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LUBRICANT

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This invention relates, as indicated, to lubricating oils and more particularly to such compositions as new compositions of matter.

This application is a continuation in part of our copending application Serial 293,276, filed September 2, 1939.

The present design of mechanical devices including internal combustion engines calls for high pressures on rubbing surfaces and the tendency is toward a still greater increase in such pressures. While conventional hydrocarbon lubricants vary somewhat in film strength the best of them are unable to withstand the extreme pressures imposed by modern design and the still higher pressures designers of mechanical devices would like to employ to take advantage of the improvements which might be achieved with higher rubbing pressures.

For many uses, as in the crankcase of an internal combustion engine, it is necessary that the lubricant employed be also noncorrosive and stable to the rather high operating temperatures.

Other desirable properties include high oiliness, low pour point and resistance to sludge formation.

It is therefore a principal object of our invention to provide an effective extreme pressure lubricating composition capable of withstanding the high pressures imposed on rubbing surfaces by modern mechanical design.

Another object is to provide such a lubricant which also has the desirable property of high oiliness.

Still another object is to provide a lubricant having the foregoing advantages and which is stable and noncorrosive in use.

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

To the accomplishment of the foregoing and related ends this invention, then, consists of the means hereinafter fully described and particularly pointed out in the claims.

The following description sets forth in detail certain approved combinations of ingredients embodying 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 a lubricating composition comprising a major amount of a lubricating oil and minor amounts of both a halogen and sulfur bearing organic compound and a thionic material. The thionic material which may be either an organic sulfur compound or elemental sulfur and when thus

employed may have sulphur present in either relatively active or inactive form, depending upon the particular use to which the composition is to be placed.

More particularly, both the halogen and sulfur bearing addition agent and the thionic material will preferably have a vapor pressure less than atmospheric at 140° C. and for certain uses, a vapor pressure less than atmospheric at 170° C. In the case of compounds which are stable at temperatures up to their boiling points, this condition may be expressed by stating that the boiling point of the compound should, in general, be higher than 140° C., and, for certain uses, such as in internal combustion engines, higher than 170° C.

While all of the halogens are effective when employed in accordance with the present invention chlorine is generally preferred since it is the least expensive and one of the most effective of the halogens. Bromine and fluorine may be employed but are relatively expensive and the latter is somewhat difficult to handle. Iodine, while effective, is at present too expensive to be employed on a large scale. It should also be noted that two or more different halogens may be present in the same molecule. The brom-chlor and fluorinated chlorine or bromine sulfur compounds give particularly satisfactory results.

The following list includes a number of typical halogen and sulfur bearing aliphatic organic compounds found generally suitable for use in accordance with this invention. It will be understood, however, that such list is intended for purposes of illustration only and is not intended to limit the scope of the invention to those compounds herein enumerated.

HALOGEN AND SULFUR BEARING ORGANIC COMPOUNDS

I. ALIPHATIC

A. Compounds of C, H, S, and X

Chloroamyl disulfide
Chlorolauryl mercaptan
Chlorolauryl thiocyanide

B. Compounds of C, H, S, X, and O

1. Esters and salts
Chloroamyl sulfate
Chlor-naphtha xanthate
2. Ethers
Chloromercapto ethyl ether
3. Carbonyl compounds
Chloromethyl mercaptoamylketone
4. Acids
Chloromercaptostearic acid

5. Sulfones and sulfoxides

Beta-chloroethyl sulfone

The thionic material to be employed in this invention may be either elemental sulfur or an organic sulfur compound. The organic sulfur compound may be carbocyclic, aliphatic or heterocyclic in nature. We have also found that those thionic materials made by the direct sulfurizing of organic compounds by the use of sulfur or a sulfur compound are of value in our invention. Of particular value are those thionic materials made by sulfurizing chemically unsaturated olefinic organic compounds.

I. CARBOCYCLIC COMPOUNDS

Examples of materials within this classification are:

Diphenyl sulfide
Dibenzyl sulfide
Di naphthyl sulfide
Di paratolyl sulfide
Di xylyl sulfide
Di phenyl disulfide
Di benzyl disulfide
Di naphthyl disulfide
Di para tolyl disulfide
Di xylyl disulfide
Dibenzyl trisulfide
Di phenol disulfide
Diphenyl sulfone
Dibenzyl sulfone
Di paratolyl sulfone
Di naphthyl sulfone
Di xylyl sulfone
Di phenyl sulfoxide
Dibenzyl sulfoxide
Dipara tolyl sulfoxide
Di xylyl sulfoxide
Di naphthyl sulfoxide
Diphenyl thio urea
Dibenzyl thio urea
Dibenzyl thio urea
Ortho tolyl thio urea
Phenyl thio cyanate
Benzyl thio cyanate
Naphthyl thio cyanate
Methyl phenyl thio ether
Ethyl benzyl thio ether
Propyl naphthyl thio ether
Thioanthraquinone
Thio phenol
Ortho thio cresol
Thio carvacrol
Thio anisol
Thio naphthol
Ortho nitro thio phenol
Phenyl thio carbonic chloride
Chlor phenyl mercaptan
Phenyl thio glycolic acid
Thio benzoic acid
Sodium thio benzoate
Calcium thio benzoate
Tin thio benzoate
Benzene sulfonic acid
Naphthalene sulfonic acid

Thio aldehydes $R-CHS$ in which R is any carbocyclic radical including phenyl, tolyl, naphthyl, xylyl, etc.

Thio ketones $R.CS.R'$ in which either R or R' is any carbocyclic radical including phenyl, tolyl, xylyl, naphthyl, etc.

Thiophenates such as calcium thiocresolate

Heterocyclic

Dibenzo thiophene
Thianthrene (diphenylene disulfide)
5 Trithioacetaldehyde
Trithioacetaldehyde trisulfone
Tetrahydrofurfuryl sulfide
Methylmercaptobenzothiazole
8-sulfhydryl quinoline
10 Mercaptodibenzofurane
Methylmercaptochlorodioxane
Ethylene sym.-dithiocarbonate

Aliphatic compounds

15 Butyl sulfide
Amyl sulfide
Hexyl sulfide
Octadecyl sulfide
Heptyl sulfide
20 Butyl disulfide
Amyl disulfide
Hexyl disulfide
Heptyl disulfide
Octadecyl disulfide
25 Amyl sulfone
Butyl sulfone
Hexyl sulfone
Heptyl sulfone
Octadecyl sulfone
30 Ethyl thio cyanate
Butyl thio cyanate
Hexyl thio cyanate
Heptyl thio cyanate
Octadecyl thio cyanate
35 Naphtha xanthate
Ethyl thio carbonic acid
Amyl thio carbonic acid
Thio ethyl carbonic ethyl ester
40 Methyl ester of dithio carbonic acid
Amyl ester of dithio carbonic acid
Sodium ethyl xanthate
Calcium amyl xanthate
Tri thio carbonic amyl ester
45 Dithiodiglycol
Ethyl di thio-oxalate
Amyl sulfoxide
Octadecyl mercaptan
Sodium amyl thisulfate
50 Thiocarbamylamine (reaction product of amyl amine and CS_2)
Amyl sulfate
Mercapto stearic acid
Calcium mercaptostearate
Methyl mercaptostearate

Sulfurized materials

Sulfurized methyl linoleate
Sulfurized methyl oleate
Sulfurized methyl aryl substituted linoleate
60 Sulfurized animal and vegetable oils
Sulfurized lard oil
Sulfurized corn oil
Sulfurized cottonseed oil
Sulfurized sperm oil
65 Sulfurized oleic acid
Sulfurized olefinic hydrocarbons from petroleum
Sulfurized olefinic material derived by halogenating, dehalogenating, and sulfurizing petroleum wax
70 Sulfurized calcium oleate
Sulfurized calcium linoleate
Sulfurized tin oleate
Sulfurized tin linoleate
Sulfurized potassium oleate
75 Sulfurized potassium linoleate

Where extreme or violent extreme pressure characteristics are encountered, the thionic material to be used will be selected from those which will turn a copper strip black in less than 30 minutes at 210° F. An example of such active thionic material is obtained by employing a physical solution or colloidal suspension of elemental sulphur in the lubricating composition. For many uses, however, where stability and freedom from corrosion and the like are of greater importance than extreme pressure characteristics, then the thionic material will be selected from those which will not turn a copper strip black in less than 30 minutes at a temperature of 210° F. The copper strip test as above indicated is conducted by mixing 10% of the addition agent with 90% of the base oil and then maintaining a clean copper strip therein for a period of 30 minutes at a temperature of 210° F.

Sulfur compounds for use in this invention may be made by controlling the composition and by varying the physical and chemical factors involved in manufacturing until a sulfur compound is formed that will not blacken a copper strip when blended with mineral oil and heated to 210° F. for 30 minutes. For example, a chemically unsaturated glyceride may be sulfurized with 5, 10, or 15 percent of sulfur and mineral oil blends of each of these may turn a copper strip black in less than 30 minutes at 210° F. However, control of the time and temperature of sulfurizing will convert all three of these to compounds that will not blacken a copper strip under the conditions of the foregoing test. Obviously, less time and lower temperatures will satisfactorily condition the glyceride containing 5 per cent sulfur than will be required for the glyceride containing 15 percent sulfur. To accomplish this result we regularly test the batch during manufacture and impose the minimum severity of manufacturing conditions. For some lubricating problems, it is necessary to have a controlled amount of both active and inactive sulfur in the lubricant.

In some instances sulfur compounds for use in this invention may be manufactured according to the above general method and the manufacturing process stopped short of complete conditioning of the sulfur compound to the copper strip test. In these instances, only small amounts of sulfur or sulfur compounds present in the desired product have a tendency to blacken the copper strip in the test prescribed. In these instances we remove the small amount of objectionable material by contacting the entire mass with treating agents that make the product satisfactory. Examples of these treating agents are finely divided metal such as copper, iron, mercury, etc., either as such or mixed with inert carriers like clay, fuller's earth, pumice, kieselguhr, and the like. Other treating methods are known and may be employed to accomplish the desired ends.

The oil base employed may be any suitable lubricating oil such as mineral oil or animal and vegetable oils of lubricating viscosity, and including synthetic, hydrogenated and volatilized oils.

It is also within the contemplation of this invention to provide the addition agents in the form of a concentrate in a suitable oil, said oil containing a rather high percentage of the addition agents. Such concentrates may be employed for future blending with a lubricating oil in the proportions desired for the particular conditions of use.

The addition agents must, of course, be soluble in the oil base in which they are employed although often the degree of solubility need not be very great since quite small quantities of the addition agents may supply the effect desired. By the term "soluble," as used herein, it is intended to indicate the ability to form not only true solutions but also any form of substantially permanently homogeneous composition when incorporated in the oil base.

In general, the invention contemplates the employment of from about .5 percent to about 10 percent by weight of the aliphatic halogen and sulfur bearing compound, based on the amount of mineral oil, and an equal or less amount of the thionic material. However, as little as .02 percent of one or the other addition agent may be effective for certain uses, while for other uses as much as 20% may be employed.

For each combination of a specific halogen and sulfur compound and a specific thionic material, it will be found that there is a certain optimum proportional relationship which may be found by comparative tests. This also holds true where the halogen and sulfur or sulfur bearing component is in the form of a complex material.

It has been found that the addition of the thionic material in which the sulfur is present in relatively inactive form and the addition of the halogen and sulfur bearing organic compound to the same mineral oil results in lubricants far superior to lubricants made with the same mineral oil and only one or the other of the two classes of compounds. The lubricants of this invention are superior in one or more respects depending upon the particular thionic material and halogen and sulfur bearing compound added to the mineral oil. For example, the corrosion or metal wear is less with the combination lubricant than with a lubricant containing only one of the addition agents. The sludging and oxidation characteristics of the lubricant in use are usually improved to a marked degree. The load-carrying capacity of the lubricants of this invention may be higher than a lubricant made with the same mineral oil and only a thionic material or a halogen and sulfur compound as such are defined by the invention. The load-carrying capacity of lubricants of this invention will remain fairly constant throughout the entire period of use of the lubricant which is one of the greatest practical advantages of these lubricants. The oiliness character of the lubricants of this invention reflects the combined oiliness effect of the two separate types of compounds, namely, thionic material and halogen and sulfur compounds. The unexpected joint effect of the halogen and sulfur compound and the thionic material makes these lubricants outstanding. From these unexpected results we are of the opinion that there is a specific but incompletely understood effect of the thionic material on the halogen and sulfur compound and of the latter on the former.

The addition agents, should of course, be stable at the operating temperatures to which they will be subjected.

While the lubricating compositions which have been described herein as illustrating one embodiment of the invention have been generally referred to as "oils," i. e., liquids, this invention is, however, also applicable to the solid and semi-solid types of lubricants commonly referred to in the trade as greases, bodied oils, etc., which contain metallic or nonmetallic salts or soaps such as calcium oleate, sodium stearate, aluminum naph-

thenate, calcium phenyl stearate, calcium dichlorostearate, ammonium oleate, or cadmium, nickel, zinc, or tin salts or soaps of various organic acids.

The following examples of our invention are not given as a limitation but to show certain practical combinations:

	Per cent
(1) SAE 10 mineral oil.....	98
Chlorolauryl mercaptan.....	1
Sulfurized methyl linoleate.....	1
(2) SAE 20 mineral oil.....	98
Chloro amyl disulfide.....	1
Sulfurized methyl oleate.....	1
(3) SAE 30 mineral oil.....	97
Chloro lauryl thio cyanide.....	2
Dibenzyl disulfide.....	1
(4) SAE 50 mineral oil.....	98
Chloroamyl sulfate.....	1
Butyl disulfide.....	1
(5) SAE 60 mineral oil.....	98
Chloro naphtha sulfate.....	1
Benzyl thiocyanate.....	1

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

1. A lubricating composition comprising a major proportion of lubricating oil and a minor amount of a halogen and sulfur bearing aliphatic compound and a minor amount of a thionic material.

2. A lubricating composition comprising a major proportion of lubricating oil and a minor amount of a halogen and sulfur bearing aliphatic compound and a minor amount of elemental sulfur.

3. A lubricating composition comprising a major proportion of lubricating oil and a minor amount of a halogen and sulfur bearing aliphatic compound and a minor amount of an organic sulfur compound.

4. A lubricating composition comprising a major proportion of lubricating oil and a minor amount of a halogen and sulfur bearing aliphatic compound and a separate organic sulfur compound of the type which does not blacken a copper strip placed in the composition at a temperature of 210° F. for thirty minutes.

5. A lubricating composition comprising a major proportion of lubricating oil and minor amounts of a halogen and sulfur bearing aliphatic compound and a relatively inactive organic sulfur compound.

6. A lubricating composition comprising a major proportion of lubricating oil and from about .02 percent to 20 percent of a halogen and sulfur bearing aliphatic compound having a vapor pressure less than atmospheric at 140° C. and from about .02 percent to 20 percent of a separate organic sulfur compound of the type which does not blacken a copper strip placed in the composition at a temperature of 210° F. for thirty minutes.

7. A lubricating composition comprising a major proportion of lubricating oil and from

about .5 percent to about 10 percent each of a halogen and sulfur bearing aliphatic compound having a vapor pressure less than atmospheric at 140° C. and a relatively inactive organic sulfur-bearing compound having a vapor pressure less than atmospheric at 140° C.

8. A lubricating composition comprising a major proportion of lubricating oil and minor proportions of both an organic sulfur bearing compound and a halogen and sulfur bearing aliphatic hydrocarbon, said addition agents having vapor pressures of less than atmospheric at 140° C.

9. A lubricating composition comprising a major proportion of lubricating oil and minor proportions of both an organic sulfur-bearing compound and a halogen and sulfur bearing aliphatic ester, said addition agents having vapor pressures of less than atmospheric at 140° C.

10. A lubricating composition comprising a major proportion of lubricating oil and minor proportions of both an organic sulfur-bearing compound and a halogen and sulfur bearing salt of an aliphatic acid, said addition agents having vapor pressures of less than atmospheric at 140° C.

11. A lubricating composition comprising a major proportion of lubricating oil and a minor amount of an aliphatic organic compound containing halogen, sulphur and oxygen in the molecule, and a minor amount of an organic sulphur compound.

12. A lubricating composition comprising a major proportion of lubricating oil and from about .02% to 20% of a halogen and sulphur bearing aliphatic compound having a vapor pressure less than atmospheric at 140° C. and from about .02% to 20% of a separate organic sulphur compound of the type which will blacken a copper strip placed in the composition at a temperature of 210° F. for thirty minutes.

13. A lubricating composition comprising a major proportion of lubricating oil and from about .02% to 20% of a halogen and sulphur bearing aliphatic hydrocarbon having a vapor pressure less than atmospheric at 140° C. and from about .02% to 20% of a separate organic sulphur compound.

14. A lubricating composition comprising a major proportion of lubricating oil and minor proportions of both an organic sulphur bearing compound and a chlor naphtha xanthate, said addition agents having vapor pressures of less than atmospheric at 140° C.

15. A lubricating composition comprising a major proportion of lubricating oil and minor proportions of both an organic sulphur bearing compound and a chlor amyl disulphide, said addition agents having vapor pressures of less than atmospheric at 140° C.

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