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LUBRICATING COMPOSITION

Carl F. Prutton, East Cleveland, Albert K. Smith, Shaker Heights, and Harry E. Johnson, Willoughby, Ohio, assignors, by mesne assignments, to The Lubri-Zol Development Corporation, Cleveland, Ohio, a corporation of Delaware

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28 Claims. (Cl. 252—48)

This application is a continuation in part of our copending applications Serial No. 170,501 filed October 22, 1937, and Serial No. 300,232 filed October 19, 1939.

As disclosed in the patent of Carl F. Prutton No. 2,051,744, granted August 18, 1936, certain desirable improvements in the lubricating properties of lubricating oils may be secured by the combination therewith of certain halogenated organic compounds.

The use by themselves of elemental sulphur and active compounds of sulphur in substantial amounts for the purpose of imparting extreme pressure characteristics to lubricating compositions has been known for some time. It has been well recognized that in order for sulphur when used alone to impart extreme pressure characteristics to lubricaintg compositions it is necessary that such sulphur be present in active or corrosive form. It has also been well known that certain organic compounds of sulphur contain sulphur in such stably bound condition that when such compounds were added in minor amounts to a lubricating composition there was no appreciable increase in film strength.

We have discovered that by the combined use in a suitable oil base of organic sulphur compounds in conjunction with certain other organic compounds and we are able to produce a lubricating composition superior in certain respects to those which have been heretofore available. The lubricating composition according to our invention is particularly applicable for use as an extreme pressure lubricant. The term "extreme pressure lubrication" is believed to be sufficiently well known to those familiar in the art that more particular definition thereof in this specification is unnecessary.

It is among the objects of our invention, therefore, to provide a lubricating composition which shall be superior in certain respects to any which has heretofore been available.

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

To the accomplishment of the foregoing and related ends, said invention, then, consists of the means hereinafter fully described and particularly pointed out in the claims, the following description setting forth in detail one approved combination of ingredients embodying our invention, such disclosed means constituting, however, but one of various forms in which the principle of the invention may be used.

Broadly stated, the improved lubricating compositions of our invention comprise the combination of:

(a) a major proportion of lubricating oil;

(b) a minor amount of an organic halogen compound;

(c) a relatively inactive organic sulphur compound in an amount in which such sulphur compound would not substantially increase the extreme pressure characteristics of a plain mineral oil; and

(d) a minor amount of an organic oxygen compound.

From the foregoing statement of our invention it will be observed that the lubricating compositions which comprise the same may be divided into four components. These four components will first be considered separately and directions then given for the manner in which they may be blended in order to achieve the improved results.

The oil base

The oil base of our lubricating compositions is a lubricating oil of the type best suited for the particular use for which the ultimate composition is designed. When the lubricating compositions of our invention are designed for the lubrication of automobiles, the oil base will of course preferably consist of a refined mineral lubricating oil of lubricating viscosity for the particular point of application. In other words, a conventional gear oil may be used for the lubrication of the gears and generally a lighter, more highly refined, oil will be used in the crank case.

This invention is applicable to lubricating compositions in which the base may consist either entirely or in part of synthetic oils, hydrogenated oils, and voltolized oils.

The oil base may also desirably contain other well known constituents such as those which improve the oiliness, pour point, cold test, and oxidation properties, etc., of the oil. In general, compositions of our invention may be employed with any commercially available addition agents for the above defined purposes since they are generally compatible with the same in the amounts usually used.

The halogen compounds

The halogen compounds used should first be oil-soluble to the extent that the required amounts may be incorporated in the oil base in a stable form of true solution or colloidal suspension so that there will be no separation on storage, even over periods of considerable length and at reduced temperatures.

The halogen compound must be sufficiently non-volatile so that it will not be driven off from the lubricating composition during use. It will generally be found that the halogen compounds should have a vapor pressure less than atmospheric at a temperature of 140° C. and preferably at a temperature of 170° C.

The halogen compounds which may be employed as components of the composition may be divided into two broad classes, cyclic or ring compounds and aliphatic or chain compounds.

In general, the ring compounds are more stable and less subject to hydrolysis than are the chain compounds particularly when the halogen is attached to a benzenoid ring structure. Therefore, where moisture and other conditions are encountered which tend to hydrolyze the halogen compounds, the ring compounds are generally preferable. The chain compounds are usually more active than the ring compounds and thus may be employed for the purpose of giving very high extreme pressure characteristics where such is necessary and where the conditions of use permit the employment of the relatively less stable chain compounds.

Examples of the various halogen bearing compounds which may thus be employed as one component of our composition are as follows:

A.—Aliphatic, such as halogenated:
- I.—Hydrocarbons, e. g.
  - Hexachlorethane, and notably, those chlorinated or fluorinated hydrocarbons which contain from four to ten or more carbon atoms, e. g.
  - Chlorinated hexane
  - Chlorinated octane
  - Chlorinated decane
  - Butylene dichloride
  - Monochlorhexane
  - 1,2 dichlorhexane
  - Amylene dichloride

Other halogen substitution or addition products of commercial materials such as petroleum fractions including the paraffins, paraffin wax, foots oil, kerosene, mineral oil, etc.

- II.—Amines
  - Primary, secondary and tertiary, e. g. chlorinated or fluorinated, hexylamines, di-amylamines, tri-amylamines, such as:
  - Chlorinated tri-amyl amines
  - Chlorinated tributyl amines
  - Chlorinated hexyl amines
- III.—Nitriles, e. g.
  - Chlorinated or fluorinated:
    - Ethyl cyanide
    - Butyl cyanide
    - Octyl cyanide
    - Lauryl nitrile
    - Stearyl nitrile
- IV.—Sulphides, e. g.
  - Chlorinated or fluorinated:
    - Di-ethyl sulphide
    - Di-butyl sulphide
    - Di-octyl sulphide
    - Di-amyl sulphide
    - Di-lauryl sulphide
    - Di-cetyl sulphide
- V.—Mercaptans, e. g.
  - Chlorinated or fluorinated:
    - Lauryl mercaptan
    - Cetyl mercaptan
    - Carnaubyl mercaptan
    - Ceryl mercaptan
    - Montanyl mercaptan
    - Melissyl mercaptan
    - Myricyl mercaptan
- VI.—Thiocyanates (rhodanates) e. g.
  - Chlorinated or fluorinated:
    - Ethyl thiocyanate
    - Butyl thiocyanate
    - Lauryl thiocyanate
    - Cetyl thiocyanate
    - Ceryl thiocyanate

B.—Cyclic compounds, such as halogenated:
- I.—Benzene and related compounds such as:
  - (1) Halogenated benzene, e. g.
    - (a) Chlorinated benzene, e. g.
      - The dichlorbenzenes, notably the ortho compound
    - (b) Brominated benzene, e. g.
      - Ortho-dibrom benzene
    - (c) Fluorinated benzene
  - (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 dichlor benzenes
      - Propyl 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 xylidines
      - Chlorinated diphenylamine
    - (c) Halogenated hydrobenzenes, e.g.
      - Hydrogenated dichlor-benzenes
      - Dichlorhexahydrobenzene (Dichlor cyclohexane)
- II.—Polyphenyls, and related compounds, including diphenyl, diphenyl benzenes, etc., such as
  - (1) Halogenated diphenyl, e. g.
    - (a) Chlorinated diphenyl, e. g.
      - Mono-chlor diphenyls
      - Dichlor diphenyls
      - Tri-chlor diphenyls
    - (b) Brominated diphenyl, e. g.
      - The mono-brom diphenyls
    - (c) Fluorinated diphenyl
  - (2) Halogenated derivatives of diphenyl, such as
    - (a) Halogenated homologs of diphenyl, e. g.
      - Chlorinated phenyl-toluenes
      - Ethylated, or propylated, chlorinated diphenyl, e. g.
      - di-ethyl tetrachlor diphenyl
    - (b) Halogenated amino derivatives of diphenyl, e. g.
      - Chlorinated phenyl anilines
      - Chlorinated phenyl-toluidines
      - Chlorinated diphenyl amines
      - Chlorinated xenyl amines
    - (c) Halogenated hydrodiphenyls, e. g.
      - Chlorinated phenyl hexahydrobenzene
      - Chlorinated dodecahydrodiphenyl
- III.—Naphthalene and related compounds, such as
  - (1) Halogenated naphthalene
    - (a) Chlorinated naphthalene, e. g.
      - α-mono-chlor naphthalene
    - (b) Brominated naphthalenes, e. g.
      - α-mono-brom naphthalene
    - (c) Fluorinated naphthalene

(2) Halogenated derivatives of naphthalenes, such as:

(a) Halogenated homologs of naphthalenes, e. g.
Chlorinated methyl naphthalenes, such as α-methyl naphthalene
Chlorinated ethyl, propyl, or isopropyl naphthalenes

(b) Halogenated amino derivatives of naphthalene, e. g.
Chlorinated naphthylamines
Mono-chlor naphthyl amine

(c) Halogenated hydronaphthalenes, e. g.
Chlorinated decahydronaphthalene
Chlorinated tetrahydronaphthalene

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, e. g.
Chlorinated 1-methyl phenanthrene
Chlorinated 3-methyl phenanthrene
Chlorinated 9,10 dimethyl phenanthrene
Chlorinated propyl and isopropyl derivatives of phenanthrene such as retene
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. monochlor pyridine.

VIII.—Nitriles derived from any of the above compounds, e. g.
Chlorinated:
Benzonitrile
Tolunitriles
Benzyl cyanide
Naphthyl cyanide
Xenyl cyanide
Cyclohexyl cyanide

IX.—Sulphides derived from any of the above compounds, e. g.
Chlorinated:
Diphenyl sulphide
Dibenzyl sulphide
Dixylyl sulphides
Di-naphthyl sulphides
Dixenyl sulphides
Dicyclohexyl sulphide

X.—Mercaptans derived from any of the above compounds, e. g.
Chlorinated:
Benzyl mercaptan
Phenyl benzyl mercaptans
Naphthyl mercaptans
Phenyl propyl mercaptans
Cyclohexyl mercaptan

XI.—Thiocyanates, e. g.
Chlorinated:
Benzyl thiocyanate
Phenyl ethyl thiocyanate
Phenyl propyl thiocyanate
Cyclohexyl thiocyanate

It will be noted that the above enumerated examples of the organic ring compounds which are usually preferred when stability is a particularly desired characteristic are, in general, compounds of the aryl type, i. e., compounds containing benzenoid ring structures and also of the type in which the halogen is directly attached to an atom which is a part of such ring structure. Very satisfactory results may be obtained when two or more different halogens are present in the same molecule, ortho brom chlor benzene being a good example of such a compound. If the aromatic compounds have been alkylated, they are often especially effective.

Especially good results are generally secured when the halogen in the composition is present in the form of an oxygen containing or bearing organic compound. This class of addition agents has the desirable property of increased oiliness, and generally a greater degree of activity than the corresponding oxygen-free compounds. In general, the halogen and oxygen bearing organic ring compounds possess greater stability as compared with the chain compounds generally, and at the same time a sufficient amount of activity so as to impart the necessary properties to the ultimate composition.

The oxygen and halogen containing or bearing organic compounds, above referred to, may be classified as follows, viz:

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, di-hydrophenol,
Tetra-hydro-phenol.

(2) Hydrogenation products of naphthalene (e. g. decahydronaphthalene, tetrahydronaphthalene, etc.):
Such as the hydrogenated naphthols.

(3) Naphthenes, such as naphthenic acid, etc.

(c) Of mixed type such as derivatives of indene, hydrindene, hydranthracene, etc.

B.—"Heterocyclic type" compounds

(a) Of the aromatic or allied type including derivatives of pyridine, quinoline, etc.

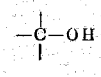
(b) Other types such as furan and its derivatives; and derivatives of thiophene, pyrrole, etc.

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
Sulphone
Sulphonic acid
Sulphoxide
Thio-sulphate

The following table indicates some of the specific compounds found suitable for use in accordance with this invention:

Organic oxygen compounds
Ring compounds
Aromatic
Phenols
Halogenated phenol
Halogenated α-naphthol
Halogenated amino phenols
Halogenated butyl phenol
Halogenated phenyl phenol
Halogenated xylenol
Halogenated "tar acids" (preferably refined by distillation)
Alcohols
Halogenated benzyl alcohol
Halogenated phenyl ethyl alcohol
Aldehydes
Halogenated benzaldehyde
Ketones
Halogenated benzophenone
Halogenated phenyl tolyl ketones
Halogenated dinaphthyl ketone
Halogenated methyl benzophenones
Amide and substituted amides
Halogenated phenyl amide
Halogenated acetanilide
Halogenated stearanilide
Acids
Halogenated phenyl fatty acids, e. g.
Phenyl acetic acid
Phenyl stearic acid
Halogenated salicylic acid
Esters
Halogenated phenyl acetate
Halogenated phenyl carbonate
Halogenated ethyl benzoate
Halogenated butyl benzoate
Halogenated di-ethyl phthalate
Halogenated dibutyl
Halogenated esters of phenyl fatty acids, e. g. ethyl and butyl esters of phenyl acetic acid and phenyl stearic acid
Halogenated methyl salicylate
Halogenated benzyl acetate
Salts
Halogenated pyridine acetate
Halogenated quinoline acetate
Halogenated aniline stearate
Halogenated calcium chlorphenyl stearate

- Halogenated magnesium chlorphenyl stearate
- Halogenated cobalt chlorphenyl stearate

Ethers
- Halogenated diphenyl ether
- Halogenated pheny ethyl ether
- Halogenated dixenyl ether
- Halogenated dinaphthyl ether
- Halogenated alkylated diphenyl ether

Non-aromatic oxygen-bearing organic ring compounds
- Halogenated cyclo-hexanol
- Halogenated naphthenic acids
- Halogenated esters of naphthenic acids
- Halogenated salts of naphthenic acids, e. g.
  - Calcium
  - Nickel
  - Cobalt
  - Lead chlor-naphthenates

Oxygen-bearing heterocyclic compounds
- (1) Halogenated furane and derivatives, e. g. halogenated esters of pyromucic acid (furoates), halogenated furfuryl and hydrofurfuryl esters of fatty acids such as the acetates and stearates.
- (2) Halogenated oxygen-bearing derivatives of thiophene and pyrrole, e. g. esters of thiophene carboxylic acids and esters of pyrrole carboxylic acid.

Chain compounds

Alcohols
- Halogenated octyl alcohol
- Halogenated decyl alcohol
- Halogenated lauryl alcohol
- Halogenated cetyl alcohol

Esters
- Halogenated methyl stearate
- Halogenated lauryl acetate
- Halogenated tri-lauryl phosphate

Hydroxy-amines
- Halogenated tri-ethanol amine
- Halogenated tri-butanol amine

Ethers
- Halogenated dibutyl ether
- Halogenated diamyl ether
- Halogenated dioctyl ether

Ketone
- Halogenated dipropyl ketone
- Halogenated dibutyl ketone
- Halogenated di-amyl ketone
- Halogenated di-octyl ketone

Acids
- Halogenated propionic acid
- Halogenated butyric acid
- Halogenated lauric acid
- Halogenated oleic acid
- Halogenated stearic acid

Salts
- Halogenated tri-ethanol-amine acetate

Complex commercial organic material

Halogenated:
- Animal and vegetable oils, fats and waxes (and complex derivatives)
- Oxidized hydrocarbons (e. g. oxidized petroleum or petroleum products) and complex derivatives obtained from such oxidation products (e. g. "alox")

As a class the halogenated oxygen-bearing compounds are particularly desirable on account of their unusual effectiveness in themselves imparting extreme pressure characteristics and in their unexpected cooperation with the organic sulfur compounds. The following are examples of such referred compounds:

- Halogenated diphenyl ether
- Halogenated benzophenone
- Halogenated methyl benzophenones
- Halogenated butyl phenyl ketone
- Halogenated phenyl acetate
- Halogenated phenol
- Halogenated O-phenyl phenol
- Halogenated cyclo hexanol
- Halogenated dibutyl phthalate
- Halogenated methyl salicylate
- Halogenated lauryl alcohol
- Halogenated methyl stearate
- Halogenated di-amyl ether
- Halogenated oxidized petroleum hydrocarbons

In addition to the substituents containing oxygen, other substituents may also be present without destroying, and in certain cases improving, the effect on the lubricating qualities of the oil such as other aryl groups, alkyl groups, and amino and substituted amino groups, imino, azo, hydrazo, hydrazine, nitrile, mercapto, sulphide, polysulphide.

Specific examples of compounds of the various classes of halogen and oxygen containing ring compounds are listed in the copending application of Carl F. Prutton, Ser. No. 737,070, filed July 26, 1934.

Other specific examples of halogen and oxygen containing organic compounds useful in the present invention will be found referred to in our copending application Ser. No. 318,624 filed by us even date herewith.

The organic sulphur compounds

As previously indicated, the third component of our composition is sulphur in the form of a relatively inactive organic sulphur compound in an amount in which such sulphur compound would not substantially increase the extreme pressure characteristics of a plain mineral oil.

In other words, our invention comprises the combined use of a halogen compound and relatively inactive sulphur to the end that the cooperation between the second and third components of our composition results in the achievement of a film strength in the resultant composition which is due to the cooperation between such second and third components. In other words, the organic sulphur compound is of the type or present in amounts such that it, when used alone without the halogen, does not substantially increase the film strength of plain mineral oil but which, when used in conjunction with a halogen compound, is activated by the latter to the production of an unexpected result flowing from the cooperative effect of the second and third components of our composition.

While there is no generally accepted standard machine or test procedure in universal use to-day for the purpose of determining extreme pressure characteristics of a lubricating composition, nevertheless there are a number of machines available to-day which are currently being used with fairly uniform and satisfactory results. The well-known Almen machine was employed in making determinations referred to herein. When in our specification and claims we refer to the fact that the sulphur compound is of the type or present in such amounts as to not substantially increase the extreme pressure characteristics of a plain mineral oil, we mean such characteristics

as would be determined by the use of the Almen machine under the conditions of test prescribed by the manufacturer.

The effect of sulphur compounds in increasing film strength is enormously enhanced by the presence of halogen-containing, or of halogen- and oxygen-containing, organic compounds, especially if the relative proportions of such sulphur and halogen compounds are within certain ranges. Sulphur compounds in amounts which have a negligible effect in increasing film strength when used by themselves are very effective when used in combination with the proper proportion of halogen-bearing organic compounds. Organic sulphides, disulphides, mercaptans, mercaptoles, thio-acids, and their esters, dithio-acids, and their esters, sulphones, sulphoxides, sulphonic acids, and their esters, sulphinic acids, and their esters sulphone amides, sulphone chlorides, thio-amides, thio-anilides, organic thiocyanates, organic xanthates, etc., (which may or may not contain a ring structure, that is they may be either aliphatic, cycloaliphatic or aromatic) are examples of sulphur compounds which act in this way.

Included among the sulphur bearing materials contemplated by our invention are the materials which may be prepared by sulphurizing various organic compounds and complex materials such as esters of fatty acids and particularly unsaturated fatty acid esters, (for example methyl linoleate), also fatty oils such as sperm oil, lard oil and vegetable oil (e. g. corn oil).

For examples of sulphur bearing materials, reference may be had to our copending application Ser. No. 318,624 filed even date herewith.

This invention, as previously indicated relates to the discovery that by the use of such a relattively inactive organic sulphur compound, or an organic sulphur compound in such small amounts that, by itself, the extreme pressure characteristics of a plain mineral oil are not substantially increased, will, however, when employed in the same amounts in conjunction with other organic compounds, give unexpected film strength improvement. Generally, the halogen bearing organic sulphur compounds are sufficiently active so that they are satisfactory extreme pressure addition agents when used by themselves. Such halogen bearing organic sulphur compounds, however, may be used in such small amounts that they do not impart any substantial degree of film strength. However, when used in the same amount in conjunction with the other components of our improved composition will be found to give unexpectedly high film strength as well as other improvements in such combination. Halogen containing aromatic sulphur compounds, in general, are examples of halogen bearing organic sulphur compounds which act in this way. Specific examples of these are the halogen containing aromatic mercaptans, sulphides, and disulphides, e. g. chlorbenzyl sulphides, chlorbenzyl disulphides, and chlorbenzyl mercaptans.

Following is a list of additional specific examples of organic sulphur compounds which have been found satisfactory for use:

Tallow mercaptan (the reaction product of chlorinated tallow with NaHS)
Trio-o-cresyl thiophosphate
Di (di-isobutylene) disulphide
Dibutyl sulphide
Di-amyl sulphide
Di-amyl disulphide
Dihydroxy diphenyl disulphide
Alkylated hydroxy phenyl disulphides
Lauryl thiocyanate
Benzyl thiocyanate
Benzyl ester of xanthic acid

For other specific examples of organic sulphur compounds which may thus be employed as the third component of the composition of our invention, reference may be had to the list of organic sulphur compounds contained in the copending application of Carl F. Prutton, Ser. No. 193,960 filed March 4, 1938.

The organic oxygen compound

As previously indicated, the fourth component of our composition is oxygen in the form of an oil soluble organic oxygen compound. Specific examples of this fourth component are 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
(1) 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.
(2) Of the class including the cycloparaffins, cyclo-olefines, etc. Examples of this class are oxygen-bearing derivatives of the following:
(*a*) Hydrogenation products of benzene (e. g. cyclohexane, cyclohexene, cyclohexadiene), such as hydrogenated phenol, notably
Cyclohexanol
Di-hydro phenol
Tetra-hydro phenol.
(*b*) Hydrogenation products of naphthalene (e. g., decahydronaphthalene, tetrahydronaphthalene, etc.), such as the hydrogenated naphthols.
(*c*) Naphthenes, such as naphthenic acid, etc.
(3) Of mixed type such as derivatives of indene, hydrindene, hydranthracene, etc.
B. "Heterocyclic" type compounds
(1) Of the aromatic or allied type including derivatives of pyridine, quinoline, etc.
(2) Other types such as furane 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

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radicle, such as 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 a ring structure, e. g. compounds containing the furyl or hydro-furyl groups.

(5') Compounds with an inorganic radicle where the oxygen is directly attached to a carbon atom, e. g.

Arsenites
Hypochlorites
Phosphites
Thiophosphates
Thiophosphites
β-hydroxylamines
Borates

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
Thiophosphate
Thiophosphite
Thio-sulphate

(Note: This class includes salts of organic bases with inorganic oxy-acids.)

The following table indicates some of the compounds which are especially suitable, halogenated or unhalogenated, as the case may be:

Organic oxygen compounds

Ring compounds	Unhalogenated	Halogenated
Aromatic: Phenols	Phenol α-naphthol Amino phenol Butyl phenol Phenyl phenol Resorcinol Xylenol "tar acids" (preferably refined by distillation) Cyclohexyl phenol	O-chlor phenol Monochlor α-naphthol Chlor-resorcinols
Alcohols	Benzyl alcohol Phenyl ethyl alcohol	Chlor benzyl alcohols
Aldehydes (less desirable because of polymerization)	Benzaldehyde	
Ketones	Benzophenone Alkylated benzophenones, e. g.— Methyl benzophenones Dimethyl benzophenones Ethylated benzophenones Propylated benzophenones Phenyl tolyl ketones Dinaphthyl ketone Aryl-alkyl ketones, e. g.— Acetophenone Butyl phenyl ketones	Monochlor benzophenone Alkylated chlor-benzophenones, e. g.— Methyl chlor-benzophenones Dimethyl chlor-benzophenones Ethylated chlor-benzophenones Propylated chlor-benzophenones Chlorinated aryl-alkyl ketones, e. g.— Monochlor acetophenone Butyl chlorphenyl ketones
Amides	Acetanilide Stearanilide	Stear-chloranilides
Acids	Aromatic fatty acids, e. g.— Phenyl acetic acid Phenyl stearic acid Salicylic acid	Chlorphenyl acetic acids Chlorphenyl stearic acids Chor-salicylic acids
Esters and salts	Phenyl acetate Phenyl carbonate Ethyl benzoate Butyl benzoate Di-methyl phthalate Di-ethyl phthalate Dibutyl phthalate Methyl salicylate Benzyl acetate Pyridine acetate Quinoline acetate Quinoline oleate Quinoline stearate Pyridine stearate Esters and salts of aromatic fatty acids, e. g., esters of phenylacetic and phenyl stearic acids, including the methyl, ethyl, butyl, lauryl, cetyl and ceryl esters; calcium, magnesium and cobalt phenyl-stearate	Ethyl chlorbenzoates Butyl chlorbenzoates Di-methyl chlorphthalates Di-ethyl chlorphthalates Di-butyl chlorphthalates Methyl chlor salicylates Chlorbenzyl acetates Esters of chlor-aromatic fatty acids, e. g., esters and chlorphenyl acetic and chlorphenyl stearic acids including the methyl, ethyl, butyl, lauryl, cetyl and ceryl esters; calcium magnesium and cobalt chlorphenyl-stearates
Ethers	Diphenyl ether Phenyl ethyl ether Dixenyl ether Dinaphthyl ether Alkylated diphenyl ether	Chlorinated diphenyl ether Chlorphenyl ethyl ethers Chlorinated dixenyl ether Chlorinated dinaphthyl ether Alkylated chlor-diphenyl ether

Non-aromatic oxygen-bearing organic ring compounds
- Cyclo-hexanol
- Cyclo-hexyl esters, e. g. cyclo-hexyl stearate, cyclo-hexyl laurate, tri-cyclo-hexyl phosphate, tri-cyclo-hexyl phosphite, tri-(methyl cyclohexyl) and tri-(iso-amyl cyclohexyl) phosphites.
- Naphthenic acids
- Esters of naphthenic acids, e. g. methyl naphthenates
- Salts of naphthenic acids, e. g. calcium, nickel, cobalt and lead naphthenates

Oxygen-bearing heterocyclic compounds
- (1) Furane and derivatives, e. g.
  - Esters of pyromucic acid (furoates), e. g. methyl furoate, butyl furoate
  - Furfuryl alcohol and esters of it, e. g. furfuryl acetate, furfuryl stearate
  - Tetrahydrofurfuryl alcohol and esters of it, e. g. tetrahydrofurfuryl acetate and stearate
- (2) Oxygen-bearing derivatives of thiophene and pyrrole, e. g. esters of thiophene carboxylic acids and esters of pyrrole carboxylic acids.

since the use of too high a concentration will reduce the film strength of the composition. For example, when the organic oxygen compound used is of the class consisting of fatty acids and esters and salts of fatty acids, a relatively small percentage of such organic oxygen compound should be used, particularly in the case of the acids, since a disadvantageous reduction in film strength will result from too high a concentration. Other organic oxygen compounds which are not so readily adsorbed on metallic surfaces, such as for example ketones, may be used in higher proportions with advantageous results.

It will be observed that among the specific examples listed above which may be used as this fourth component in our improved lubricating composition are halogen bearing organic oxygen compounds. Thus, it is within the contemplation of our invention to form a lubricating composition which comprises a halogen bearing oxygen-free organic compound, plus a relatively inactive organic sulphur compound, plus a halogen bearing organic oxygen compound, all of them dissolved in a lubricating oil base. The oxygen-free halogen compound in such a composition will serve the purpose of a reservoir of halogen in the

Chain compounds	Unhalogenated	Halogenated
Alcohols		
	Octyl alcohol	Fluorinated octyl alcohol
	Decyl alcohol	Fluorinated decyl alcohol
	Lauryl alcohol	Fluorinated lauryl alcohol
	Cetyl alcohol	Fluorinated cetyl alcohol
	Carnaubyl alcohol	Fluorinated carnaubyl alcohol
	Ceryl alcohol	Fluorinated ceryl alcohol
	Montanyl alcohol	Fluorinated montanyl alcohol
	Melissyl alcohol	Fluorinated melissyl alcohol
	Myricyl alcohol	Fluorinated myricyl alcohol
Esters and salts		
	Methyl palmitate	Methyl dichlor palmitate
	Methyl stearate	Methyl dichlor stearate
	Methyl lactate	Sodium chlorhydroxystearate
	Butyl lactate	Calcium dichlor stearate
	Lauryl acetate	Cobalt dichlor stearate
	Cetyl acetate	
	Ceryl acetate	
	Tri-ethanol-amine acetate	
	Tri-lauryl phosphate	
	Tri-lauryl phosphite	
	Di-ethyl oxalate	
	Di-butyl oxalate	
	Di-lauryl oxalate	
	Di-cetyl oxalate	
	Di-ceryl oxalate	
	Dimethyl malonate	
	Dibutyl malonate	
	Dimethyl succinate	
	Dibutyl succinate	
	Dimethyl tartrate	
	Dibutyl tartrate	
	Dilauryl tartrate	
	Tributyl citrate	
	Trilauryl citrate	
Hydroxy-amines		
	Tri-ethanol amine	
	Tri-butanol amine	
	Dibutyl ethanolamine	
Ethers	Butyl ether	Chlorinated or fluorinated ethyl ether (notably β, β' dichlor ethyl ether)
	Amyl ether	Butyl ether
	Octyl ether	Amyl ether
	Lauryl ether	
Ketones		
	Dipropyl ketone	Chlorinated or fluorinated:
	Dibutyl ketone	
	Di-amyl ketone	Laurone
	Di-octyl ketone	Palmitone
	Laurone	Stearone
	Palmitone	
	Stearone	
Acids		
	Propionic acid	Chlorinated or fluorinated:
	Butyric acid	
	Lauric acid	Lauric acid
	Palmitic acid	Palmitic acid
	Stearic acid	Stearic acid
	Hydroxystearic acid	Chlorhydroxystearic acid

The amount of such organic oxygen compound to be used will depend upon its tendency to be adsorbed by the metallic bearing surfaces. Relatively smaller amounts of organic oxygen compounds which tend to highly adsorb are used form required to maintain a high film strength, and the halogen and oxygen containing compound will serve to increase the oiliness of the composition without, however, having as great a tendency to reduce the film strength of the com-

position as would be the case with a similar oxygen compound which did not contain halogen. Accordingly, when the fourth component, i. e. the oxygen compound also contains halogen, it may be used in concentrations somewhat greater than those specified above for use when the fourth component is halogen free.

Thus, any of the halogen bearing organic oxygen compounds given as specific examples for use as the second component may be used instead as the fourth component. Conversely, any of the halogen and oxygen bearing organic compounds which have been given as specific examples of the fourth component may be used instead as the second component. When this is done, of course, a different compound will be used as the constituent representing either the second or the fourth component, as the case may be. Similarly included among the examples of organic sulphur compounds useful as the third component have been given compounds which are halogen bearing and may thus be used instead as the second component. A specific example of such are the halogen bearing xanthates and the like. Where such halogen and sulphur compound also contains oxygen, it may be used as the fourth component with other compounds which are respectively the second and third component of the composition.

It will also be observed that certain other organic sulphur compounds identified for use as the third component are likewise oxygen containing organic compounds, and may thus be used instead as the fourth component, however, when used as the fourth component, they will be employed in conjunction with other compounds representing the second and third components.

Listed among the specific examples of compounds useful as the second component of the composition are halogen bearing organic compounds which also contain sulphur (examples of such are the chlorinated organic thiocyanates) which can be used to advantage as the third component with any of the other specific examples listed as representative of the second component.

It will, of course, be understood that in any particular finished lubricant made in accordance with our invention, each of components 2, 3 and 4 will be represented by a different specific compound. While chlorbenzyl disulphide is a specific example of an organic sulphur compound, i. e. component 3, it may, nevertheless, be used in a finished lubricant as component 2, i. e. the halogen compound. When such is the case then, of course, some other sulphur compound will be used as the 3rd component. The same will be true of other compounds which may fall in different classes and thus be representative of more than one component.

In the case of an organic compound containing the three elements, halogen, oxygen, and sulphur, the compound will be most useful as the second component of our composition when the halogen is in a relatively active state, and will be most useful as the third component of our composition when the sulphur is in a relatively more active state as compared with the halogen.

In order to protect bearings, gears, etc. from very severe overloads, it is sometimes advisable to use a halogen-containing compound which is so active as to be appreciably corrosive under normal conditions. Since chain compounds are generally more corrosive, i. e. more active than ring compounds, they are admirably suited for this purpose. In these circumstances the corrosive effect of such chain compounds and of halogenated organic ring compounds of the addition type for example, may be greatly inhibited by the addition of certain other oil-soluble compounds, such as (1) organic bases, aromatic and alkyl amines, triethanolamine, quinoline, etc., (2) organic phosphates, e. g., tri-butyl phosphate, tri-phenyl phosphate, tri-cresyl phosphate, etc. Also certain of the halogen and sulphur compounds referred to above have similar corrosion-inhibiting effects, notably (1) the phosphates of chlorinated ring compounds, e. g. tri-chlorphenyl phosphate, (2) mercaptans and chlor-mercaptans. For other specific examples of corrosion inhibitors reference may be had to copending applications Ser. Nos. 119,132; 297,872; 297,873; 297,874; 297,875 and 297,876.

In general, the addition agents which are added to the lubricating oil base should have a vapor pressure less than atmospheric at the temperatures to which the finished product is subjected either during storage or use. For the lubrication of ice machines, one type of addition agent would be suitable which however might be entirely unsuited for the lubrication of internal combustion engines operating at extremely high temperatures. In general, the addition agents which comprise the second, third and fourth components of our composition should have a vapor pressure less than atmospheric at 140° C. and preferably at 170° C.

Percentages and proportions

The percentages and proportions within which the several components of our improved lubricating compositions are employed will depend largely upon the purpose for which the lubricating composition is designed and the character of the several components themselves.

The second component of our composition, i. e. the halogen bearing compound will be employed in percentages which are dictated by the results desired and the type of oil base and sulphur compound with which they are combined, etc. For most purposes, the halogen bearing compounds will be employed in percentages less than 20% of the total composition. In most cases, amounts less than 10% will be employed and for certain uses such as for crank case oils in internal combustion engines, amounts less than 5% will be employed. In general, the halogen bearing compound will be required to be present in amounts in excess of .02% in order to be effective. The ranges of percentages which may be given therefore for the amount of the second component which is employed may be given as from about .02% to about 20%; from about .1% to about 10% and from about .5% to about 5%.

The organic sulphur compounds employed as the third component of our composition will generally be employed in the range of from about .01% to about 20%. For most uses, this range will be from about .1% to about 10%, the range of from about .5% to about 5% being usually preferred.

The organic oxygen compound which is employed as the fourth component of our composition will generally be employed in amounts from about .01% to about 10%, due regard being given to the statements previously made as to the best proportional relationship between the second and fourth components. Generally very low concentrations, on the order of .01% to .10%, of this fourth component will be used in many cases.

Especially good results are secured when the

halogen compound employed is selected from the general class which contains from about 25% to about 50% of halogen. With this class of halogen compounds optimum results will be secured in high-temperature lubricants by the employment of from one-tenth to 2% of the halogenated compounds.

As above indicated, optimum results are secured by maintaining a certain proportional relationship between the second and third components depending upon the relative activity of these components. Thus for example, with a relatively very inactive sulphur compound and a relatively very active halogen compound the proportional relationship would be in the range of one part of the sulphur compound to one part of the halogen compound. With the sulphur compound relatively less inactive and the halogen compound of relatively low activity, the proportional relationship would be in the range of one part of the sulphur compound to about ten parts of the halogen compound. Intermediate ranges which have been successfully employed have been one part of sulphur compound to five parts of halogen compound and one part of sulphur compound to two parts of halogen compound. For the most part good results will be obtained with a proportional relationship of about one part of sulphur compound to three parts of halogen compound.

Throughout the foregoing description of our invention, reference has been made generally to the use of "halogen bearing" or "halogenated" organic compounds. Of the halogen containing compounds which are thus indicated as useful, it will be understood, of course, that the chlorine containing compounds are usually preferred, largely due to their inherently lower cost and their general superiority over the other halogens. The bromine containing species will generally be found less desirable than the corresponding chlorine compounds, due to higher cost. The iodine containing compounds are, as a class, less desirable than any of the other halogens because of the high cost and difficulty of preparation. For the most part, the practical advantages which may be achieved by the use of the iodine compounds may be gotten in a more satisfactory manner by the use of the corresponding chlorine compounds.

The fluorinated compounds are again usually less desirable than the chlorinated compounds. However, it is generally true that, with regard to a particularly active chlorine compound, the corresponding fluorinated compound will be more stable and for certain purposes preferable for this reason.

In the light of the foregoing, it will be observed that wherever a particular class or sub-class of compounds, or a specific compound, is identified as being halogen containing material, we prefer the use of the corresponding chlorine compound.

In the definition in the foregoing specification of the various materials which may be used as the respective components of our composition, a large number of rather broad classes and subclasses of organic compounds have been mentioned. Of such broad class, there may be, of course, some few cases where the specific material is unsuited for use in a lubricant. Those skilled in the art will be able to readily appreciate and discard those which, while included along with compounds of greater utility, may, however, be such that they would obviously not be used as a constituent in a lubricating composition in the light of the teachings of this specification. Generally, the characteristics which render certain specific examples unsatisfactory for use are lack of stability, lack of oil solubility, high volatility, etc. All of the compounds which are suggested for use, therefore, by the present specification are limited to those classes which do have sufficient stability, sufficient oil solubility, and a sufficiently low volatility so that they may be satisfactorily employed in lubricating compositions, always having in mind the particular characteristics of the composition required by the use for which it is designed.

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.

We therefore particularly point out and distinctly claim as our invention:

1. A lubricating composition comprising a major proportion of mineral oil and a relatively inactive organic sulphur compound in an amount in which such sulphur compound would not substantially increase the extreme pressure characteristics of a plain mineral oil and minor amounts of both a halogen bearing organic compound and an organic oxygen compound, said compounds being oil soluble within the percentages present in the oil, of sufficiently low volatility and of such stability so as not to be substantially evaporated from or decomposed in the lubricating composition during use.

2. A lubricating composition comprising a major proportion of mineral oil and a relatively inactive organic sulphur compound in an amount in which such sulphur compound would not substantially increase the extreme pressure characteristics of a plain mineral oil and minor amounts of both a halogen bearing organic compound and a halogenated organic oxygen compound, all of said compounds having a vapor pressure less than atmospheric at a temperature of 140° C., said compounds being oil soluble within the percentages present in the oil, of sufficiently low volatility and of such stability so as not to be substantially evaporated from or decomposed in the lubricating composition during use.

3. A lubricating composition comprising a major proportion of mineral oil and a relatively inactive organic sulphur compound in an amount in which such sulphur compound would not substantially increase the extreme pressure characteristics of a plain mineral oil and minor amounts of both a halogen bearing organic ring compound and an organic oxygen compound, all of said compounds having a vapor pressure less than atmospheric at a temperature of 140° C., said compounds being oil soluble within the percentages present in the oil, of sufficiently low volatility and of such stability so as not to be substantially evaporated from or decomposed in the lubricating composition during use.

4. A lubricating composition comprising a major proportion of mineral oil and a relatively inactive organic sulphur compound in an amount in which such sulphur compound would not substantially increase the extreme pressure characteristics of a plain mineral oil and minor amounts of both a halogen bearing aromatic compound and an organic oxygen compound, all of said compounds having a vapor pressure less than atmospheric at a temperature of 140° C., said compounds being oil soluble within the percentages present in the oil, of sufficiently low vola-

tility and of such stability so as not to be substantially evaporated from or decomposed in the lubricating composition during use.

5. A lubricating composition comprising a major proportion of mineral oil and a relatively inactive organic sulphur compound in an amount in which such sulphur compound would not substantially increase the extreme pressure characteristics of a plain mineral oil and minor amounts of both a halogen bearing aromatic compound and a halogenated organic oxygen compound, all of said compounds having a vapor pressure less than atmospheric at a temperature of 140° C., said compounds being oil soluble within the percentages present in the oil, of sufficiently low volatility and of such stability so as not to be substantially evaporated from or decomposed in the lubricating composition during use.

6. A lubricating composition comprising a major proportion of mineral oil and a relatively inactive organic sulphur compound in an amount in which such sulphur compound would not substantially increase the extreme pressure characteristics of a plain mineral oil and minor amounts of both a halogen bearing aliphatic compound and an organic oxygen compound, all of said compounds having a vapor pressure less than atmospheric at a temperature of 140° C., said compounds being oil soluble within the percentages present in the oil, of sufficiently low volatility and of such stability so as not to be substantially evaporated from or decomposed in the lubricating composition during use.

7. A lubricating composition comprising a major proportion of mineral oil and a relatively inactive organic sulphur compound in an amount in which such sulphur compound would not substantially increase the extreme pressure characteristics of a plain mineral oil and minor amounts of both a halogen bearing aliphatic compound and a halogenated organic oxygen compound, all of said compounds having a vapor pressure less than atmospheric at a temperature of 140° C., said compounds being oil soluble within the percentages present in the oil, of sufficiently low volatility and of such stability so as not to be substantially evaporated from or decomposed in the lubricating composition during use.

8. A lubricating composition comprising a major proportion of mineral oil and a relatively inactive organic sulphur compound in an amount in which such sulphur compound would not substantially increase the extreme pressure characteristics of a plain mineral oil and minor amounts of both a halogen and oxygen bearing organic compound and an organic oxygen compound, all of said compounds having a vapor pressure less than atmospheric at a temperature of 140° C., said compounds being oil soluble within the percentages present in the oil, of sufficiently low volatility and of such stability so as not to be substantially evaporated from or decomposed in the lubricating composition during use.

9. A lubricating composition comprising a major proportion of mineral oil and a relatively inactive organic sulphur compound in an amount in which such sulphur compound would not substantially increase the extreme pressure characteristics of a plain mineral oil and minor amounts of both a halogen and oxygen bearing aromatic compound and an organic oxygen compound, all of said compounds having a vapor pressure less than atmospheric at a temperature of 140° C., said compounds being oil soluble within the percentages present in the oil, of sufficiently low volatility and of such stability so as not to be substantially evaporated from or decomposed in the lubricating composition during use.

10. A lubricating composition comprising a major proportion of mineral oil and a relatively inactive organic sulphur compound in an amount in which such sulphur compound would not substantially increase the extreme pressure characteristics of a plain mineral oil and minor amounts of both a halogen and oxygen bearing aliphatic compound and an organic oxygen compound, all of said compounds having a vapor pressure less than atmospheric at a temperature of 140° C., said compounds being oil soluble within the percentages present in the oil, of sufficiently low volatility and of such stability so as not to be substantially evaporated from or decomposed in the lubricating composition during use.

11. A lubricating composition comprising a major proportion of mineral oil and a sulphur bearing organic ring compound in an amount in which such sulphur compound would not substantially increase the extreme pressure characteristics of a plain mineral oil and minor amounts of both a halogen bearing organic compound and an organic oxygen compound, all of said compounds having a vapor pressure less that atmospheric at a temperature of 140° C., said compounds being oil soluble within the percentages present in the oil, of sufficiently low volatility and of such stability so as not to be substantially evaporated from or decomposed in the lubricating composition during use.

12. A lubricating composition comprising a major proportion of mineral oil and a sulphur bearing aromatic compound in an amount in which such sulphur compound would not substantially increase the extreme pressure characteristics of a plain mineral oil and minor amounts of both a halogen bearing organic compound and an organic oxygen compound, all of said compounds having a vapor pressure less than atmospheric at a temperature of 140° C., said compounds being oil soluble within the percentages present in the oil, of sufficiently low volatility and of such stability so as not to be substantially evaporated from or decomposed in the lubricating composition during use.

13. A lubricating composition comprising a major proportion of mineral oil and a sulphur bearing aliphatic compound in an amount in which such sulphur compound would not substantially increase the extreme pressure characteristics of a plain mineral oil and minor amounts of both a halogen bearing organic compound and an organic oxygen compound, all of said compounds having a vapor pressure less than atmospheric at a temperature of 140° C., said compounds being oil soluble within the percentages present in the oil, of sufficiently low volatility and of such stability so as not to be substantially evaporated from or decomposed in the lubricating composition during use.

14. A lubricating composition comprising a major proportion of mineral oil and an organic sulphide in an amount in which such sulphur compound would not substantially increase the extreme pressure characteristics of a plain mineral oil and minor amounts of both a halogen bearing organic compound and an organic oxygen compound, all of said compounds having a vapor pressure less than atmospheric at a temperature of 140° C., said compounds being oil soluble within the percentages present in the oil, of sufficiently low volatility and of such stability

so as not to be substantially evaporated from or decomposed in the lubricating composition during use.

15. A lubricating composition comprising a major proportion of mineral oil and an organic polysulphide in an amount in which such sulphur compound would not substantially increase the extreme pressure characteristics of a plain mineral oil and minor amounts of both a halogen bearing organic compound and an organic oxygen compound, all of said compounds having a vapor pressure less than atmospheric at a temperature of 140° C., said compounds being oil soluble within the percentages present in the oil, of sufficiently low volatility and of such stability so as not to be substantially evaporated from or decomposed in the lubricating composition during use.

16. A lubricating composition comprising a major proportion of mineral oil and an organic polysulphide in an amount in which such sulphur compound would not substantially increase the extreme pressure characteristics of a plain mineral oil and minor amounts of both a halogen bearing aromatic compound and an organic oxygen compound, all of said compounds having a vapor pressure less than atmospheric at a temperature of 140° C., said compounds being oil soluble within the percentages present in the oil, of sufficiently low volatility and of such stability so as not to be substantially evaporated from or decomposed in the lubricating composition during use.

17. A lubricating composition comprising a major proportion of mineral oil and an organic polysulphide in an amount in which such sulphur compound would not substantially increase the extreme pressure characteristics of a plain mineral oil and minor amounts of both a halogen bearing aliphatic compound and an organic oxygen compound, all of said compounds having a vapor pressure less than atmospheric at a temperature of 140° C., said compounds being oil soluble within the percentages present in the oil, of sufficiently low volatility and of such stability so as not to be substantially evaporated from or decomposed in the lubricating composition during use.

18. A lubricating composition comprising a major proportion of mineral oil and an organic disulphide in an amount in which such sulphur compound would not substantially increase the extereme pressure characteristics of a plain mineral oil and minor amounts of both a halogen bearing organic compound and an organic oxygen compound, all of said compounds having a vapor pressure less than atmospheric at a temperature of 140° C., said compounds being oil soluble within the percentages present in the oil, of sufficiently low volatility and of such stability so as not to be substantially evaporated from or decomposed in the lubricating composition during use.

19. A lubricating composition comprising a major proportion of mineral oil and an aromatic disulphide in an amount in which such sulphur compound would not substantially increase the extreme pressure characteristics of a plain mineral oil and minor amounts of both a halogen bearing organic compound and an organic oxygen compound, all of said compounds having a vapor pressure less than atmospheric at a temperature of 140° C., said compounds being oil soluble within the percentages present in the oil, of sufficiently low volatility and of such stability so as not to be substantially evaporated from or decomposed in the lubricating composition during use.

20. A lubricating composition comprising a major proportion of mineral oil and an aromatic disulphide in an amount in which such sulphur compound would not substantially increase the extreme pressure characteristics of a plain mineral oil and minor amounts of both a halogen bearing organic compound and a halogenated organic oxygen compound, all of said compounds having a vapor pressure less than atmospheric at a temperature of 140° C., said compounds being oil soluble within the percentages present in the oil, of sufficiently low volatility and of such stability so as not to be substantially evaporated from or decomposed in the lubricating composition during use.

21. A lubricating composition comprising a major proportion of mineral oil and an aromatic disulphide in an amount in which such sulphur compound would not substantially increase the extreme pressure characteristics of a plain mineral oil and minor amounts of both a halogen bearing aromatic compound and an organic oxygen compound, all of said compounds having a vapor pressure less than atmospheric at a temperature of 140° C., said compounds being oil soluble within the percentages present in the oil, of sufficiently low volatility and of such stability so as not to be substantially evaporated from or decomposed in the lubricating composition during use.

22. A lubricating composition comprising a major proportion of mineral oil and an aromatic disulphide in an amount in which such sulphur compound would not substantially increase the extreme pressure characteristics of a plain mineral oil and minor amounts of both a halogen bearing aliphatic compound and an organic oxygen compound, all of said compounds having a vapor pressure less than atmospheric at a temperature of 140° C., said compounds being oil soluble within the percentages present in the oil, of sufficiently low volatility and of such stability so as not to be substantially evaporated from or decomposed in the lubricating composition during use.

23. A lubricating composition comprising a major proportion of mineral oil and an aromatic disulphide in an amount in which such sulphur compound would not substantially increase the extreme pressure characteristics of a plain mineral oil and minor amounts of both a halogen bearing aromatic compound and a halogenated organic oxygen compound, all of said compounds having a vapor pressure less than atmospheric at a temperature of 140° C., said compounds being oil soluble within the percentages present in the oil, of sufficiently low volatility and of such stability so as not to be substantially evaporated from or decomposed in the lubricating composition during use.

24. A lubricating composition comprising a major proportion of mineral oil and an aromatic disulphide in an amount in which such sulphur compound would not substantially increase the extreme pressure characteristics of a plain mineral oil and minor amounts of both a halogen bearing aliphatic compound and a halogenated organic oxygen compound, all of said compounds having a vapor pressure less than atmospheric at a temperature of 140° C., said compounds being oil soluble within the percentages present in the oil, of sufficiently low volatility and of such

stability so as not to be substantially evaporated from or decomposed in the lubricating composition during use.

25. A lubricating composition comprising a major proportion of mineral oil and a halogen bearing organic sulphur compound in an amount in which such sulphur compound would not substantially increase the extreme pressure characteristics of a plain mineral oil and minor amounts of both a halogen bearing organic compound and an organic oxygen compound, all of said compounds having a vapor pressure less than atmospheric at a temperature of 140° C., said compounds being oil soluble within the percentages present in the oil, of sufficiently low volatility and of such stability so as not to be substantially evaporated from or decomposed in the lubricating composition during use.

26. A lubricating composition comprising a major proportion of mineral oil and a halogen bearing organic sulphur compound in an amount in which such sulphur compound would not substantially increase the extreme pressure characteristics of a plain mineral oil and minor amounts of both a halogen bearing aromatic compound and an organic oxygen compound, all of said compounds having a vapor pressure less than atmospheric at a temperature of 140° C., said compounds being oil soluble within the percentages present in the oil, of sufficiently low volatility and of such stability so as not to be substantially evaporated from or decomposed in the lubricating composition during use.

27. A lubricating composition comprising a major proportion of mineral oil and a halogen bearing organic sulphur compound in an amount in which such sulphur compound would not substantially increase the extreme pressure characteristics of a plain mineral oil and minor amounts of both a halogen bearing aliphatic compound and an organic oxygen compound, all of said compounds having a vapor pressure less than atmospheric at a temperature of 140° C., said compounds being oil soluble within the percentages present in the oil, of sufficiently low volatility and of such stability so as not to be substantially evaporated from or decomposed in the lubricating composition during use.

28. A lubricating composition comprising a major proportion of mineral oil and a halogen bearing organic sulphur compound in an amount in which such sulphur compound would not substantially increase the extreme pressure characteristics of a plain mineral oil and minor amounts of both a halogen bearing aliphatic compound and a halogenated organic oxygen compound, all of said compounds having a vapor pressure less than atmospheric at a temperature of 140° C., said compounds being oil soluble within the percentages present in the oil, of sufficiently low volatility and of such stability so as not to be substantially evaporated from or decomposed in the lubricating composition during use.

CARL F. PRUTTON.
ALBERT K. SMITH.
HARRY E. JOHNSON.