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LUBRICATING COMPOSITION

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

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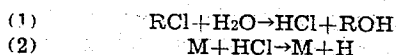
In U. S. Patents Nos. 1,986,645 and 1,986,651 it is taught that the lubricating properties of a lubricating composition may be materially improved and extreme pressure characteristics imparted to lubricants such as mineral lubricating oil, by the addition thereto of minor amounts of halogenated carbon ring compounds.

This application is a continuation in part of our co-pending application Serial No. 241,606, filed November 21, 1938, now issued as Patent No. 2,255,085.

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 hydrolysis of the chlorine compound as a simultaneous intermediate reaction. These reactions may be expressed as follows:



where R is an organic radicle 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 of oxygen and halogen bearing organic compounds and more specifically, oxygen and halogen bearing organic ring compounds, either used alone or incorporated with any suitable oil base.

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 absorbed 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.

We have found that certain oxygen-containing organic ring compounds which have been chlorinated and added to a lubricating oil are capable of improving the properties of such oil, particularly when employed for "thin-film" lubricating purposes. The addition of these certain oxygen containing organic ring compounds which have been chlorinated and added to the lubricating oil have been found to improve the properties thereof to an even greater extent than certain similar chlorinated hydro-carbons, notably when added in very small amounts.

The halogen and oxygen-containing organic ring compounds added to a suitable oil base are, as above indicated, preferably of the chlorinated species and particularly the compounds which have been found to produce very satisfactory results, may be classified as follows; viz:

I. "Carbon ring" type compounds

- (a) Of the aromatic, or allied type, including oxygen and halogen bearing derivatives of benzene, diphenyl, naphthalene, anthracene, etc., and homologs of them, also such derivatives of compounds of the bridged ring type, such as the terpenes, and related compounds.
- (b) Of the class including such derivatives of the cyclo-aliphatic compounds such as cycloparaffins, cyclo-olefines, cyclo-acetylenes. Examples of this class are oxygen and halogen-bearing derivatives of hydrogenated aromatic compounds, such as the following:

- (1) Hydrogenation products of benzene (e. g. cyclohexane, cyclohexene, cyclohexadiene).
- (2) Hydrogenation products of naphthalene (e. g. decahydronaphthalene, tetrahydronaphthalene etc.)
- (3) Naphthenes, naphthenic acid, etc.

- (c) Of mixed type such as oxygen and halogen-bearing derivatives of indene, hydrindene, hydranthracene, etc.

II. "Heterogeneous ring" type compounds

- (a) Of the aromatic or allied type including oxygen and halogen-bearing derivatives of pyridine, quinoline, etc.
- (b) Other types such as oxygen and halogen-bearing derivatives of furan and its derivatives and of thiophene, pyrrole etc.

Included in Class II are two principal types of compounds, viz: Compounds in which all of the ring structures are of the heterogeneous type and compounds containing both heterogeneous ring structures and carbon ring structures.

The foregoing compounds may also be classified according to the nature of the attachment of the oxygen to the compound, viz:

10 I'. Directly attached to one or more carbon atoms, as in the case of:

- (1') Ethers and analogous compounds
- (2') Compounds containing the $\equiv\text{C}-\text{OH}$ radicle, such as alcohols and other derivatives of carbinol (including phenols, cresols, naphthols etc.)
- (3') Compounds containing the carbonyl ($=\text{C}=\text{O}$) 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 the ring structure, e. g. furan and its derivatives, anthraquinone, etc.

25 II'. Indirectly attached through the means of some other atom, i. e., in the form of an inorganic radicle, e. g.:

Amide
Arsenate
Arsenite
Chlorate
Chlorite
Cyanate
Hydroxylamine
Hypochlorite
Nitrate
Nitrite
Nitro
Nitroso
Perchlorate
Phosphate
Phosphite
Sulphate
Sulphite
Sulphinic acid
Sulphone
Sulphonic acid
Sulphoxide
Thiocyanate
Isothiocyanate
Thio-sulphate
Thio-phosphate
Isocyanate.

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

1. Esters and salts of an aromatic acid;
2. Esters formed by the combination of a phenol, cresol, naphthol, etc. with an organic acid of either the fatty or aromatic type;
3. An ester formed by the combination of an aromatic alcohol (either mono-hydric or poly-hydric) with an organic acid of either the fatty or aromatic type.

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

75 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 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.

	Class
Acetanilide.....	I (a)-I' (3')
Acetophenone.....	I (a)-I' (3')
Aluminum phenyl mercaptostearate.....	I (a)-I' (3')
Aluminum phenyl stearate.....	I (a)-I' (3')
Amyl salicylate.....	I (a)-I' (2') and (3')
Amino phenol.....	I (a)-I' (2')
Anethole.....	I (a)-I' (3')
Aniline oleate.....	I (a)-I' (2')
Aniline stearate.....	I (a)-I' (2')
Anthraquinone.....	I (a)-I' (2')
Anthranol.....	I (a)-I' (2')
Azobenzonic acid.....	I (a)-I' (3')
Azophenol.....	I (a)-I' (2')
Benzaldehyde.....	I (a)-I' (3')
Benzaldoxime.....	I (a)-II'
Benzamide.....	I (a)-II'
Benzene sulphonie acid.....	I (a)-II'
Benzene sulphoxide.....	I (a)-II'
Benzil.....	I (a)-I' (2')
Benzoic acid.....	I (a)-I' (3')
Benzoin.....	I (a)-I' (2') and (3')
Benzophenone.....	I (a)-I' (3')
Benzylic acetate.....	I (a)-I' (3')
Benzylic alcohol.....	I (a)-I' (2')
Benzylic cyanate.....	I (a)-II'
Benzylic mercapto stearate.....	I (a)-I' (3')
Benzylic naphthenate.....	I (b) (3)-I' (3')
Benzylic nitrate.....	I (a)-II'
Benzylic nitrite.....	I (a)-II'
Benzylic stearate.....	I (a)-I' (3')
Benzylic sulphate.....	I (a)-II'
Benzylic sulphite.....	I (a)-II'
Benzylic sulphone.....	I (a)-II'
Benzylic thio-sulphate.....	I (a)-II'
Borneol.....	I (a)-I' (2')
Bornyl acetate.....	I (a)-I' (2')
Butyl azobenzoate.....	I (a)-I' (3')
Butyl esters of:	
Pyrrole carboxylic acid.....	II (b)-I' (3')
Thiophene carboxylic acid.....	II (b)-I' (3')
Butyl benzoate.....	I (a)-I' (3')
Butyl thio-benzoate.....	I (a)-I' (3')
Butyl ester of mercapto rosolic acid.....	I (a)-I' (3')
Butyl ester of phenyl acetic acid.....	I (a)-I' (3')
Butyl ester of phenyl stearic acid.....	I (a)-I' (3')
Butyl furoate.....	II (b)-I' (3') and (4')
Butyl mercapto benzoate.....	I (a)-I' (3')
Butyl naphthenate.....	I (a)-I' (3')
Butyl phenyl ketone.....	I (a)-I' (3')
Butyl toluate.....	I (a)-I' (3')
Calcium naphthenate.....	I (b)-I' (3')
Calcium phenyl mercapto stearate.....	I (a)-I' (3')
Calcium phenyl stearate.....	I (a)-I' (3')
Camphor.....	I (a)-I' (2')
Cinnamic acid and esters.....	I (a)-I' (3')
Cresyl acetate.....	I (a)-I' (3')
Cresyl naphthenate.....	I (b) (3)-I' (3')
Cresyl stearate.....	I (a)-I' (3')
Cyclohexanol.....	I (b) (1)-I' (2')
Cyclohexanone.....	I (b) (1)-I' (3')
Decahydronaphthol.....	I (b) (2)-I' (2')
Dibenzoyldimethyl disulphide.....	I (a)-I' (3')
Dibenzoyldimethyl sulphide.....	I (a)-I' (3')
Dibenzoyl disulphide.....	I (a)-I' (3')
Dibenzoyl sulphide.....	I (a)-I' (3')
Dibenzoyldisulphide.....	I (a)-I' (3')
Dibenzyl ether.....	I (a)-I' (1')
Dibutyl phthalate.....	I (a)-I' (3')
di-Disulphide of tertiary amyl phenol.....	I (a)-I' (2')
Dihydroxy dibenzyl disulphide.....	I (a)-I' (2')
Dihydroxy diphenyl disulphide.....	I (a)-I' (2')
Dihydroxy diphenyl sulphide.....	I (a)-I' (2')
Dinaphthyl ether.....	I (a)-I' (1')
Dinaphthyl ketone.....	I (a)-I' (3')
Diphenyl acetic acid and esters.....	I (a)-I' (3')
Diphenyl ether.....	I (a)-I' (1')
Dixenyl ether.....	I (a)-I' (1')
Ethyl ester of phenyl acetic acid.....	I (a)-I' (3')
Ethyl naphthyl ether.....	I (a)-I' (1')
Ethyl salicylic acid and esters.....	I (a)-I' (2') and (3')
Ethyl toluate.....	I (a)-I' (3')
Furan.....	II (b)-I' (4')
Furfural.....	II (b)-I' (3') and (4')
Furil.....	II (b)-I' (3') and (4')
Furoin.....	II (b)-I' (2') (3') and (4')
Hexahydrophenyl acetate.....	I (b) (1)-I' (3')
Hexahydrophenyl mercapto stearate.....	I (b) (1)-I' (3')
Hexahydrophenyl stearate.....	I (b) (1)-I' (3')
Hydroxyazobenzene.....	I (a)-I' (2')
Hydroxy-benzyl mercaptan.....	I (a)-I' (2')
Hydroxy-diphenylamine.....	I (a)-I' (2)
Hydroxy-indene.....	I (c)-I' (2)
Hydroxy-methyl-aniline.....	I (a)-I' (2)
Hydroxy-phenyl-hydrazine.....	I (a)-I' (2')
Hydroxyphenyl mercaptan.....	I (a)-I' (2')
Hydroxy-quinoline.....	II (c)-I' (2')
Hydroxythiophene.....	II (b)-I' (2')
Iminophenol.....	I (a)-I' (2)
Indoxyl.....	I (c) (2)-I' (2)
Ketopentamethylene.....	I (b)-I' (3')
Mercapto benzoic acid.....	I (a)-I' (3')
Mercapto rosolic acid.....	I (a)-I' (3')
Methyl salicylate.....	I (a)-I' (2') and (3')
Methyl toluate.....	I (a)-I' (3')
Naphthol.....	I (a)-I' (2')
Naphthol ethyl ether.....	I (a)-I'
Nitrodiphenyl.....	I (a)-I'
Nitrosobenzene.....	I (a)-II'
Nitrosophenol.....	I (a)-II'
Nitrotoluene.....	I (a)-II'
Phenol.....	I (a)-I' (2')
Phenyl acetate.....	I (a)-I' (3')
Phenyl acetic acid.....	I (a)-I' (3')
Phenyl amyl nitrate.....	I (a)-II'
Phenyl amyl nitrite.....	I (a)-II'
Phenyl amyl ether.....	I (a)-I' (1')
Phenyl benzoate.....	I (a)-I' (3')
Phenyl ethyl alcohol.....	I (a)-I' (2')
Phenyl ethyl chlorate.....	I (a)-II'
Phenyl ethyl chlorite.....	I (a)-II'
Phenyl ethyl cyanate.....	I (a)-II'
Phenyl ethyl ether.....	I (a)-I' (1')
Phenyl ethyl hypochlorite.....	I (a)-II'
Phenyl ethyl perchlorate.....	I (a)-II'
Phenyl ethyl sulphate.....	I (a)-II'
Phenyl ethyl sulphite.....	I (a)-II'
Phenyl ethyl sulphone.....	I (a)-II'
Phenyl ethyl thiosulphate.....	I (a)-II'
Phenyl hydroxylamine.....	I (a)-II'
Phenyl mercapto stearate.....	I (a)-I' (3')
Phenyl mercapto stearic acid and esters.....	I (a)-I' (3')
Phenyl naphthenate.....	I (b) (3)-I' (3')
Phenyl naphthyl ketone.....	I (a)-I' (3')
Phenyl nitrite.....	I (a)-II'
Phenyl oleate.....	I (a)-I' (3')
Phenyl oxydisulphide.....	I (a)-I' (3')
Phenyl phenol.....	I (a)-I' (2)
Phenyl phenyl-acetate.....	I (a)-I' (3')
Phenyl phenyl-naphthenate.....	I (b) (3)-I' (3')
Phenyl phenyl-stearate.....	I (a)-I' (3')
Phenyl propionic acid and esters.....	I (a)-I' (3')
Phenyl propyl alcohol.....	I (a)-I' (2')
Phenyl stearate.....	I (a)-I' (3')
Phenyl stearic acid.....	I (a)-I' (3')
Pyridine stearate.....	II (a)-I' (3')
Pyrrol stearate.....	II (b)-I' (3')
Sodium phenylmercaptostearate.....	I (a)-I' (3')
Sodium phenylstearate.....	I (a)-I' (3')
Sodium thiobenzoate.....	I (a)-I' (3')
Stearanilid.....	I (a)-I' (3')
Tertiary amyl phenol.....	I (a)-I' (2')
Thiobenzoic acid.....	I (a)-I' (3')
Toluic acid.....	I (a)-I' (3')
Tricresyl phosphate.....	I (a)-II'
Triphenyl arsenate.....	I (a)-II'
Triphenyl arsenite.....	I (a)-II'
Triphenyl phosphate.....	I (a)-II'
Triphenyl phosphite.....	I (a)-II'
Tri-tertiary amyl phenyl phosphate.....	I (a)-II'
Zinc benzoate.....	I (a)-I' (3')
Zinc phenylstearate.....	I (a)-I' (3')

In the following table are given examples of aromatic acids, halogen-bearing derivatives of which may be employed as addition agents in accordance with our invention:

Benzoic acid
Benzoic acid derivatives
Azobenzonic acid
Mercapto benzoic acid
Lauryl benzoic acid
Salicylic acid
Salicylic acid derivatives
Ethyl salicylic acid
Carboxylic acid
Carboxylic acid derivatives
Pyrrole carboxylic acid
Thiophene carboxylic acid
Acetic acid
Acetic acid derivatives
Phenyl acetic acid
Diphenyl acetic acid

Stearic 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
 Mercapto rosolic acid

Among the esters and salts, halogen derivatives of which are likewise suitable for use as addition agents, are the esters and salts which may be derived from the aromatic acids listed immediately above and mono and polyhydric alcohols, or other hydroxy compounds (including phenols). Specific examples of such alcohols and hydroxy compounds are those specifically identified under (6) in next column.

Among the salts of aromatic acids, the halogen-bearing derivatives of which may also be employed as addition agents, are the salts of the aromatic acids listed above, including the sodium, calcium aluminum, magnesium, zinc and lead salts, and salts derived from ammonia, substituted ammonias, and other organic bases such as quinoline and pyridine.

A very important group of esters, halogen-bearing derivatives of which are particularly suited for use as addition agents, especially in certain types of lubricants, are the esters of alcohols of the benzenoid type. Specific examples of such alcohols are the following:

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

This class of esters may be derived from alcohols of the benzenoid type, such as those listed above and organic acids, either aliphatic or aromatic or from such alcohols and inorganic acids. Examples of such organic and inorganic acids are those listed under (6) (b) in next column.

The class of unsaturated oxygen compounds is particularly suited, after halogenation or halogen treatment, for use as addition agents in accordance with our invention. The following is a classification of these unsaturated oxygen compounds along with specific examples of the various groups within this sub-class:

(1) Unsaturated alcohols, e. g.

Vinyl ethyl alcohol
 Allyl alcohol
 Crotonyl alcohol
 Oleyl alcohol
 Propargyl alcohol

(2) Unsaturated aldehydes, e. g.

Acrolein
 Crotonaldehyde
 Hexadienal
 Octatrienal
 Citral
 Propargylic aldehyde

(3) Unsaturated ketones, e. g.

Allyl acetone
 Di-allyl ketone
 Mesityl oxide
 Phorone
 Vinyl lauryl ketone
 Acetylenic ketones
 (e. g. $R-C\equiv C-CO-R'$)

such as

Allylene methyl ketone
 Allylene lauryl ketone

(3a) Ketenes

Ketene
 Acetyl ketene

(4) Unsaturated ethers, e. g.

Di-vinyl ether
 Di-allyl ether
 Allyl ethyl ether
 Vinyl ethyl ether
 Allyl iso-amyl ether
 Allyl lauryl ether
 Propargyl ethyl ether

(5) Unsaturated acids, e. g.

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

(6) Unsaturated esters, e. g.

(a) Esters of unsaturated acids (e. g. those listed under (5) above as well as unsaturated aromatic acids such as cinnamic and coumaric) with mono- and polyhydric alcohols, or other hydroxy compounds (including phenols). Examples of such alcohols and hydroxy compounds are:

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
 Phenol
 Polyhydroxy-benzenes
 Alkylated phenols
 Naphthols
 Unsaturated alcohols
 (e. g. those listed under (1) above)

(b) Esters of unsaturated alcohols (e. g. those listed under (1) above) with organic acids, either aliphatic or aromatic, or with inorganic acids. Examples of such acids are:

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 those listed under (5) above

Aromatic acids, including:

Benzoic acid
 Phthalic acids
 Salicylic acid
 Anthranilic acid
 Cinnamic acid

Cyclo-aliphatic acids, including:

Naphthenic acids
 Hexahydrobenzoic acid

Heterocyclic acids including:

Furoic acid
 Pyrrol carboxylic acids

Inorganic acids, including:

Hydro-halogen acids
 Oxy-halogen acids
 Sulphurous acid
 Sulphuric acid
 Thiosulphuric acid
 Carbonic acid
 Thiocarbonic acids
 Hydrogen sulphide
 Phosphorous acid
 Thiophosphorous acids
 Phosphoric acid
 Thiophosphoric acids
 Cyanic acid
 Thiocyanic acid
 Hydrocyanic acid
 Boric acid

- (7) Salts of unsaturated acids, including the Ammonium and substituted ammonium
 Sodium
 Calcium
 Aluminum
 Magnesium
 Zinc
 Lead

Salts of unsaturated acids generally, and more specifically of such acids as those listed under (5) above and of unsaturated aromatic acids.

In addition to the compounds listed above, commercial products comprising complex mixtures of unsaturated oxygen-bearing organic compounds may be used as the "unsaturated" reactant. Examples of such materials are the fatty oils of unsaturated character, e. g.

Castor oil
 Chinawood oil
 Corn oil
 Cottonseed oil
 Croton oil
 Lard oil
 Linseed oil
 Menhaden fish oil
 Rape seed oil
 Soya bean oil
 Sperm oil

Useful additional unsaturated oxygen compounds which may be derived from any of the above fatty oils are, e. g.

- (1) Acids, extracted from the oils by direct hydrolysis, or by saponification and subsequent hydrolysis, or otherwise.
- (2) Esters, produced by esterifying the acids of (1) e. g. to form esters analogous to any of those listed under (6) in Table No. 2.
- (3) Soaps, produced by saponifying the oils directly or by neutralizing the acids of (1) with alkalies, e. g. to form salts analogous to those listed under (7) in Table No. 2.

The unsaturated oxygen compounds are of particular importance and may, therefore, be classified in further detail according to the nature of the attachment of the oxygen atom to the molecule, viz:

Table No. 3

I'. Directly attached to one or more carbon atoms, as in the case of:

- (1') Ethers and analogous compounds
- (2') Compounds containing the —C—OH radicle, such as alcohols and other derivatives of carbinol (including phenols, cresols, naphthols etc.)
- (3') Compounds containing the carbonyl C=O radicle, such as amides, aldehydes, ketones, organic acids, esters and salts of organic acids (including such salts of both inorganic and organic bases), thioacids and esters and salts of thioacids
- (4') Compounds in which oxygen forms a part of the ring structure, e. g. furan and its derivatives, etc.
- (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).

In addition to the unsaturated compounds above described, certain unsaturated cyclic compounds are also of use, such as the cyclo-olefines (e. g. cyclo-hexene) and derivatives of them.

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

This invention also contemplates the use of halogen-bearing acids (and salts and esters derived from them) which may be derived from compounds formed by condensing unsaturated acids (such as those included among the unsaturated oxygen-bearing compounds referred to above) with an aromatic compound in the presence of a catalyst such as anhydrous aluminum chloride. It also contemplates the use of such halogen-bearing salts and esters as may be derived from compounds formed by similarly condensing unsaturated salts and esters (such as those included among the unsaturated oxygen-bearing compounds referred to above) with an aromatic compound.

Examples of other halogen-bearing aromatic acids, esters and salts of the type contemplated hereby (for example those which may be derived from compounds formed by condensing an aromatic acid, ester, or salt, with an unsaturated aliphatic compound) will be found in the copending application of Carl F. Prutton, Ser. No. 216,153, filed June 27, 1938.

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 to 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 their pure state.

Experiments have shown that when compounds which readily hydrolyze, such as chlorinated open chain compounds, are added to the only base, hydrolysis will take place to such an extent that the metal parts of any machine being lubricated will be seriously attacked and corroded by the acid generated. On the other hand, the addition of chlorinated organic ring compounds of the above enumerated class does not cause corrosion.

Certain of the halogen and oxygen-bearing open chain or aliphatic compounds, in their pure state, or when added to a suitable base do result, however, in a lubricant particularly suitable for certain purposes. Examples of the foregoing are halogenated fatty oils such as chlorinated cotton-seed oil and chlorinated coconut oil. As above indicated, such compounds readily hydrolyze and while thus not preferred as a lubricant for use in the crank case of internal combustion engines, are nevertheless, admirably suited for use as lubricants in metal working such as drawing, extruding, rolling, etc., where the lubricant is in contact with the metallic surface for only relatively a short length of time and where the very slight amount of corrosion which may result is not particularly objectionable. Furthermore, such compounds are admirably suited for use in lubricants in die drawing or similarly working certain corrosion resistant materials such as stainless steel and the like.

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 pres-

sure range, below that obtained with ordinary lubricants.

In the foregoing description of our invention we have listed a large number of classes and specific examples of addition agents, the halogen-bearing derivatives of which are contemplated for use as addition agents in the preparation of lubricating compositions in accordance with our invention. Many of these materials themselves, i. e., the unhalogenated materials named, as well as the halogen-free analogs of the halogenated or halogen-bearing materials named, may be employed to advantage in lubricating compositions since many of such possess valuable properties as addition agents.

These unhalogenated materials may be used as the sole addition agent to impart improved lubricating properties to a mineral oil (or other lubricating medium) or may advantageously be used in conjunction with other addition agents, such as organic halogen compounds, organic phosphorus compounds (e. g. esters of phosphoric and phosphorous acids), organic sulphur compounds, soaps, oiliness agents, oxidation inhibitors, viscosity index improvers, or such other addition agents as may be employed for the same or other purposes.

Other modes of applying the principle of our 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.

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

1. A lubricating composition comprising in combination, a major proportion of a suitable oil base and a minor proportion of a halogen and oxygen bearing aromatic compound containing the carbonyl radical.

2. A lubricating composition comprising in combination, a major proportion of a suitable oil base and a minor proportion of a halogen bearing aromatic aldehyde.

3. A lubricating composition comprising a major proportion of a suitable oil base and a minor proportion of an oxygen and halogen bearing organic ring compound containing the carbonyl



radical.

4. A lubricating composition comprising in combination a major proportion of a suitable oil base and a minor proportion of a halogen bearing organic compound including a



group directly attached to a ring structure.

5. A lubricating composition comprising in combination a major proportion of a suitable oil base and a minor proportion of a halogen bearing organic compound including a



group directly attached to a benzenoid ring structure.

6. A lubricating composition comprising in combination a major proportion of a suitable oil base and a minor proportion of a halogen bearing organic compound including a



group directly attached to an aromatic group.

7. A lubricating composition comprising in combination a major proportion of a suitable oil base and a minor proportion of a halogen bearing organic compound including a



group in a ring structure.

CARL F. PRUTTON.
ALBERT K. SMITH.