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LUBRICATING COMPOSITION

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This invention relates, as indicated, to lubricants and more particularly to lubricating compositions and methods of lubricating having certain advantages over such compositions and methods now familiar to those skilled in the art.

This application is a continuation in part of co-pending application Serial No. 737,070, filed July 26, 1934, and copending application Serial No. 755,987, filed December 4, 1934.

At the present time there is an increasing demand for lubricating compositions capable of resisting the effects of extreme pressures and temperatures under conditions of use and it is an object of the present invention to provide such a composition.

By "extreme pressures," as referred to above, is meant pressures of or in excess of 10,000 pounds per square inch, such pressures being now commonly encountered in hypoid gears, bearings, contact surfaces of cylinders and piston rings in internal combustion engines, and many other points. Such pressures tend to cause the rupture of the continuous "thick film" of lubricant which separates bearing surfaces under more moderate conditions. A region of "thin film" lubrication results which is also sometimes described as "boundary" lubrication.

A particular object of my invention is, therefore, to provide a lubricant and method of lubricating which will function to advantage under conditions of extreme pressure and effectively prevent seizure and scoring of the relatively moving metallic surfaces being lubricated.

Other objects of this invention will appear as the description proceeds.

To the accomplishment of the foregoing and related ends, this invention, then, comprises the means hereinafter fully described and particularly pointed out in the claims. The following description sets forth in detail certain approved combinations of ingredients embodying my invention, such disclosed means constituting, however, but certain of the various forms in which the principle of the invention may be employed.

Broadly stated, this invention contemplates the combined use in lubricating compositions of a soap (salt) or ester of a naphthenic acid and a separate halogenated organic compound.

When liquid compositions are desired, as, for instance, in the lubrication of Diesel engines, it is obvious that only relatively small proportions of the soap should be added to the hydrocarbon base oil. Since, however, it has been found that the presence of even small amounts of the naphthenate will considerably enhance the effectiveness of the separate halogen compound, liquid compositions are satisfactory for many purposes

and may contain as little as 0.1% of the soap or ester although from about 1% to about 5% by weight, based on the amount of oil, is generally more desirable and where solid or semi-solid greases are to be employed much larger percentages of the soap may be suitable, up to about 60%.

The base oil employed in the composition of this invention is generally mineral oil but it is to be understood that any other suitable hydrocarbon lubricating oil, whether naturally occurring or synthetic, may be employed as the oil base.

It is also within the contemplation of this invention to provide the addition agents in the form of a concentrate in a suitable oil, said oil containing rather high percentages of the addition agents. Such concentrates may be employed for future blending with a lubricating oil in the proportions desired for the particular conditions of use.

The following list of naphthenates suitable for use in accordance with the invention is intended to be illustrative only and it is to be understood that various other compounds coming within the group of salts (soaps) and esters of naphthenic acids broadly are included within the scope of the invention:

- A. Salts (soaps) of naphthenic acids
 - (1) Salts of alkali metals, e. g.,
Sodium naphthenate
Potassium naphthenate
 - (2) Salts of alkaline earth metals, e. g.,
Barium naphthenate
Calcium naphthenate
Strontium naphthenate
Magnesium naphthenate
 - (3) Salts of other metals such as,
Aluminum naphthenate
Lead naphthenate
Zinc naphthenate
 - (4) Salts of organic bases, e. g.,
Aniline naphthenate
Toluidene naphthenate
Dimethyl aniline naphthenate
Quinoline naphthenate
Pyridine naphthenate
Tri-ethyl amine naphthenate
Tri-ethanolamine naphthenate
- B. Esters of naphthenic acids
 - (1) Aliphatic esters, e. g.,
Methyl naphthenate
Ethyl naphthenate
Butyl naphthenate
Amyl naphthenate
Lauryl naphthenate
 - (2) Aromatic esters, e. g.,
Phenyl naphthenate
Benzyl naphthenate

These naphthenates have the effect, when employed in lubricating compositions in conjunction with a separate organic halogen compound, of rendering the halogen more active so that the extreme pressure characteristics of the lubricant are considerably improved over those afforded by the same halogen compound when employed as

the sole addition agent. This activation permits the use of halogenated organic compounds which would otherwise be too inactive for a particular purpose and also so enhances the effectiveness of various other organic halogen compounds that they may be employed to good advantage in cutting, drawing and other metal-working operations.

For purposes of classification the halogenated organic compounds may be conveniently grouped as "oxygen-free" and "oxygen-bearing."

In the case of the halogenated aromatic oxygen-free compounds, it is preferable for certain uses that the halogen be attached to a carbon atom of the benzenoid ring. These latter compounds are sometimes more desirable because of their non-corrosive character and general stability.

The halogenated oxygen-free organic compounds as noted may be either:

A. Aliphatic, such as halogenated:

I. Hydrocarbons,

Notably, those containing from four to ten carbon atoms, e. g.,
Chlorinated or fluorinated hexane
Chlorinated or fluorinated octane
Chlorinated or fluorinated decane

II. Amines

Primary, secondary and tertiary, e. g., hexylamines, di-amylamines, tri-amylamines such as:
Chlorinated or fluorinated tri-amyl amine
Chlorinated or fluorinated hexyl amines
Also:
Chlorinated or fluorinated tributyl amine

III. Nitriles

Halogenated ethyl nitrile
Halogenated butyl nitrile

or (preferable for certain types of uses as noted above):

B. Cyclic compounds, such as halogenated:

I. Benzene and related compounds such as:

- (1) Halogenated benzene, e. g.,
The dichlorobenzenes, notably the ortho compound
Ortho-dibrom benzene
The fluorinated benzenes
- (2) Halogenated derivatives of benzene such as:

(a) Halogenated homologs of benzene, e. g.,

Mono-chlor toluene
Mono-chlor xylene
Mono-chlor cymene
Ethyl mono-chlor benzenes
Propyl mono-chlor benzenes
Di-ethyl mono-chlor benzenes
Ethyl dichlor benzenes
Propyl dichlor benzenes
Di-ethyl dichlor benzenes
Di-ethyl tetrachlor benzenes

(b) Halogenated amino derivatives of benzene, e. g.,

Chlorinated aniline
Mono-chlor aniline (preferably the ortho compound)
Mono-chlor di-methyl aniline
Chlorinated toluidines
Chlorinated xylenidines
Chlorinated diphenylamine

(c) Halogenated hydrobenzenes, e. g.,

Hydrogenated dichlor-benzenes such as dichlorhexahydrobenzene (dichlor cyclohexane)

- (3) Halogenated aromatic nitriles, e. g.,
Chlorinated phenyl nitrile

II. Polyphenyls, and related compounds, including diphenyl, diphenyl benzenes, etc., such as,

- (1) Chlorinated diphenyl, e. g.,
Mono-chlor diphenyls
Tri-chlor diphenyls
- (2) Brominated diphenyl, e. g.,
The mono-brom diphenyls
- (3) Fluorinated diphenyl
- (4) Halogenated derivatives of diphenyl, such as,

(a) Halogenated homologs of diphenyl, e. g.,

Chlorinated methyl diphenyls
Chlorinated ethyl diphenyls

(b) Halogenated amino derivatives of diphenyl, e. g.,

Chlorinated amino-diphenyls
Chlorinated amino methyl diphenyls

- (c) Halogenated hydrodiphenyls, e. g.,
Chlorinated phenyl hexahydrobenzene
Chlorinated dodecahydrodiphenyl

III. Naphthalene, such as

- (1) Chlorinated naphthalene, e. g.,
 α -mono-chlor naphthalene
- (2) Brominated naphthalenes, e. g.,
 α -monobrom naphthalene
- (3) Fluorinated naphthalene
- (4) Halogenated derivatives of naphthalene such as:

(a) Halogenated homologs of naphthalenes, e. g.,

Chlorinated methyl naphthalene notably the alpha compound, chlorinated propyl, and isopropyl substitution products of naphthalene

(b) Halogenated amino derivatives of naphthalene, e. g.,

Chlorinated naphthylamines

(c) Halogenated hydronaphthalenes, e. g.,

Chlorinated decahydronaphthalene

IV. Phenanthrene and anthracene and related compounds, such as:

- (1) Chlorinated phenanthrene, chlorinated anthracene
- (2) Halogenated derivatives of phenanthrene and anthracene, such as:

(a) Halogenated homologs

Chlorinated 1-methyl phenanthrene

Chlorinated 3-methyl phenanthrene

Chlorinated 9,10 dimethyl phenanthrene

Chlorinated propyl and isopropyl derivatives of phenanthrene

Chlorinated dimethyl anthracenes

Chlorinated α -methyl anthracene

Chlorinated β -methyl anthracene

Chlorinated propyl and isopropyl derivatives of anthracene

(b) Halogenated amino derivatives, e. g.,

Chlorinated phenanthrylamines

Chlorinated anthramines

(c) Halogenated hydrophenanthrenes and halogenated hydroanthracenes, e. g.,

Chlorinated retene oil (contains hydro retene)

V. Chrysene, picene, and related compounds, including their derivatives, such as homologs, amino derivatives and other substitution products.

VI. Bridged ring compounds, such as the terpenes and related compounds, and their derivatives, e. g., chlorinated pinene.

VII. Heterocyclic compounds, such as pyridine, quinoline, pyrrole, thiophene, and derivatives of them, e. g., mono-chlor pyridine.

Very satisfactory results may be obtained when two or more different halogens are present in the same molecule, orthobrom-chlor benzene, ethylbrom chlor benzenes, and the fluorinated chlorine compounds being good examples of such compounds. If the aromatic compounds have been alkylated they are often especially effective.

As a matter of convenience, the halogenated diphenyls and substituted diphenyls, as well as halogenated substituted benzenes where two or more phenyl groups are directly linked, may be inclusively referred to as halogenated polyphenyls.

Some of the best examples of the aromatic compounds are:

- Chlorinated benzene, B-I (1) e. g.,
Di-chlor benzene (notably the ortho compound)
Mono-chlor toluene, B-I (2) (a)
Di-ethyl tetrachlor benzene
Chlorinated diphenyl B-II (1)
Chlorinated aniline B-I (2) (b)
Chlorinated pyridine B-VIII
Chlorinated quinoline B-VII

Good examples of halogenated aliphatic hydrocarbons are:

- Fluorinated pentane
Fluorinated hexane
Fluorinated octane
Fluorinated di-iso-butene
Halogenated petroleum derivatives, particularly halogenated petroleum oils and waxes.

Halogenated oxygen bearing organic compounds

Here, as above, compounds of the aromatic series with the halogen attached to the ring are

avored for purposes in which it is desirable to have the halogen present in its most stable combined form. However, for certain uses the halogenated oxygen-bearing aliphatic compounds have been found to be more effective and satisfactory.

The oxygen-bearing compounds may, for convenience, be classified as follows:

- I. Aliphatic, or carbon chain type
 - Oxygen-bearing derivatives of:
 - A. Hydrocarbons of the paraffin series,
 - B. Hydrocarbons of the olefine series and
 - C. Hydrocarbons of the acetylene series.
- II. Organic ring type
 - Oxygen-bearing derivatives of:
 - A. "Carbon ring" type compounds
 - (a) Of the aromatic, or allied type, including oxygen-bearing derivatives of benzene, naphthalene, anthracene, etc., also compounds of the bridged ring type, such as the terpenes, and related compounds.
 - (b) Of the class including the cycloparaffins, cyclo-olefines, etc. Examples of this class are oxygen-bearing derivatives of the following:
 - (1) Hydrogenation products of benzene (e. g. cyclohexane, cyclohexene, cyclohexadiene);
Such as hydrogenated phenol, notably: Cyclohexanol, dihydro-phenol, tetrahydro-phenol.
 - (2) Hydrogenation products of naphthalene (e. g. decahydronaphthalene, tetrahydronaphthalene, etc.);
Such as the hydrogenated naphthols.
 - (3) Naphthalenes, such as naphthenic acid, etc.
 - (c) Of mixed type such as derivatives of indene, hydrinene, hydranthracene, etc.
 - B. "Heterocyclic" type compounds
 - (a) Of the aromatic or allied type including derivatives of pyridine, quinoline, etc.
 - (b) Other types such as furfural, furan and its derivatives and derivatives of thiophene, pyrrole, etc.

The oxygen-bearing derivatives of the foregoing compounds may also be classified according to the nature of the attachment of the oxygen to the molecule, viz.:

- I'. Directly attached to one or more carbon atoms, as in the case of:
 - (1') Ethers and analogous compounds
 - (2') Compounds containing the —C—OH radicle, such as alcohols and other derivatives of carbinol (including phenols, cresols, naphthols, etc.)
 - (3') Compounds containing the carbonyl >C=O radicle, such as amides, aldehydes, ketones, organic acids, esters and salts of organic acids, thio-acids and esters of thio-acids
 - (4') Compounds in which oxygen forms a part of the ring structure, e. g., furan and its derivatives, etc.
 - (5') Compounds with inorganic radicle where the oxygen is directly attached to carbon atom:
 - Arsenite
 - Hypochlorite
 - Phosphite
 - Thiophosphate
 - Thiophosphite
 - β -Hydroxylamines
- II'. Indirectly attached through the means of some other atom, i. e., in the form of an inorganic radicle, e. g.:
 - Arsenate
 - Chlorate
 - Chlorite
 - Cyanate
 - α -Hydroxylamine
 - Nitrate
 - Nitrite
 - Nitro
 - Nitroso
 - Oxime
 - Perchlorate
 - Phosphate
 - Sulphate
 - Sulphite
 - Sulphinic acid
 - Sulphone
 - Sulphonic acid
 - Sulphoxide
 - Thio-sulphate

The following table indicates some of the compounds which are particularly suitable for use in accordance with the present invention:

- A. Aromatic
 - (1) Phenols, e. g.;
o-Chlor phenol
Monochlor α -naphthols
 - (2) Alcohols, e. g.,
The chlor-benzyl alcohols
 - (3) Ketones, e. g.,
Mono-chlor benzophenones
Chlor naphthyl ketones
Chlor-methyl-benzophenones
 - (4) Acids, e. g.,
Chlorphenyl acetic acids
Chlor salicylic acids
Chlor phenyl stearic acids
 - (5) Esters, e. g.,
Methyl chlorbenzoates
Ethyl chlorbenzoates
Butyl chlorbenzoates
Dimethyl chlorphthalates
Di-ethyl chlorphthalates
Dibutyl chlorphthalates
Methyl chlor salicylates
Methyl chlor-phenyl-stearates
 - (6) Ethers, e. g.,
Chlorinated diphenyl ether
Chlorphenyl ethyl ethers
Chlorinated dixenyl ether
Chlorinated dinaphthyl ether
Alkylated chlor-diphenyl ethers
 - (7) Non-aromatic oxygen-bearing organic ring compounds
Halogenated cyclohexanol
Halogenated esters of naphthenic acids
 - (8) Oxygen-bearing heterocyclic compounds
 - (a) Halogenated furane and derivatives of furane, e. g.,
Halogenated esters of pyromucic acid (furoates).
Halogenated furfuryl alcohol and esters of it, e. g.,
Chlorinated furfuryl acetate
 - (b) Halogenated oxygen-bearing derivatives of thiophene and pyrrole, e. g.,
Chlorinated esters of thiophene carboxylic acids and chlorinated esters of pyrrole carboxylic acids
- B. Chain compounds
 - (1) Alcohols
Fluorinated octyl alcohol
Fluorinated decyl alcohol
Fluorinated lauryl alcohol
Fluorinated cetyl alcohol
 - (2) Esters
Methyl dichlorstearate
Chlorinated tri-lauryl phosphate
Chlorinated tri-ethyl phosphate
 - (3) Ketones
Chlorinated dibutyl ketone
Chlorinated di-amyl ketone

It is, of course, to be understood that the above lists of compounds are intended merely to illustrate the type of compound suitable as one component of the addition agent of this invention and are not to be construed as limiting said component to the particular groups or examples there disclosed.

It is believed that under conditions of extreme pressure the halogenated addition agents of this invention react chemically or physico-chemically with the metallic surfaces to form a non-fluxing surface which will not seize or score. This invention is not intended to be limited, however, by any particular theory or explanation of the action upon the metallic surfaces.

All of the various halogens are effective when employed in accordance with the present invention but chlorine is generally preferred inasmuch as it is the least expensive and one of the most effective of the halogens. Bromine and fluorine are more expensive and the latter is relatively difficult to handle but they are each usable in accordance with this invention. Iodine is not so readily obtainable as the other halogens and is quite expensive but it also is satisfactory in providing effective addition agents. It should also be noted that two or more different halogens may be present in the same molecule. The brom-chlor and fluorinated chlorine or bromine compounds give especially satisfactory results. When used in conjunction with a naphthenate, an amount of from about 0.1% to about 20% by

weight, based on the amount of oil, of the separate halogen compound is all that is required to render the finished lubricant efficient under conditions of extreme pressure. Seldom is there any need to employ more than 10% and usually about 3% of the halogenated addition agent will be found to be ample for most purposes.

Since, in general, the loss of the addition agent by volatilization will be less for compounds having a low volatility, the vapor pressure of the compounds should, for most purposes, be less than atmospheric pressure at temperatures up to 140° C. It is usually desirable, especially for use in internal combustion engines, that the vapor pressure be less than atmospheric at temperatures up to 170° C. In the case of compounds which are stable at temperatures up to their boiling points, this condition may be expressed by stating that the boiling point of the compound should, in general, be higher than 140° C., and for certain uses, such as in internal combustion engines, higher than 170° C.

While mineral oil generally is the principal ingredient of the lubricant, it is not essential that it be the only ingredient other than the addition agent, provided that there be no additional ingredient which is incompatible with such addition agent. It is within the contemplation of this invention to include, if necessary or desirable, such other addition agents as are commonly added to improve the viscosity index or cold test of the lubricant and a lubricating composition according to this invention which also has a separate oiliness increasing agent has been found to be especially effective.

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims, or the equivalent of such, be employed.

I therefore particularly point out and distinctly claim as my invention:

1. A lubricating composition comprising a hydrocarbon oil, from about .1% to about 5% of a naphthenate, and a separate halogenated organic compound.

2. A lubricating composition comprising a hydrocarbon oil, from about .1% to about 5% of a naphthenate, and a separate halogenated organic ring compound.

3. An extreme pressure crank-case lubricant for internal combustion engines comprising a major proportion of a hydrocarbon oil, from about .1% to about 5% of a naphthenate, and a separate halogenated organic compound.

4. A lubricating composition having as a prin-

cipal lubricating constituent, the combination of mineral lubricating oil, from about .1% to about 5% of an oil-soluble naphthenate, and a stable, oil-soluble, halogenated organic compound, said compound having a vapor pressure less than atmospheric at a temperature of 140° C. and present in an amount less than 10%, based on the amount of mineral oil, but sufficient to provide a lubricating composition effective to prevent seizure and scoring of relatively moving metallic surfaces under pressures substantially in excess of 10,000 pounds per square inch.

5. An extreme pressure crank-case lubricant for internal combustion engines comprising a major proportion of a hydrocarbon oil, from about .1% to about 5% of a naphthenate, and a separate chlorinated organic compound.

6. An extreme pressure crank-case lubricant for internal combustion engines comprising a major proportion of a hydrocarbon oil, from about .1% to about 5% of a naphthenate, and a separate chlorinated organic ring compound.

7. A lubricating composition comprising a hydrocarbon oil, from about 0.1% to about 10% of a chlorinated organic compound, and from about 0.1% to about 5% of a salt of a naphthenic acid.

8. A lubricating composition comprising a hydrocarbon oil, from about 0.1% to about 10% of a chlorinated aromatic compound, and from about 0.1% to about 5% of a salt of a naphthenic acid.

9. A lubricating composition comprising a hydrocarbon oil, from about 0.1% to about 3% of a chlorinated aromatic compound, and from about 0.1% to about 5% of a salt of a naphthenic acid.

10. A lubricating composition comprising a hydrocarbon oil, from about 0.1% to about 5% of aluminum naphthenate, and from about 0.1% to about 10% of a separate halogenated organic compound.

11. A lubricating composition comprising a hydrocarbon oil, from about 0.1% to about 5% of aluminum naphthenate, and from about 0.1% to about 3% of a separate chlorinated organic ring compound.

12. A lubricating composition comprising a hydrocarbon oil, from about 0.1% to about 5% of calcium naphthenate, and from about 0.1% to about 10% of a separate halogenated organic compound.

13. A lubricating composition comprising a hydrocarbon oil, from about 0.1% to about 5% of lead naphthenate, and from about 0.1% to about 10% of a separate halogenated organic compound.

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