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LUBRICATING COMPOSITION

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This invention relates as indicated to lubricating compositions and more particularly to compositions for use in connection with the lubrication of relatively moving metallic surfaces which are subjected to or liable to be subjected to extreme pressures. More particularly, this invention relates to a lubricating composition which is especially adapted for use in connection with the lubrication of the transmission and differential gears and bearings of motor vehicles, etc., and it is among the objects of the invention to provide compositions obviating the disadvantages of the usual petroleum oils.

In our co-pending application, Serial No. 649,734, filed December 31, 1932, there is defined the conditions which obtain when relatively moving metallic surfaces are subjected to extreme pressure, i. e., for the definition of extreme pressure lubrication and the distinction thereof over low pressure or thick film lubrication, reference may be had to the specification of the above mentioned application.

It is among the objects of this invention to provide a lubricating composition which may be employed to reduce the friction between relatively movable metallic surfaces under pressures and other factors which result in what has been above explained as thick film lubrication and a composition which may be employed for thin film lubrication and without a material increase in the coefficient of friction between the parts over that found during thick film lubrication.

In the co-pending application of Carl F. Prutton, Serial No. 679,594, filed July 10, 1933, there is disclosed the use of halogenated organic compounds as addition agents to lubricating compositions such as comprise principally mineral oil and as stated in the specification of such application, the addition of the halogenated organic compounds to the oil base impart extreme pressure characteristics to the composition not possessed by the pure petroleum oil.

It is a further object of this invention to provide an additional improvement in such lubricating compositions as disclosed in the last above-mentioned application by the further addition thereto of certain materials.

Other objects of this 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 in-

vention, such disclosed means constituting, however, but one of various forms in which the principle of the invention may be used.

Particularly stated, this invention comprises the combined use as a lubricating composition of organic halogen bearing compounds and sulphur in active form; and the combined use of both such materials as addition agents to lubricating compositions which also contain a suitable lubricating oil such as mineral oil.

The suitable oil which may be used in providing one of the lubricating compositions contemplated by this invention may be any vegetable or mineral oil or a sulphur treated oil. For the definition of the term "sulphur-treated oil" reference may be had to the portion of this specification referring to the form in which sulphur may be present in the oil.

Our invention, as above explained, contemplates the use of halogenated compounds in such proportions as not to materially reduce the viscosity of the lubricating composition.

Since the loss of such additions by volatilization will in general be less for higher boiling materials, the boiling point should be at least 125° C. and preferably above 140° C. In other words, in order that the addition agents may not be driven off from the ultimate composition during elevated temperatures encountered during use they should have a vapor pressure less than atmospheric at a temperature of 125° C. and preferably at a temperature of 140° C.

The halogenated organic compounds used are preferably of such nature as to be sufficiently stable so that they will not cause corrosion of the bearings and other metallic parts exposed to the lubricant. These requirements in general are met more specifically by the halogenated organic ring compounds as distinguished from open chain compounds. The chlorinated species of these compounds is preferred particularly due to their low cost and superiority of performance. The halogenated organic ring compounds which have been found to produce very satisfactory results are as follows:

Halogen bearing derivatives of:

I Benzene such as:

(1) Halogenated benzene, e. g.,
Monchlorbenzene;

The dichlorbenzenes, notably the ortho compound; the trichlorbenzenes, notably the 1, 2, 4 compound,

- (2) Halogenated derivatives of benzene such as
- (a) Halogenated homologs of benzene, e. g.
 - chlorinated toluene
 - chlorinated xylene
 - chlorinated cymene
 - (b) Halogenated amino derivatives of benzene, e. g.
 - chlorinated aniline
 - chlorinated toluidines
 - chlorinated xylidines
 - (c) Halogenated hydrobenzenes, e. g.
 - dichlorhexahydrobenzene (dichlorcyclohexane)
- II Polyphenyls, including diphenyl, diphenyl benzenes, etc., such as,**
- (1) Chlorinated diphenyl
 - (2) Halogenated derivatives of diphenyl, such as,
 - (a) Halogenated homologs of diphenyl, e. g.
 - chlorinated phenyl-toluenes
 - (b) Halogenated amino derivatives of diphenyl, e. g.
 - chlorinated phenyl-anilines
 - chlorinated phenyl-toluidines
 - (c) Halogenated hydrodiphenyls, e. g.
 - chlorinated phenyl hexahydrobenzene
 - chlorinated dodecahydrodiphenyl
- III Naphthalene, such as**
- (1) Chlorinated naphthalene
 - (2) Halogenated derivatives of naphthalene such as:
 - (a) Halogenated homologs of naphthalenes, e. g. chlorinated methyl naphthalene notably the alpha compound, chlorinated propyl, and isopropyl substitution products of naphthalene
 - (b) Halogenated amino derivatives of naphthalene, e. g. chlorinated naphthylamines
 - (c) Halogenated hydronaphthalenes, e. g. chlorinated decahydronaphthalene
- IV Phenanthrene and anthracene, 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 α -methyl anthracene
 - chlorinated β -methyl anthracene
 - chlorinated dimethyl anthracenes
 - chlorinated propyl and isopropyl derivatives of anthracene
 - (b) Halogenated amino derivatives, e. g.
 - chlorinated phenanthrylamines
 - chlorinated anthramines
 - (c) Halogenated hydrophenanthrenes and halogenated hydroanthracenes
- V Chrysene, and picene, including halogenation products of their derivatives including homologs and other substitution products.**
- VI Bridged ring compounds, such as derivatives of the terpenes and related compounds.**
- VII Heterocyclic compounds, such as halogen bearing derivatives of pyridine, quinoline, pyrrole, thiophene and furan.**

It will be noted that the above enumerated examples of organic ring compounds which are preferably employed 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.

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

Of the chain compounds which may be employed, such as hexachlorethane, acetylene, tetrachloride, butylene dichloride (1-2 di-chlorbutane), monochlorhexane, 1-2 dichlor hexane, amylene dichloride, etc. or any other halogen substitution or addition products of the paraffins, olefines or acetylenes or derivatives of them, the less volatile and more stable are preferred for the reasons above set forth.

Certain halogenated commercial products which are mixtures of such compounds are also adapted for this use, such as: chlorinated wax, chlorinated kerosene, chlorinated motor oil, etc.

It has been found that the effectiveness of halogenated organic compounds in increasing the film strength of lubricating compositions is augmented by the presence of oxygen. Such oxygen may be present in the form of a separate organic compound or preferably in the same compound as the halogen. A preferred type of composition as contemplated by this invention is therefore one in which the halogen is present in the form of a halogenated oxygen-bearing organic ring compound.

The sulphur present in the composition may occur as elemental sulphur in solution or in a stable form of colloidal suspension or as sulphur-treated oils.

By the term "sulphur-treated oil" as employed in this description is meant any suitable oil base which has been treated with sulphur, for example a composition produced by the heating of the sulphur with a fixed oil such as lard oil or fish oil or to which sulphur or a sulphur compound (e. g., di-phenyl di-sulphide) has been added so that a certain amount of sulphur is present in active or loosely combined form. It has been found that a lubricating composition containing from .50% to 2.50% of sulphur in active or loosely combined form is well suited for use as a lubricant according to the present invention. These percentages are not to be construed, however, as limitations

but merely as an indication of the proportion of sulphur in the form defined for good results.

It has been found that for optimum results a certain relationship should be maintained between the amount of halogen or more specifically, chlorine in the composition and the amount of sulphur, when the halogenated compounds of the above class are added to a sulphur-containing oil. It has been found that to a composition having a low content of sulphur in active or loosely combined form, halogenated compounds should be added in correspondingly low concentrations for best results. When sulphur-treated oil is used in combination with halogenated compounds, it should be noted that for sufficiently desirable results the major proportion of the ultimate composition need not consist entirely of sulphur-treated oil but a suitable oil base, such as a mineral oil or vegetable oil may have added thereto minor quantities or proportions of either a sulphur-treated oil or elemental sulphur in solution and a halogenated compound.

As an example of the cooperative effect of halogenated organic compounds and a sulphur compound of the type described, the table below shows the results obtained when solutions in mineral oil of a sulphurized fixed oil alone, chlorinated diphenyl ether alone and the same concentrations of both additions were tested on an Almen lubricant testing machine. The fixed oil used was cotton seed oil and contained about 9.5% of sulphur. The chlorinated diphenyl ether contained a total of about 45% chlorine. The increase in film strength of the oil caused by the compounds dissolved in it is shown and is stated in terms of additional pounds of weight applied to the loading arm of the machine required to cause breakdown as compared with the mineral oil alone:

Percent of sulphurized cottonseed oil	Percent of chlorinated diphenyl ether	Increase in breakdown load
0	1	6
5	0	6
5	1	24

For general use, a lubricating composition in accordance with our invention may comprise a major proportion of a suitable oil base and minor proportions, i. e., less than 50% of the previously named addition agents. More specifically, our invention contemplates incorporating with a suitable oil base a total of less than 20% of addition agents of the previously enumerated types.

The optimum amount of the addition agents to be employed will depend largely upon their physical characteristics and especially their effect on the viscosity of the oil to which they are added. The particular use for which the lubricant is intended is also a governing factor in determining the amount of the compound to be added.

The limit of the amount of the addition agents which may be added to the previously mentioned oil base and which will produce improved results depends, as above indicated, upon the reduction in viscosity of the composition caused by the addition of such compounds. For particular uses and when certain of the more viscous addition agents are employed, such addition agents may be present in amounts up to 100%.

For example, chlorinated diphenyl ether has a sufficiently high viscosity especially when it contains more than 40% of combined chlorine, so that it may be used as a lubricant in the pure

state. Halogenated ring compounds of this nature are therefore suitable as a base to which to add the sulphur or sulphur-treated oil directly without any other oil base such as mineral oil to form one type of lubricating composition contemplated by this invention.

It is to be understood that the "so-called" addition agents referred to herein shall be substantially oil-soluble or of such nature that they may be included in the composition in the form of a stable colloidal suspension. It should also be noted that certain of the addition agents contemplated by this invention, while soluble in oil do not dissolve readily therein. When such compounds are used they may be first dissolved in materials such as, benzene, the chlorobenzenes, the higher alcohols such as amyl alcohol, acetone, petroleum naphtha, carbon tetrachloride, tetrachloroethylene, aniline, tricresyl phosphate, etc., and the resulting solution then added to the lubricating composition.

The lubricating compositions herein described are particularly useful for the purpose of lubricating the engaging surfaces of gears especially those of the worm and of the hypoid types, and for lubricating any such surfaces when operating under heavy loads or whenever extremely high unit pressures between such surfaces are encountered. These compositions are also well adapted for lubricating bearings and especially those of the heavy duty, slow speed type.

The lubricating compositions herein described are particularly useful for the purpose of lubricating gears and such bearings and wearing surfaces generally as are not subjected to high temperatures. Since the so-called "addition agents" employed in lubricating compositions made in accordance with the present invention are in general too active when subjected to high temperatures, they are not particularly adapted for use as lubricants in the crank cases of internal combustion engines.

This application is a continuation in part of pending application Serial Number 649,734 filed December 31, 1932 and Serial Number 744,600 filed September 17, 1934.

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 in carrying out the process, provided the ingredient or ingredients stated in any of the following claims or the equivalent of such stated ingredient or ingredients be employed.

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

1. A lubricating composition including as a principal lubricating constituent the combination of a halogenated organic ring compound and sulphur in solution in active form.

2. A lubricating composition including a principal lubricating constituent comprising the combination of a halogenated organic ring compound and a sulphur-treated oil.

3. A lubricating composition including as a principal lubricating constituent the combination of a halogenated organic ring compound and a sulphur treated fixed oil.

4. A lubricating composition including as a principal lubricating constituent the combination of a lubricating oil, a halogenated organic ring compound and sulphur in solution in active form.

5. A lubricating composition including as a principal lubricating constituent the combination of a suitable oil base, a fixed oil, a halogenated

organic ring compound and sulphur in solution in active form.

5 6. A lubricating composition including as a principal lubricating constituent the combination of a fixed oil containing sulphur in chemical combination in active or loosely combined form, and a minor proportion of a halogenated organic ring compound.

10 7. A lubricating composition including as a principal lubricating constituent the combination of a fixed oil containing sulphur in chemical combination in active or loosely combined form, and a minor proportion of a chlorinated organic ring compound.

15 8. A lubricating composition including as a principal lubricating constituent the combination of a fixed oil containing sulphur in chemical combination in active or loosely combined form, and a minor proportion of a halogen bearing derivative of at least one compound of the class including benzene, naphthalene, and diphenyl.

20 9. A lubricating composition including a major proportion of mineral oil and minor proportions of both a halogenated organic ring compound and sulphur in solution in active form.

25 10. A lubricating composition including as a principal lubricating constituent the combination of a major proportion of mineral oil and in solution therein minor proportions of both a halogenated organic compound and a separate organic compound containing sulphur in active or loosely combined form.

30 11. A lubricating composition including as a principal lubricating constituent the combination of a major proportion of mineral oil and in solution therein minor proportions of both a halogenated organic ring compound and an organic compound containing sulphur in active or loosely combined form.

40 12. A lubricating composition including as a principal lubricating constituent the combination of a halogenated oxygen bearing organic ring compound, and sulphur in solution in active form.

45 13. A lubricating composition including as a principal lubricating constituent the combination of at least one compound of the class including halogen and oxygen bearing derivatives of benzene, naphthalene, and diphenyl, and sulphur in solution in active form.

50 14. A lubricating composition including as a principal lubricating constituent the combination of a lubricating oil, a minor proportion of

at least one compound of the class including halogen and oxygen bearing derivatives of benzene, naphthalene, and diphenyl, and sulphur in solution in active form.

5 15. A lubricating composition including as a principal lubricating constituent the combination of a halogenated diphenyl ether and sulphur in solution in active form.

10 16. A lubricating composition comprising a major proportion of a sulphur treated oil and a minor proportion of a stable, oil-soluble halogenated organic compound having a vapor pressure less than atmospheric at a temperature of 140° C.

15 17. A lubricating composition comprising a major proportion of a sulphur treated oil and a minor proportion of a stable, oil-soluble halogenated ring compound having a vapor pressure less than atmospheric at a temperature of 140° C.

20 18. A lubricating composition comprising a major proportion of a sulphur treated oil and a minor proportion of a stable, oil-soluble halogenated hydrocarbon having a vapor pressure less than atmospheric at a temperature of 140° C.

25 19. A lubricating composition comprising a major proportion of mineral lubricating oil and minor proportions of both a halogenated organic compound and an organic sulphur compound, said compounds being oil soluble, having vapor pressure less atmospheric at a temperature of 140° C. and present in amounts less than 20% based on the amount of lubricating oil.

30 20. A lubricating composition comprising a major proportion of mineral lubricating oil to which have been added minor proportions of both a chlorinated organic compound and sulphur in solution in active form, said chlorinated organic compound having a vapor pressure of less than atmospheric at a temperature of 140° C.

40 21. A lubricating composition including as a principal lubricating constituent the combination of a chlorinated organic compound to which has been added sulphur in solution in active form.

45 22. A lubricating composition comprising a major proportion of a sulphur treated oil and a minor proportion of a stable, oil-soluble, halogenated hydrocarbon ring compound having a vapor pressure less than atmospheric at a temperature of 140° C.

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