mineral lubricating oil of viscosity 500" Redwood at 140° F.
+ 1.0% Phenyl-*β*-naphthylamine
0.2% Tin petroleum sulphonate

(3) 87.5% Firsts castor oil
12.5% Mineral lubricating oil of viscosity 44" Redwood at 140° F.
+ 1.0% Phenyl-*β*-naphthylamine
0.2% Tin petroleum sulphonate
2.0% Di (3 - carbomethoxy-4-hydroxyphenyl) thioether cresyl phosphite
0.2% Dimorpholinyl phenyl methane.

By "tin petroleum sulphonate" is meant the tin salt of the oil-soluble petroleum sulphonic acids commonly known as "mahogany acids." The organic compounds of tin may be replaced by the corresponding compounds of antimony.

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