

Patented Jan. 27, 1948

14,978

UNITED STATES PATENT OFFICE

2,434,978

ANTICORROSION ADDITIVES FOR
SYNTHETIC LUBRICANTS

William A. Zisman, Washington, D. C., and Hay-
ward R. Baker, Mt. Rainier, Md., assignors to
the United States of America, as represented by
the Secretary of the Navy

No Drawing. Application April 15, 1944,
Serial No. 531,240

7 Claims. (Cl. 352—32)

(Granted under the act of March 3, 1883, as
amended April 30, 1928; 370 O. G. 757)

1

This invention relates to anti-corrosion addi-
tives for use with a new type of oil made by the
polymerization of alkylene oxides, and to such
oils containing the same.

In the effort to develop lubricants and hydraulic
oils of less inflammability than the petroleum
hydrocarbons, and of lower viscosity at low tem-
peratures, a new type of oil, or series of oils, has
been developed wherein mixed alkylene oxides
play an important part in the molecular struc-
ture. These oils, briefly, are copolymers of vari-
ous alkylene oxides, such as ethylene oxide and
propylene oxide, and they are known in the trade
as B-O-100 oils.

In spite of their unusual physical properties,
these oils, by themselves, are rather limited in
application because they are relatively corrosive
when compared to the best protected hydrocar-
bon oils.

This invention provides a group of organic com-
pounds which are soluble and compatible with the
B-O-100 oils at high and low temperatures and
which inhibit the corrosive action of the oils when
dissolved therein in small quantities. The inven-
tion also includes these oils containing the anti-
corrosion additives referred to, as new composi-
tions of matter.

Not all organic compounds which are soluble in
these oils are capable of inhibiting their corrosive
action. The group of the compounds which are
effective may be classified generally in the form
of several sub-groups, namely:

Naphthenic acids having molecular weights be-
tween about 180 and 440, metal naphthenates of
said acids, n-alkoxy derivatives of benzoic acid
wherein the alkyl chain has from 6 to 18 carbon
atoms, esters of anhydro-sorbitol and anhydro-
mannitol with aliphatic monocarboxylic acids
having from 6 to 18 carbon atoms, saturated and
unsaturated aliphatic amines having from 6 to 18
carbon atoms, metal soaps of aliphatic acids from
caproic to stearic, aliphatic alpha-hydroxy acids
from alpha-hydroxy caproic to alpha-hydroxy
stearic, saturated aliphatic acids from caproic to
palmitic, monocarboxylic aliphatic acids contain-
ing a triple bond and having from 6 to 18 carbon
atoms, alkaryl derivatives of aliphatic acids from
caproic to stearic the alkaryl group consisting of
an alkyl chain from 1 to 18 carbon atoms and an
aryl group, and acid-amide complexes formed by
reacting unsubstituted and aryl-substituted ali-
phatic acids from caproic to stearic with aromatic
amines and with aliphatic amines having from
8 to 18 carbon atoms.

2

Typical, preferred compounds within these
groups are described more in detail as follows:

The aliphatic series of acids from lauric to
palmitic protects steel from corrosion when in a
mixture of B-O-100 oil and water. Also the acids
from caproic to lauric are useful, although larger
quantities will be required to give complete pro-
tection. The shorter chain acids are useful at
very low temperatures such as minus 40° F. for
lauric acid and even lower for those with 6 or 8
carbon atoms. Naphthenic acids with molecular
weights of 180 to 440 are highly effective at tem-
peratures as low as minus 40° F., and other naph-
thenic acids of lower molecular weights are useful
at still lower temperatures, although greater
quantities are necessary.

The aliphatic amines from decyl amine to
octadecyl amine are effective for temperatures
ranging from minus 40° F. upward, depending
upon the chain length of the amine. The quan-
tity used to secure protection, in general, is less
within increasing chain lengths.

Other amines which are useful are those from
decenyl and decendienyl to octadecenyl and octa-
decendienyl amine and mixtures of these. (In
the table given below, a mixture of n-mono-octo-
decenyl amine and n-mono-octadecendienyl
amine is illustrated.) These amines serve effec-
tively as anti-corrosion agents in the B-O-100
oils of extreme temperature ranges including
temperatures much lower than minus 40° F.

Ethylphenyl stearic acids and the related com-
pounds from methyl to octadecyl and phenyl,
benzyl, tolyl, xylyl and naphthyl substituted ali-
phatic acids from caproic to stearic are excellent
additives and are useful from temperatures at the
upper limits of normal use to below minus 40° F.
Preferably a combination of shorter chain acids
is used in the oils which are to be subjected to
extremely low temperatures. Some of the addi-
tives covered within this sub-group and which
are particularly useful are as follows: phenyl
stearic acid, xylyl stearic acid, tolyl stearic acid,
xenylyl stearic acid, cumyl stearic acid, pseudo
cumyl stearic acid, diethylphenyl stearic acid, di-
isopropyl phenyl acid, tetrahydronaphthyl stearic
acid, chlorophenyl stearic acid.

The various metal naphthenates are useful, dif-
ferent ones having particular merit over different
temperature ranges. Zinc naphthenate is one
which serves at high temperatures and is also
effective down to minus 40° F.

Other metallic soaps from caproates to stea-
rates are satisfactory corrosion preventatives,

some for temperatures in the higher range and others over a wider range of temperatures. Zinc stearate is effective both in the higher ranges and as low as minus 20° F.

Alpha hydroxy substituted acids from caproic to stearic are satisfactory addition agents, of which alpha hydroxy palmitic acid is effective at temperatures even below minus 40° F.

Para-n-dodecyloxy benzoic acid and the related ortho, meta and para acids from hexyl to octadecyloxybenzoic acids serve at both high and low temperatures. Stearolic acid, 9-octadecynoic acid (an 18 carbon atom acid with an unsaturated triple bond) and similar unsaturated aliphatic acids from hexanoic to stearic acid are useful at high temperatures and down to temperatures below minus 40° F.

Sorbitan mono-oleate, which is an ester of an anhydro polyhydric alcohol, and esters resulting from the esterification of one or more hydroxyl groups of an anhydro-sorbitol or an anhydro-mannitol with one or more of the aliphatic monocarboxylic acids are effective additives over the average temperature range and to temperatures below minus 40° F.

A series of compounds or mixtures of compounds or complexes made by combining equivalent weights of aliphatic acids from caproic to stearic, or phenyl, benzyl, tolyl, or naphthyl substituted aliphatic acids with an equivalent weight of amine from octyl to octadecyl or aromatic amines or aromatic substituted aliphatic amines, are highly effective anti-corrosion additives. These complexes are most easily prepared by dissolving the acid and amine in alcohol warming slightly and mixing well. Then the alcohol is allowed to evaporate, leaving the acid amine complex which is used as the additive for the B-O-100 oils. All of these series of complexes are useful over very wide temperature ranges and some of them are desirable additives for use at temperatures below minus 40° F. *

Mixtures of any of these additives may be used in the B-O-100 oils to achieve characteristics dependent on more than one type of additive. A comparison of the effects of different specific additives on the B-O-100 oils is shown in the following table, the meaning of the abbreviations being given below:

Table

Additive	Lubricant used	Corrosion rating	Per cent Additive by Weight	Solubility in Lubricant used	Effect of cold storage in two weeks
				° C.	° F.
lauric acid.....	250-B-O-100	0	0.5	S 25	S 40
myristic acid.....	400-B-O-100	0	0.5	S 25	S 20
palmitic acid.....	250-B-O-100	0	0.5	S 100	S 0
naphthenic acid M. W.—240.....	400-B-O-100	0	1.0	S 25	S 40
naphthenic acid M. W.—440.....	250-B-O-100	0	0.5	S 25	S 40
hexadecyl amine.....	250-B-O-100	0	1.0	S 25	S 0
mixture of n-mono octadecenyl and n-mono octadecendienyl amine.....	400-B-O-100	0	1.0	S 25	S 40
and	250-B-O-100				
ethyl phenyl stearic acid.....	250-B-O-100	0	0.75	S 25	S 40
phenyl stearic acid.....	250-B-O-100	0	0.5	S 25	S 40
xylyl stearic acid.....	250-B-O-100	0	0.5	S 25	S 40
zinc naphthenate.....	250-B-O-100	0	0.5	S 100	S 40
zinc stearate.....	250-B-O-100	0	0.2	S 100	S 20
palmitic 2-hydroxy acid.....	400-B-O-100	0	0.5	S 25	S 40
p. n. dodecyloxy benzoic acid.....	250-B-O-100	0	0.2	S 25	S 40
stearolic acid.....	250-B-O-100	0	1.0	S 25	S 40
sorbitan monooleate.....	250-B-O-100	0	1.0	S 25	S 40
stearic acid and phenyl alpha naphthyl amine complex.....	250-B-O-100	0	0.75	S 100	S 0
stearic acid and dodecyl amine complex.....	250-B-O-100	0	1.0	S 100	S 20
stearic acid and tetradecyl amine complex.....	250-B-O-100	0	0.75	S 100	S 0
stearic acid and hexadecyl amine complex.....	250-B-O-100	0	0.75	S 100	S 0
stearic acid and octadecyl amine complex.....	250-B-O-100	0	0.75	S 100	S 0

S=soluble. The number preceding the "B-O-100" in column 2 indicates the relative degree of polymerization of the oil. In some cases the additive is soluble in the lubricant used only on long standing. If, however, it is warmed slightly it is soluble immediately.

The corrosion rating was determined by a modification of the A. S. T. M. turbine corrosion test D-665-42-T. The modification consisted of using a flat bottom pyrex cylindrical container 80 by 18 mm. in size. The specimen was a piece of cold rolled steel 4.25 by 0.25 by 0.03 inch in size. The specimen was attached directly to the shaft of a motor and serves as its own stirrer, revolving at approximately 1080 R. P. M. The lower 1.78 inches of the specimen is the only part considered in the test as it alone is in contact with the liquid sample. The sample consists of 9 parts by volume of B-O-100 oil, 1 part of distilled water containing the additive compound, thus giving a mixture of 90% B-O-100 oil and about 10% water. The steel specimen was rotated in the mixture for 48 hours at 140° F.

Many variations will be apparent to those skilled in the art, and the invention should not be limited other than as defined by the appended claims.

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

We claim:

1. A synthetic hydraulic and lubricating fluid composition which comprises essentially a polyalkylene oxide fluid having dissolved therein a corrosion inhibitor, which inhibitor comprises at least one compound selected from the group consisting of aliphatic acids, alkaryl derivatives of aliphatic acids, and metal soaps of said acids, wherein the aliphatic acid is one having from about 6 to 18 carbon atoms in the aliphatic chain.

2. A synthetic hydraulic and lubricating fluid composition which comprises essentially a polyalkylene oxide fluid and about 0.1 to about 2 per cent by weight of an inhibitor dissolved therein, which inhibitor comprises at least one compound selected from the group consisting of aliphatic acids, alkaryl derivatives of aliphatic acids, and metal soaps of said acids, wherein the aliphatic acid is one having from about 6 to about 18 carbon atoms in the aliphatic chain.

3. A synthetic fluid lubricating composition which comprises essentially a polyalkylene oxide fluid and about 0.1 to about 2 per cent by weight

5

of an inhibitor dissolved therein which comprises at least one alkaryl derivative of aliphatic acids from caproic to stearic, the alkaryl group consisting of an alkyl chain from 1 to 18 carbon atoms and an aryl group.

4. A synthetic hydraulic and lubricating fluid composition which comprises essentially a polyalkylene oxide fluid and about 0.1 to about 2 per cent by weight of ethyl phenyl stearic acid dissolved therein.

5. A synthetic fluid lubricating composition which comprises essentially a polyalkylene oxide fluid and about 0.1 to about 2 per cent by weight of an inhibitor dissolved therein which comprises at least one alpha-hydroxy acid from alpha hydroxy caproic to alpha hydroxy stearic.

6. A synthetic fluid lubricating composition which comprises essentially a polyalkylene oxide fluid and about 0.1 to about 2 per cent by weight of an inhibitor dissolved therein which comprises at least one saturated aliphatic acid from caproic to palmitic.

6

7. A synthetic hydraulic and lubricating fluid composition which comprises essentially a polyalkylene oxide fluid and about 0.1 to about 2 per cent by weight of lauric acid dissolved therein.

WILLIAM A. ZISMAN.
HAYWARD R. BAKER.

REFERENCES CITED

- 10 The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
15 2,308,502	Farrington	Jan. 19, 1943
2,296,342	Gaylor et al.	Sept. 22, 1942
2,293,868	Toussaint	Aug. 25, 1942
2,281,676	Cock	May 5, 1942
2,268,608	McNulty et al.	Jan. 6, 1942
20 2,152,683	Eichwald	Apr. 4, 1939
2,149,498	Bludworth	Mar. 7, 1939