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2,991,251 CORROSION INHIBITING LUBRICATING COMPOSITION

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This invention relates to materials and methods for in-
hibiting the lead corroding tendency of compositions con-
taining partial esters of aliphatic polyhydroxy alcohols.
Particularly, it relates to oil compositions comprising partial
esters of polyhydroxy alcohols and minor amounts,
sufficient to inhibit lead corrosion, of mercaptobenzothiazole
or its derivatives and/or hydroxy benzoic acid or
its derivatives.

Fatty acid partial esters of aliphatic polyhydric alcohols,
e.g., sorbitan monooleate, have found widespread use for
inhibiting the corrosion of iron. However, in certain ap-
plications where the composition containing the partial
ester also comes in contact with lead, the partial ester
causes excessive corrosion of lead, even though inhibiting
the corrosion of iron. For example, mineral oil com-
positions containing sorbitan monooleate have been used
in the crankcase of piston-type aircraft engines to pre-
vent rusting during storage. For this use, the engine is
run for a short period of time to circulate the composi-
tion through the engine, after which the engine is turned
off, and the oil drains back to the crankcase, leaving a
protective film on the cylinder walls and other internal
parts of the engine. Recently, for purposes of economy,
it has become desirable to use the same composition for
actual operation of the engine, rather than to remove
the rust preventive oil composition and replace it with
fresh lubricating oil. However, when the oil composi-
tion containing the partial ester was later used as lubricat-
ing oil, such that the composition was circulated through
the engine for long periods of time, excessive corrosion of
the lead in the copper-lead bearings in the engine oc-
curred. It has now been found that the lead corroding
tendencies of these partial esters may be effectively curbed,
without interfering with their rust inhibiting properties,
by the addition of a minor amount of mercaptobenzothiazole
and its derivatives, or hydroxy benzoic acid and
its derivatives.

The compositions of the invention will generally com-
prise an oil base, about 1 to 25, e.g., 2 to 10 weight
percent of the partial ester, and about 0.01 to 2.0, e.g.,
0.03 to 1.0 weight percent of the lead corrosion inhibiting
material.

The oil base will generally be a mineral lubricating oil,
although other petroleum bases such as kerosene, gas oil,
naphthas, petrolatum, etc. may be used.

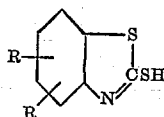
The partial esters used as rust preventives include the
C₁₂ to C₂₂ fatty acid partial esters of aliphatic polyhydric
alcohols having about 3 to 12, e.g., 3 to 8 carbon atoms,
and about 2 to 8, e.g., 3 to 6 hydroxy groups per mole-
cule. Preferred materials are the mono- and diesters of
C₃ to C₆ alcohols having about 3 to 6 hydroxyl groups
and prepared from C₁₂ to C₁₈ fatty acids. The above type
of partial esters includes the partial esters of the mono-
dehydrated aliphatic polyhydric alcohols, which are well
known in the art, for example, see U.S. Patent 2,434,490,
as well as partial esters of non-dehydrated aliphatic poly-
hydric alcohols, e.g. pentaerythritol monooleate.

Specific examples of the above types of partial esters
will therefore include: glyceryl monooleate, pentaerythritol
monooleate, sorbitan monooleate, the dioleates of
sorbitan, mannitan, pentaerythritol and related polyhydric
alcohols, the corresponding partial stearic and palmitic

acid esters of these alcohols, and partial esters of these
alcohols made from mixtures of these fatty acids.

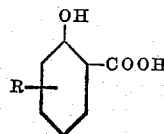
The lead corrosion inhibiting agents are organic mate-
rials containing an aromatic nucleus, and are of two
general types as follows:

Mercaptobenzothiazoles and its derivatives having the
general formula:



wherein each R is hydrogen or a C₁ to C₈, e.g., C₁ to C₄
alkyl group. Specific examples of such materials include:
2-mercaptobenzothiazole; 2-mercapto, 4,6-dimethyl benzo-
thiazole; 2-mercapto, 4-methyl, 6-octyl benzothiazole; 2-
mercapto, 4-tertiary butyl benzothiazole; etc.

Salicylic acid and its derivatives having the general
formula:



wherein R is hydrogen or a C₁ to C₈ straight or branched-
chain alkyl group.

Specific examples of the salicylic acid materials of
the above formulas include: salicylic acid, 2-hydroxy-3-
methyl benzoic acid, 2-hydroxy-4 octyl benzoic acid, etc.

Other additive materials, to adapt the composition of
the invention to special applications, may also be in-
cluded in the composition in amounts of about 0.05 to
10.0 wt. percent based on the weight of the total composi-
tion. For example, it may be desirable to add other rust
preventive additives, such as petroleum sulfonates and
lecithin; viscosity index improvers, such as polymeth-
acrylates and polyisobutylene; oxidation inhibitors; etc.
Materials of increased consistency may also be prepared
by thickening the oil composition of the invention with
appropriate soaps, polymers, waxes, etc. In some cases,
the addition of a C₁ to C₁₈, e.g. C₂ to C₈, alkyl amine to
the composition seems to aid in inhibiting lead corrosion,
particularly when it is used in conjunction with the sali-
cyclic acid type inhibitor.

The lead corrosion inhibitors of the invention were
found to be the only effective materials of a wide number
of similar type materials and other known inhibiting agents
which were tested. This is shown by the following ex-
amples:

EXAMPLE I

The test for lead corrosion was the S.O.D. lead cor-
rosion test, which was carried out by suspending rotat-
ing copper and lead strips for one hour in the oil com-
position maintained at a temperature of 325° F. Fol-
lowing this, the lead strip was removed and the change
in weight of the strip, in terms of milligrams per square
inch of strip, was measured. The above test was carried
out on: the base oil per se, which was a solvent extracted
Mid-Continent mineral lubricating oil having a viscosity
of 100 SUS at 210° F.; a composition consisting of 95
weight percent of the base oil and 5 weight percent of
a commercial sorbitan monooleate sold under the trade
name of Span 80; and the oil-sorbitan monooleate com-
position containing various different additives. The re-

sults of this series of tests are summarized in the following table:

Table I

S.O.D. LEAD CORROSION TEST
[1 hour at 325° F. with copper catalyst]

Wt. Percent Inhibitor Added to Oil-Sorbitan Monooleate Composition	Lead Strip Weight Loss (mg./sq. in.)
Oil, per se.....	6
95% oil and 5% sorbitan monooleate.....	249
1.0 Ditertiary butyl para cresol.....	231
1.0 Phenyl alpha naphthylamine.....	262
1.0 Hydroquinone monomethyl ether.....	308
1.0 Lecithin.....	395
1.0 Amine from hydrogenated tallow acids.....	194
0.5 2-Ethyl hexyl amine.....	195
1.0 adduct of salicylaldehyde and ethylene diamine.....	361
0.5 Dioctyl phosphoric acid.....	268
0.5 Trioctyl phosphate.....	187
0.5 Zinc dioctyl dithiophosphate.....	278
1.0 Cetyl mercaptan.....	312
0.5 Tridodecyl borate.....	308
0.5 Methyl thluram disulfide.....	207
1.0 Phenothiazine.....	199
1.0 Mercaptobenzothiazole.....	+4
0.1 Mercaptobenzothiazole.....	132

As seen from the above tests, the base oil per se showed a lead strip weight loss of only 6 mg., yet when 5 weight percent of sorbitan monooleate was added to this oil, it then gave a weight loss of 249 mg. Of the numerous inhibitors tested above, it is seen that only the mercaptobenzothiazole was effective. Thus, one weight percent of mercaptobenzothiazole had actually resulted in a small gain of +4 mg., and as little as one-tenth of 1 percent of mercaptobenzothiazole had effectively reduced the corrosivity about in half.

EXAMPLE II

Another series of compositions was tested by adding various inhibitors to the oil-sorbitan monooleate composition of Example I. However, in these tests the lead strip was exposed for two hours at 325° F. and no copper was present. Results are reported in Table II.

Table II

MODIFIED S.O.D. LEAD CORROSION TEST
[2 hrs. at 325° F. without copper catalyst]

Wt. Percent Inhibitor Added to Oil-sorbitan Monooleate Composition	Weight Loss of Lead Test Strip (mg./sq. in.)
95% oil and 5% sorbitan monooleate.....	121
0.1 Salicylic acid.....	10
0.05 Salicylic acid.....	100
0.1 Salicylic acid+0.1 n-butyl amine.....	5
0.05 Salicylic acid+0.05 n-butyl amine.....	101
0.1 Salicylic acid+0.05 mercaptobenzothiazole.....	18
0.05 Salicylic acid+0.05 mercaptobenzothiazole.....	63

As seen from Table II, the lead corrosiveness of the oil-sorbitan monooleate composition was somewhat less in the absence of the copper catalyst (cf. Table I). The salicylic acid per se was very effective in inhibiting the lead corrosion. The addition of 0.1% alkyl amine with the 0.1% salicylic acid was also found very effective,

as are blends of salicylic acid and mercaptobenzothiazole. The use of aliphatic hydroxy acids such as citric, maleic and tartaric acids was not effective.

The inhibitors of the invention can also be mixed directly with the partial ester or concentrates thereof to form a rust preventive additive mixture which is also inhibited against lead corrosion.

To further illustrate the invention, other compositions can be prepared as follows:

10 A. 0.05 wt. percent of 4-methyl, 6-n-octyl benzothiazole can be added by simple mixing to a composition consisting of 1.0 wt. percent of glyceryl monostearate and 99.0 wt. percent of mineral lubricating oil of the type used in Example I.

15 B. 2.0 wt. percent of 2-hydroxy-4-n-octyl benzoic acid can be added by simple mixing to a composition consisting of 10.0 wt. percent of the dioleate of mannitan and 90.0 wt. percent of mineral lubricating oil of the type used in Example I.

20 C. 5 wt. percent of mercaptobenzothiazole may be mixed with 95 wt. percent of Span 80 (sorbitan monooleate) to form an additive mixture.

In summary, the invention relates to materials and methods for inhibiting the lead corroding tendencies of compositions containing a fatty acid partial ester (usually the mono- or diester) of a polyhydric alcohol by mixing into said compositions about 2 to 40 wt. percent, e.g. 4 to 20 wt. percent, based on the weight of partial ester, a lead corrosion inhibitor. This lead corrosion inhibitor may be mercaptobenzothiazole, or its ring substituted alkyl derivatives or salicylic acid or its ring substituted alkyl derivatives or mixtures thereof.

What is claimed is:

1. A lubricating composition which is rust preventive and substantially non-corrosive to lead, which comprises a major proportion of mineral lubricating oil, about 1 to 25 wt. percent of sorbitan monooleate, and about .03 to 1.0 wt. percent of a material selected from the group consisting of mercaptobenzothiazole, salicylic acid, and mixtures thereof.

2. The lubricating composition of claim 1, wherein said material is mercaptobenzothiazole.

3. The lubricating composition of claim 1, wherein said material is salicylic acid.

45 4. The lubricating composition of claim 1 which also contains 0.5 to 10.0 wt. percent of a C₁ to C₁₈ alkyl amine.

50 5. A lubricating composition which is rust preventive and substantially non-corrosive to lead, comprising a major amount of mineral lubricating oil, about 2 to 10 wt. percent of sorbitan monooleate, and about 0.03 to 1.0 wt. percent of a material selected from the group consisting of mercaptobenzothiazole and salicylic acid.

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