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LUBRICATING COMPOSITION

Carl F. Prutton, Cleveland Heights, Ohio, assignor, by mesne assignments, to The Lubri-Zol Development Corporation, Cleveland, Ohio, a corporation of Delaware

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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 my copending application Serial No. 247,000, filed December 21, 1938, which has now issued into Patent No. 2,276,341, which in turn is a continuation-in-part of copending 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 use in lubricating compositions of esters of naphthenic acids used either alone or preferably in combination with a separate halogenated organic compound.

When compositions are desired suitable for use in the lubrication of internal combustion engines, it is obvious that only relatively small proportions of these esters should be added to the hydrocarbon base oil. Since, however, it has been found that the presence of even small amounts of these esters will considerably enhance the

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lubricating properties of mineral lubricating oils especially when employed in combination with separate halogen compounds, liquid compositions are satisfactory for many purposes and may contain as little as 0.1% of the ester although from about 1% to about 5% by weight, based on the amount of oil, is generally more desirable. Amounts up to 20% may be used for certain purposes. Concentrates which may be further blended with base stocks may contain up to as high as 60% of these esters of naphthenic acids.

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.

The oil base of the preferred composition of this invention is a highly refined mineral lubricating oil having a viscosity and other characteristics such as to make the same suitable for use as the crankcase lubricant for internal combustion engines. The highly refined mineral lubricating oils suitable for use as the base in the improved compositions of my invention may be conveniently classified in accordance with their viscosity index, three such classes being oils having a V. I. up to 30; oils having a V. I. from 30 to about 70; and oils having a V. I. of above 70. Obviously the oil base selected may contain appropriate constituents in addition to plain mineral oil such as pour point depressors and the like, since these conventionally employed materials have been found entirely compatible with the addition agents which characterize the final blends comprising my invention.

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 esters 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 esters of naphthenic acids broadly are included within the scope of the invention:

Esters of naphthenic acids:

(1) Aliphatic esters, e. g.,

Propyl diiso-propyl naphthenates

Methyl naphthenate

Ethyl naphthenate

Butyl naphthenates (n-, iso-, and sec-)

Amyl naphthenates

Lauryl naphthenate

Cetyl naphthenate

- (2) Aromatic esters, e. g.,
 Phenyl naphthenate
 t-Amyl-phenyl naphthenate
 Benzyl naphthenate
 Cresyl naphthenate
 Xenyl naphthenate
- (3) Cyclo-aliphatic esters, e. g.,
 Cyclopentyl naphthenate
 Cyclohexyl naphthenate
 Methyl-cyclohexyl naphthenates
 Di-methyl-cyclohexyl naphthenates
 Tri-methyl-cyclohexyl naphthenates
 Propyl-cyclohexyl naphthenates
 Amyl-cyclohexyl naphthenates
 Lauryl-cyclohexyl naphthenates
 Cetyl-cyclohexyl naphthenates
 Cyclohexyl-carbinol naphthenates
 Cyclohexyl-cyclohexyl naphthenates

Any esters may be used which are derived from naphthenic acids by substituting an organic radicle, R, for the replaceable hydrogen of the acid. Examples of R are the following:

I. Hydrocarbon radicles:

- (A) Alkyl radicles
 Amyl (n, iso, sec. and tertiary)
 Lauryl
 Cetyl
 Carnaubyl
 Ceryl
 Montanyl
 Mellisyl
 Myricyl
 Lacceryl
 Psyllisyl
- (B) Aryl radicles
 Phenyl
 Xenyl
 Naphthyl (alpha- and beta-)
 Anthracyl
 Phenanthryl
- (C) Cyclo-alkyl radicles
 Cyclopentyl
 Cyclohexyl
 Cycloheptyl
 Cyclohexyl-cyclohexyl
- (D) Alkylated aryl radicles
 Radicles formed by the alkylation of aryl radicles, such as those listed above (B), with any of the alkyl radicles, e. g., those listed above (A), or with any of the following:
 Methyl
 Ethyl
 Propyl (n-, and iso-)
 Butyl (n-, iso- and sec-)
- Specific examples of alkylated aryl radicles are as follows:
 Cresyl
 Xylol
 Trimethyl-phenyl
 Ethyl-phenyl
 Tetra-ethylphenyl
 t-Amyl phenyl
 Lauryl-phenyl
 Cetyl-phenyl
 Ceryl-phenyl
 Methyl-naphthyl
 Iso-propyl-naphthyl
 t-Amyl-naphthyl
 Lauryl-naphthyl
 Cetyl-naphthyl
 Iso-propyl-xenyl
 t-Amyl-xenyl
 Lauryl-xenyl
- (E) Alkylated cyclo-alkyl radicles
 Radicles formed by the alkylation of cyclo-alkyl radicles, such as those listed above (C), with any of the alkyl radicles, such as those listed above. Specific examples are:
 Methyl-cyclohexyl
 Dimethyl cyclohexyl
 t-Amyl cyclohexyl
 Lauryl cyclohexyl
 Cetyl cyclohexyl
- (F) Cyclo-alkylated aryl radicles, e. g.
 Cyclohexyl-phenyl
 Cyclohexyl-xenyl
 Cyclohexyl-naphthyl
- (G) Arylated-alkyl radicles, e. g.
 Benzyl
 Phenyl-ethyl
 Phenyl-amyl
 Phenyl-lauryl
 Phenyl-cetyl
 Xenyl-methyl
 Xenyl-ethyl
 Naphthyl-methyl
 Naphthyl-ethyl
- (H) Cyclo-alkylated alkyl radicles, e. g.
 Naphthyl
 Hexahydrobenzyl
 Cyclohexyl-ethyl
 Cyclohexyl-amyl

I. Hydrocarbon radicles—Continued:

- (I) Arylated cyclo-alkyl radicles, e. g.
 Phenyl-cyclohexyl
 Xenyl-cyclohexyl
 Naphthyl-cyclohexyl

- (J) Mixed radicles, e. g.
 Methylcyclohexyl-phenyl
 Amylcyclohexyl-phenyl
 Cyclohexyl-cresyl
 Cyclohexyl-xylol
 Cyclohexyl amyl-phenyl
 Cyclohexyl-benzyl
 Xylol-cyclohexyl
 Lauryl-phenyl cyclohexyl
 Cetyl-phenyl cyclohexyl
 Phenyl-methylcyclohexyl
 Phenyl-amylcyclohexyl
 Xylol-methylcyclohexyl
 Benzyl-cyclohexyl
 Benzyl-methylcyclohexyl
 Methylcyclohexyl-amyl
 Methylcyclohexyl-lauryl

II. Oxygen-containing organic radicles

- (A) Of the ether type, e. g.
 Methoxy-phenyl
 Ethoxy-phenyl
 Lauroxy-phenyl
 Cyclohexoxy-phenyl
 Phenoxy-phenyl
 Phenoxy-naphthyl
 Phenoxy-cyclohexyl
 Phenoxy-ethyl
 Phenoxy-lauryl
 Phenoxy-cetyl
 Amyl-phenoxy-ethyl
 Phenyl-ethoxy-ethyl
 —C₂H₄—O—C₂H₄— (derived from di-ethylene glycol)

- (B) Of the ketone type, e. g.
 Acetyl-phenyl
 Acetyl-xenyl
 Acetyl-naphthyl
 Acetyl-lauryl
 Acetyl-cetyl
 Acetyl-cyclohexyl
 Acetyl-naphthenyl
 Lauroyl-phenyl
 Benzoyl-phenyl
 Benzoyl-naphthyl
 Benzoyl-cyclohexyl
 Benzoyl-naphthenyl
 Benzoyl-lauryl
 Benzoyl-cetyl
 Stearoyl-phenyl
 Stearoyl-xenyl
 Stearoyl-naphthyl
 Stearoyl-amyl
 Stearoyl-lauryl
 Stearoyl-cetyl
 Stearoyl-phenoxyphenyl
 Stearoyl-cyclohexyl
 Stearoyl-naphthenyl
 Naphthenoyl-phenyl
 Naphthenoyl-xenyl
 Naphthenoyl-naphthyl
 Naphthenoyl-amyl
 Naphthenoyl-lauryl
 Naphthenoyl-cetyl
 Naphthenoyl-phenoxy-phenyl
 Naphthenoyl-cyclohexyl
 Phenoxybenzoyl-phenyl

(C) Of the ester type, i. e.

Derived from hydroxy-esters by the removal of the hydroxyl group, as for example, by the removal of the hydroxyl group from the following esters:

- (1) Esters of hydroxy acids, e. g., esters formed by substitution of any of the "R" groups listed above for one or more of the acid hydrogen atoms of the following acids:

Lactic acid
 Hydracrylic acid
 Citric acid
 Tartaric acid
 Ricinoleic acid
 Hydroxy-stearic acid
 Hydroxy-chlorstearic acid
 Cyclohexanol carboxylic acids
 Hydroxybenzoic acids
 Salicylic acid
 Hydroxy-phthalic acids
 Hydroxy-phenyl-benzoic acids
 Naphthol carboxylic acids

- (2) Esters of polyhydroxy alcohols and phenols in which at least one hydroxyl group remains unsubstituted, for example—esters formed by esterifying the following so that at least one hydroxyl group remains in the resulting ester:

Ethylene glycol
 Diethylene glycol
 Propylene glycols
 Butylene glycols
 Poly-hydroxy benzenes
 Dihydroxy-benzenes
 Resorcinol
 Catechol
 Hydroquinone
 Tri-hydroxybenzenes
 Pyrogallol

III. Sulphur-containing radicles, e. g. any of the examples of oxygen-containing radicles in which at least one oxygen atom has been replaced with sulphur. Specific examples of sulphur-containing radicles are:

(A) Of the thio-ether type

Thio-phenoxy-phenyl ($C_6H_5-S-C_6H_5$)

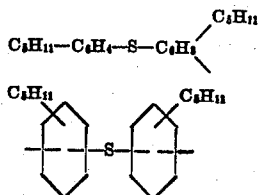
Thio-phenoxy-ethyl ($C_6H_5-S-C_2H_5$)

Thio-lauroxy-phenyl ($C_{11}H_{23}-S-C_6H_5$)

Thio-t-amyl-phenoxy-phenyl

($C_6H_5-C_4H_9-S-C_6H_5$)

Thio-t-amyl-phenoxy-t-amyl-phenyl



(B) Of the thio-ketone type

Thio-acetyl-phenyl

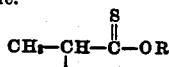
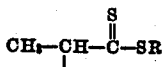
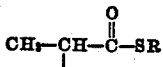
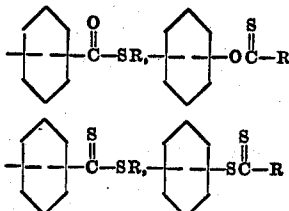
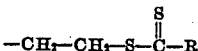
Thio-benzoyl-phenyl

Thio-stearoyl-phenyl

Thio-naphthenoyl-phenyl

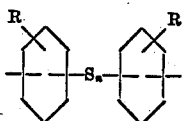
Thio-stearoyl-cyclohexyl

(C) Of the thio-ester type, e. g., derived from hydroxy-esters of thio-carboxylic acids. Examples of such radicles are:



Where R is methyl, ethyl, butyl, amyl, lauryl, stearoyl, naphthenyl, etc.

(D) Radicles derived from hydroxy-organic polysulphides by removal of the hydroxy group, e. g.



where R is hydrogen or an alkyl or cyclo-alkyl group

$R-S_n-R'$

where R is an alkyl or cyclo-alkyl group and R' is an alkylene group.

generated esters of naphthenic acids. The specific examples previously given are the unhalogenated esters which may be thus used. Each of the esters thus identified, either generically, sub-generically or specifically, may be modified by halogenation, and the halogenated ester thus derived used as the addition agent.

It is believed unnecessary to repeat the foregoing list in the more specific identification of the halogen-bearing esters, since it will be obvious to those skilled in the art what the halogen counterparts of these esters would be. The usual halogenation process, well-known to those familiar with the art, may be employed in the preparation of the halogenated esters. The usual halogenation step may be followed by subsequent stabilization treatments, such as air blowing, alkali washing, or the like, in order that the halogen retained in the ester will be sufficiently stable, and not too readily liberated during storage and use.

The following, however, is a list of specific examples of halogen-bearing esters of naphthenic acids which will be found particularly suitable and this, therefore, constitutes a preferred group of compounds for use in the lubricating compositions of my invention.

Chlorinated methyl naphthenate containing about 20% chlorine

Chlorinated butyl naphthenate containing about 10% chlorine

Chlorinated methyl-cyclohexyl naphthenate containing about 10% chlorine

Chlorinated methyl-cyclohexyl naphthenate containing about 40% chlorine

Chlorophenyl naphthenates

Chlorobenzyl naphthenates

Dichlorobenzyl naphthenates

Dichlor-xenyl naphthenates

Tetra-chlor-xenyl naphthenates

Tetra-chlor-phenoxy-phenyl naphthenates

Hexachlor-phenoxy-phenyl naphthenates

This invention thus contemplates the utilization of halogen in combination with the esters of naphthenic acid. The halogen may be, as indicated above, included in the same molecule as by halogenation of the ester, itself, or the halogen may be present in a separate molecule, i. e. a separate halogen-bearing organic compound. It has been found that the esters of naphthenic acid have a cooperative effect when employed in conjunction with a separate halogenated organic compound. This is true whether the naphthenic acid ester be halogenated or unhalogenated. This cooperation between the naphthenic acid esters and the separate organic halogen compound is manifested by the ester cooperating with the separate halogen compound in activating the latter, so that a higher film strength may be attained from the use of a given amount of halogen in the form of the separate organic halogen compound, and moreover, extremely stable halogenated organic compounds, which would have a low degree of activity, may be rendered especially active by the incorporation therewith of an ester of naphthenic acid, whether the latter be halogenated or unhalogenated.

This invention, therefore, includes the combined use of the esters of naphthenic acids, either halogenated or unhalogenated, with a separate organic halogen compound, and this combination, for the reasons above given, is the preferred embodiment of my invention, since in such combination, the greatest utility of the esters of naphthenic acids may be realized.

As previously indicated, this invention comprises the use in lubricating compositions of esters of naphthenic acid. These esters, when used alone, that is, without any other addition agent effective to cooperate therewith, are admirably suited to impart to the lubricant to which they are added, properties such as oiliness, reduction in rate of wear which enables such lubricant to be used under conditions where the plain refined mineral lubricating oil base would be unsatisfactory for use alone.

These esters of naphthenic acid, which may be used alone, may be either the straight esters or such esters halogenated, and accordingly this invention comprises the use in lubricating compositions of both the halogenated and unhalo-

For purposes of classification, the halogenated organic compounds, which thus comprise one component of the preferred embodiment of my invention, 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 xylydines
 - Chlorinated diphenylamine
 - (c) Halogenated hydrobenzenes, e. g.,
 - Di-chlor hydrobenzenes 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
 - Di-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
 - Mono-chlor α -naphthyl amine
 - (c) Halogenated hydronaphthalenes, e. g.,
 - Chlorinated decahydronaphthalene

Cyclic compounds, such as halogenated—Continued:
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, ethyl-bromchlor 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 di-phenyls 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)
 - Oi-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 favored 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, cycloolefines, 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, di-hydro-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, hydriene, 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



radicle, such as alcohols and other derivatives of carbinol (including phenols, cresols, naphthols, etc.)

(3') Compounds containing the carbonyl



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
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

Diethyl chlorphthalates

Dibutyl chlorphthalates

Methyl chlor salicylates

Methyl chlor-phenyl-stearates

A. Aromatic—Continued:

(6) Ethers, e. g.,

Chlorinated diphenyl ether

Chlorphenyl ethyl ethers

Chlorinated dioxenyl 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.

As illustrative of specific embodiments of my invention I will list below a number of specific examples of final blends which, it will be noted, are divided into two groups, the first group being motor oils adapted for use in the crankcases of internal combustion engines, and the second group being gear oils useful, for example, in the gearcases of automobiles and the like.

I. Motor oils

	Per cent
1. Mineral oil-----	99.5
Chlorinated methyl naphthenate containing about 20% chlorine-----	.5
2. Mineral oil-----	99.5
Chlorinated methyl cyclohexyl naphthenate containing about 10% chlorine-----	.5
3. Mineral oil-----	99
Dichlorobenzyl naphthenate-----	1
4. Mineral oil-----	98.5
Ortho dichlorobenzene-----	1.0
Methyl naphthenate-----	.5
5. Mineral oil-----	98.5
Chlorinated diphenyl containing about 50% chlorine-----	1.0
Butyl naphthenate-----	.5
6. Mineral oil-----	98.5
Ortho dichlorobenzene-----	.5
Hexadichlorodiphenyl ether-----	.5
Methyl naphthenate-----	.5
7. Mineral oil-----	98.75
Ortho dichlorobenzene-----	.5
Hexachlor diphenyl ether-----	.5
Chlorinated methyl naphthenate containing about 20% chlorine-----	.25

The "mineral oil" given in the foregoing list of compositions Nos. 1 to 7 inclusive, may be any suitable highly refined mineral lubricating oil having characteristics suiting the same for use as a crankcase lubricant. For example, the "mineral oil" used in each of Examples 1 to 7 may be an S. A. E. 20 Pennsylvania motor oil having a viscosity index of about 100. As previously indicated, this "mineral oil" may include, in addition to highly refined mineral lubricating oil, other constituents such as pour point depressors and the like. The S. A. E. number may, of course, vary in accordance with the usual standards which are observed in fitting an oil base to a particular use or condition of use.

II. Gear oils

	Per cent
8. Mineral oil-----	93
Chlorinated methyl cyclohexyl naphthenate containing about 40% chlorine-----	7

	Per cent
9. Mineral oil-----	92.5
Chlorinated paraffin wax containing about 40% chlorine-----	7.0
Methyl naphthenate-----	.5
10. Mineral oil-----	91
Chlorinated paraffin wax containing about 40% chlorine-----	8
Methyl naphthenate-----	1
11. Mineral oil-----	91.75
Chlorinated paraffin wax containing about 40% chlorine-----	8.00
Chlorinated methyl naphthenate containing about 20% chlorine-----	.25
12. Mineral oil-----	89.8
Chlorinated paraffin wax containing about 40% chlorine-----	7.0
Chlorobenzyl disulphide-----	3.0
Methyl cyclohexyl naphthenate-----	.2
13. Mineral oil-----	89.9
Chlorinated paraffin wax containing about 40% chlorine-----	8.0
Benzyl disulphide-----	2.0
Chlorinated methyl naphthenate containing about 20% chlorine-----	.1
14. Mineral oil-----	89
Reaction product of chlorinated paraffin wax, containing about 35% chlorine, with sodium disulphide, such reaction product containing about 20% sulphur-----	10
Methyl naphthenate-----	1
15. Mineral oil-----	89.5
Reaction product of chlorinated paraffin wax, containing about 35% chlorine, with sodium disulphide, such reaction product containing about 20% sulphur-----	10.0
Chlorinated methyl cyclohexyl naphthenate containing about 10% chlorine-----	.5

The "mineral oil" identified a component in each of compositions 8 to 15 inclusive is preferably a gear oil suitable for use as the base in lubricants designed for use in gearcases. For example, an entirely satisfactory composition may be produced by utilizing as the "mineral oil" component in each of compositions 8 to 15 inclusive an S. A. E. 90 gear oil having a viscosity index of about 70. Here again, the "mineral oil" component may include not only a refined mineral lubricating oil of properties such as those given above, but may also include other components such as thickening agents and the like.

Attention is directed particularly to Examples 12 to 15 above which are additionally characterized by the presence therein of an organic sulphur compound which, in certain instances, such as for example composition No. 12, may contain chlorine in the same molecule with the sulphur. This combination, i. e., the combination of an ester of a naphthenic acid with an organic sulphur compound, and with or without a separate organic halogen compound, has been found to be of particular utility. The organic sulphur compound and the esters of naphthenic acid, whether halogenated or unhalogenated, cooperate in the production of a final lubricating composition characterized by properties such as oiliness, film strength, and ability to reduce wear, which it is not possible to achieve with the use of either of these components alone, and which is more than

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the cumulative effect of such components when used separately.

Other modes of applying the principle of my invention may be employed instead of the one explained, change being made as regards the materials employed, provided the ingredients stated by any of the following claims or the equivalent of such stated ingredients be employed.

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

1. A lubricating composition comprising the combination of an ester of a naphthenic acid and an organic sulphur compound.

2. A lubricating composition comprising a hydrocarbon oil and minor amounts of both an ester of naphthenic acid and a separate organic compound containing an element of the class consisting of halogen and sulphur.

3. A lubricating composition comprising the combination of an ester of a naphthenic acid and an organic halogen compound having a vapor pressure less than atmospheric at 140° C.

4. A lubricating composition comprising a hydrocarbon oil, a halogenated organic compound, and from about 0.1% to about 5% by weight, based on the amount of oil, of an ester of a naphthenic acid.

5. A lubricating composition comprising a hydrocarbon oil, a halogenated organic ring compound, and from about 0.1% to about 5% by weight, based on the amount of oil, of an ester of a naphthenic acid.

6. A lubricating composition comprising a hydrocarbon oil, from about 0.1% to about 5% of an oil-soluble ester of a naphthenic acid, and a stable oil-soluble halogenated organic compound, said compound having a vapor pressure less than

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atmospheric at 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 pressure substantially in excess of 10,000 pounds per square inch.

7. A lubricating composition comprising the combination of an ester of a naphthenic acid and a chlor benzyl sulphide.

8. A lubricating composition comprising the combination of methyl naphthenate and a chlor benzyl sulphide.

CARL F. PRUTTON.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,276,341	Prutton	Mar. 17, 1942
2,224,541	Frollich	Dec. 10, 1940
2,121,976	Mikeska	June 28, 1938
1,882,816	Hagedorn	Oct. 18, 1932
2,135,092	Maverick	Nov. 1, 1938

FOREIGN PATENTS

Number	Country	Date
402,262	British	Nov. 30, 1933

OTHER REFERENCES

Industrial and Engineering Chemistry, vol. 28, #10, Oct. 1936.

Article by Lincoln et al., pages 1191-1197. (Copy in Div. 64.) 252-58.