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LUBRICATING COMPOSITION

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2 Claims. (Cl. 252—54)

In U. S. Patents Nos. 1,986,645 and 1,986,651 it is taught that the lubricating properties of a lubricating composition may be materially improved and extreme pressure characteristics imparted to lubricants such as mineral lubricating oil, by the addition thereto of minor amounts of halogenated carbon ring compounds. This application is a continuation-in-part of copending application Ser. No. 649,734 now Patent No. 2,213,532, and also of copending application Ser. No. 241,606 now Patent No. 2,255,085, which is in turn a continuation-in-part of copending applications Ser. No. 31,720 now Patent No. 2,137,782, and Ser. No. 170,500, now Patent No. 2,204,620.

It has been explained that the reason why such compounds thus improve the extreme pressure characteristics of the lubricant probably is due to the fact that such addition agents chemically react with the bearing surfaces under the conditions imposed by relative movement and extreme pressure between the bearing surfaces to form a microscopic film of a metallic halide which prevents seizing between the bearing surfaces by acting as an anti-fluxing agent.

The halogenated carbon ring compounds were indicated as preferable in said patents due to the fact that such compounds are relatively stable, i. e., they do not readily hydrolyze in the presence of moisture which usually occurs in varying quantities in mineral oils. In other words, the halogenated carbon ring compounds are sufficiently stable so that decomposition and attack thereof upon the metallic surfaces occurs only in the areas where extreme pressure is encountered, i. e., on the bearing surfaces.

One theory of the action of halogen compounds, specifically chlorine compounds, in increasing film strength, assumes that, as above indicated, under the stress of the rubbing action of bearing surfaces in motion under load, chlorides of the bearing metals are formed on their surfaces and exert an anti-fluxing effect in preventing subsequent fusing of the two surfaces. This surface reaction, however, to take place with sufficient effectiveness depends upon the hydrolyses of the chlorine compound as a simultaneous intermediate reaction. These reactions may be expressed as follows:

(1) $RCl+H_2O=HCl-ROH$

(2) $M+HCl=MCl+H$

where R is an organic radical and M is one of the metals of the bearing surfaces.

(Note: The hydrogen evolved by (2) probably would act to reduce one or more of the organic compounds rather than to appear as free hydrogen.)

The correctness of the foregoing theory is substantiated by the fact that when a chlorinated hydrocarbon is added to a hydrocarbon mineral oil and the mixture thoroughly freed from moisture by the action of dehydrating agents, the film strength is no more than that of the oil alone. Exposure of the mixture to the atmosphere so that it may absorb a slight amount of moisture will then cause an increase in the film strength.

Since the presence of a large amount of moisture and especially of free water is objectionable in a lubricant besides being a highly variable factor in normal service, it is advisable to supply an oil soluble substitute for the same.

It is the principal object of this invention, therefore, to provide a lubricating composition as the type utilizing halogenated organic compounds as the extreme pressure addition agent but so modified as to be effective in the manner defined without being dependent upon the presence in the lubricating composition of some addition material such as water.

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 sets 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, this invention comprises the use as a lubricant either used alone or incorporated with any suitable oil base of halogen bearing esters containing an aromatic nucleus, specifically esters of aromatic acids or esters prepared by esterifying an organic acid with an aromatic alcohol.

The esters used in the lubricating compositions of the present invention may therefore be identified as of the type having the following structure:

$$R-\overset{O}{\overset{\|}{C}}-Q-(CH_2)_x-R'$$

where Q is either oxygen or sulphur, x is at least 1, and R and R' are of the class consisting of hydrogen and organic radicles, at least one of which is aromatic. As hereinafter more specifically pointed out, the esters of aromatic acids are the ones which will generally be found most useful.

Of the esters which may thus be employed as addition agents, those which are of the type in which the

$$\left(R-\overset{O}{\overset{\|}{C}}-O-\right)$$

radicle is attached to a carbon atom, which is a part of an open chain structure, are preferred. This type of aromatic ester is more resistant to the hydrolyzing action of moisture which would tend to cause the decomposition of other types of aromatic esters, for instance esters of phenolic compounds.

By the term "aromatic" wherever used herein, we intend to include compounds containing a benzenoid structure including benzenoid structures other than the benzene ring, for example, the pyridine, quinoline, thiophene, pyrrole and furan structures.

Thus the present invention is concerned with the use of a particular class of halogen bearing organic ring compounds which also contain oxygen. The above defined esters as a class of halogen and oxygen bearing organic ring compounds are particularly desirable for use as addition agents since they generally result in the production of an improved lubricant in which the characteristics suiting the same for use as a lubricant over a wide field of application are generally improved.

The oxygen which is included in the molecule of the addition agent acts to increase the effectiveness of the latter in raising the film strength of a mineral oil to which the addition agent is added or to improve the lubricating properties of the halogenated compound when used without the addition of some other lubricant. The oxygen probably acts in the same way as water in making possible the formation of hydrochloric acid as an intermediate step in the surface reaction above explained.

By combining in a single molecule the halogen and the oxygen atoms, a lubricant is affected in two ways:

First: The oxygen is always available at the exact point where required; and

Second: The molecule is more strongly adsorbed by metal surfaces than similar halogen compounds which do not contain oxygen.

The latter circumstance enhances the effect of small amounts of such compounds because it is equivalent to an increase in concentration of the compound at the bearing surfaces.

The halogen and oxygen-bearing organic ring compounds of the aromatic ester type include compounds of the aromatic type which may be classified as follows:

1. Esters of aromatic acids;
2. Esters formed by the combination of an aromatic alcohol (either mono-hydric or poly-hydric) with an organic acid which may be of the aliphatic, cycloaliphatic or aromatic type.

In the following table are given examples of aromatic acids from which esters may be prepared as representative of the class of compounds included in 1 above.

Benzoic acid
Benzoic acid derivatives:
- Azobenzoic acid
- Thiobenzoic acids
- Mercapto benzoic acid
- Lauryl benzoic acid

Salicylic acid
Salicylic acid derivatives:
- Thiosalicylic acids
- Ethyl salicylic acid

Heterocyclic acids:
- Pyrrole carboxylic acids
- Thiophene carboxylic acids

Acetic acid derivatives:
- Phenyl acetic acid
- Diphenyl acetic acid

Stearic acid derivatives:
- Phenyl stearic acid
- Phenyl mercapto stearic acid
- Xenyl stearic acid
- Naphthyl stearic acid
- Tolyl stearic acid

Furoic acid
Cinnamic acid
Phthalic acid
Toluic acid

The alcohols combined with the foregoing aromatic acids may either be aromatic, aliphatic, or cycloaliphatic. Examples of such alcohols are the following:

Methyl alcohol
Ethyl alcohol
Propyl alcohols
Butyl alcohols
Amyl alcohols
Lauryl alcohols
Cetyl alcohols
Benzyl alcohol
Furfuryl alcohol
Tetrahydrofurfuryl alcohol
Ethylene glycol
Propylene glycol
Di-ethylene glycol
Glycerol
Erythritol
Unsaturated alcohols, e. g.
- Vinyl ethyl alcohol
- Allyl alcohol
- Crotonyl alcohol
- Oleyl alcohol
- Propargyl alcohol

Cyclohexanol
Methylcyclohexanol
Amylcyclohexanol
Phenyl cyclohexanol
Cyclohexyl cyclohexanol

The aromatic alcohols used in the preparation of the esters of class 2 above may be any of the following:

Benzyl alcohol
Phenyl ethyl alcohol
Benzhydrol
Tri phenyl carbinol
Phenyl propyl alcohol
Phenyl benzyl alcohol
Furfuryl alcohol
Naphthobenzyl alcohol
Cinnamyl alcohol

The organic acids of the aliphatic, cycloaliphatic or aromatic type used in the preparation of esters included in class 2 above may be any of the following:

Aliphatic acids, including:
Saturated acids, such as:
- Acetic acid
- Propionic acids
- Butyric acids
- Lauric acids
- Palmitic acid
- Stearic acid
- Oxalic acid
- Citric acid
- Lactic acid
- Glycolic acid
- Malonic acid

Unsaturated acids, such as:
- Vinyl acetic acid
- Vinyl acrylic acid
- Vinyl glycolic acid
- Acrylic acid
- Crotonic acid
- Oleic acid
- Linolenic acid
- Maleic acid
- Fumaric acid
- Linoleic acid
- Elaeostearic acid
- Propiolic acid
- Stearolic acid

Cyclo-aliphatic acids, including:
- Naphthenic acids
- Hexahydrobenzoic acid

Heterocyclic acids including:
- Furoic acid
- Pyrrol carboxylic acids

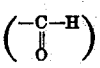
Aromatic acids, including
- Those given above in the list of aromatic acids for use in the preparation of the esters of class 1.

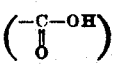
In cases where it is desired that the lubricant have a maximum stability, saturated compounds will usually be preferred in comparison with unsaturated compounds. Where stability, including the resistance to oxidation and polymerization, is not of primary importance, certain of the unsaturated compounds may be preferred for special applications, for example to improve solubility, solventicity and the like.

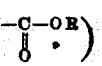
For certain uses, the esters may be used as addition agents in lubricating compositions of the present invention. Such compounds may desirably contain an oxygen bearing substituent, i. e. having oxygen present in a substituent in addition to the oxygen present in the ester group. The following is a list of such oxygen bearing substituents which may thus be desirably included in the compounds which comprise the addition agents of the present invention.

(1) Alcohol or phenol (—OH)

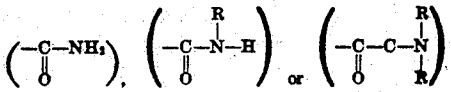
(2) Ketone 

(3) Aldehyde 

(4) Acid 

(5) Ester 

(6) Salt 

(7) Amide and substituted amide 

(8) Ether (—O—R)

(9) Inorganic radicles in which the oxygen is directly attached to a carbon atom: arsenite, hypochlorite, phosphite, thiophosphate, thiophosphite, borate and β hydroxylamines.

(10) Inorganic radicles in which the oxygen is indirectly attached through the means of some other atom, e. g.: arsenate, chlorate, chlorite, cyanate, α hydroxylamine, nitrate, nitrite, nitro, nitroso, oxime, perchlorate, phosphate, sulphate, sulphite, sulphinic acid, sulphone, sulphonic acid, sulphoxide, thiophosphates, thiophosphites and thiosulphate.

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, and thiocyanate.

Specific examples of compounds of the various classes described above are halogen derivatives of the compounds listed below. These derivatives may be substitution products, addition products, or both. They may be formed by halogenation of the compound listed, or of intermediate compounds, or by some other method.

- Amyl salicylate
- Benzyl acetate
- Benzyl benzoate
- Benzyl mercapto stearate
- Benzyl naphthenate
- Benzyl phenyl-stearate
- Benzyl stearate
- Butyl azobenzoate
- Butyl esters of:
  - Pyrrole carboxylic acid
  - Thiophene carboxylic acid
- Butyl benzoate
- Butyl thio-benzoate
- Butyl ester of phenyl acetic acid
- Butyl ester of phenyl stearic acid
- Butyl mercapto benzoate
- Butyl toluate
- Esters of cinnamic acid, e. g.:
  - Methyl and lauryl esters
- Dibutyl phthalate
- Esters of diphenyl acetic acid, e. g.:
  - Methyl and lauryl esters
- Ethyl ester of phenyl acetic acid
- Esters of ethyl salicylic acid, e. g.:
  - Methyl and lauryl esters
- Ethyl toluate
- Methyl salicylate
- Methyl phenyl-stearate
- Methyl toluate
- Esters of phenyl mercapto stearic acid, e. g.:
  - Methyl and lauryl esters
- Esters of phenyl propionic acid, e. g.
  - Methyl and lauryl esters

As a class of esters which will be found particularly useful are the halogen bearing esters derived from an acid formed by condensing an unsaturated acid such as those listed above with an aromatic compound such as:

- Benzene
- Chlorbenzene
- Alkylated benzene, e. g.
  - Toluene
  - Xylene
  - Ethyl benzenes
- Naphthalene
- Alkylated naphthalenes
- Diphenyl
- Alkylated diphenyls

in the presence of a catalyst such as anhydrous aluminum chloride. This invention also contemplates the use of such halogen bearing aromatic esters as may be derived from compounds formed by similarly condensing unsaturated esters with an aromatic compound such as those listed above.

Examples of other aromatic esters of the type contemplated for use hereby are those which may be derived from compounds formed by condensing an aromatic ester with an unsaturated aliphatic compound. For example the product derived from the condensation of methyl salicylate with an unsaturated aliphatic compound such as oleic acid. The chlorine bearing esters of this type are quite satisfactory for use.

As previously indicated, the foregoing so-called addition agents may, for most uses, be added in minor amounts to other lubricants such as mineral oil, fish oil, lard oil, castor oil, rape-seed oil, etc., and in some cases, depending upon the character of use, as well as the character of the selected agents, the latter may be effectively used in their pure state.

The optimum amount of the halogen compound to be employed is usually dependent upon various considerations such as its cost, the character of the selected compounds, the character of the addition agent to which the same is added and more particularly, the character of the use to which the same is put. For most uses, since the cost of such halogen compounds is usually considerably greater than lubricants such as mineral oil, optimum results are obtained by using minimum quantities of these halogenated addition agents. For the purpose of lubricating and reducing the friction between relatively moving parts of an internal combustion engine such as crank case bearings, piston and cylinder surfaces, as well as piston rings and valves, a composition according to our invention comprises a major proportion of a suitable oil base such as mineral oil and concentrations of from one-fourth of 1% to 2% of halogen compounds of the above defined type. If the valve structure of the engine is to be lubricated separately from the remainder of the mechanism by means acting in an auxiliary fashion such as by the addition of the lubricating composition to the engine fuel, the composition for such purposes will preferably contain a larger amount of such halogen compounds, i. e. from about 2% to about 10%.

When lubricating bearing surfaces such as gears and the like where extreme temperatures are usually not encountered a composition comprising a major proportion of a suitable oil base and a total of less than about 20% of at least one halogen and oxygen-containing organic compound of the enumerated class will be found very satisfactory.

When combined with a lubricating oil such as mineral oil, the optimum amount of the halogen compound to be employed will depend largely upon the halogen content of the particular compound, its physical characteristics and especially its effect on the viscosity of the oil to which it is added. When addition agents of the above enumerated class having very low viscosity are employed, and added to lubricants such as mineral oil, the limit of the amount of such compounds which may be added and which will produce improved results depends in a large measure upon the reduction in viscosity of the composition caused by the addition of such compounds. When, however, the more viscous compounds are employed, or where the particular use does not require thick film lubrication, the so-called addition agents may, as previously indicated, be employed in concentrations up to 100%.

With regard to the stability of the organic ring compounds contemplated, the most resistant to hydrolysis of the halogen are those in which the halogen is directly attached to an atom which is part of a benzenoid ring structure. Examples of such ring structures are aryl groups such as the phenyl and naphthyl groups. In any case, for most uses, it is preferred to have the halogen attached to an atom which is part of an organic ring structure and especially a six-membered organic ring structure.

The compositions comprising our invention have certain advantages when used as a lubricant of which the following may be mentioned:

First: By the use of this composition, it is possible to extend the pressure range between the bearing surfaces because of the reduced tendency for bearing surfaces so lubricated to become scored or to seize at higher pressures than are allowable with ordinary lubricants.

Second: The friction between the bearing surfaces is reduced, especially in the higher pressure range, below that obtained with ordinary lubricants.

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 lubricating oil with the properties of such composition affecting its use as a lubricant improved by incorporating therein a minor amount, based on the amount of lubricating oil, of a stable oil-soluble halogen bearing ester of phthalic acid.

2. A lubricating composition comprising a major proportion of mineral lubricating oil and a minor proportion of chlorinated dibutyl phthalate.

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