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LUBRICATING OIL

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Our invention relates to lubricating oils and more particularly to an improved lubricating oil of high film strength which is noncorrosive toward easily corroded bearing materials.

This application is a continuation-in-part of our co-pending application, Serial No. 275,488, filed May 24, 1939.

In the development of new automotive and other types of engines, increased power and other requirements have led to the introduction of bearing metals, alloys and mixtures which are readily attacked by oxidation products of the lubricant. Some of these newer bearing compositions are cadmium-silver, copper-lead and alloys of lead with alkali and alkaline earth metals. These comparatively soft metals are corroded readily by oils which have been used for a short time in the engine. One method of overcoming this difficulty would be to use more resistant bearing compositions, and another would be to use an oil which does not develop these corrosive materials during use. Still another method would be to use a lubricant containing a material which would react with and render inert the corrosive products as rapidly as they are formed. Our invention is not concerned with the first method but with the other two possibilities. Various addends have been proposed for addition to lubricants for the purpose of inhibiting the formation of corrosive materials during use. These may be called antioxidants, since they increase the time of use before rapid oxidation after it has started. Various addends have also been proposed to be added to lubricants for the purpose of reacting with such corrosive materials, as may in time be formed, and removing them from the oil so that they are unable to corrode the parts being lubricated. These may be called precipitants. The present invention proposes addends combining these two capabilities in the same molecule to give an unexpectedly superior activity in both respects over what would be expected from simply the additive effect alone.

Certain compounds are adsorbed or absorbed by metals forming tenacious films at the surface of metals which are able to stand high pressures. X-ray diffraction methods have shown that compounds containing highly polar molecules, that is, molecules of unsymmetrical character containing an atom or group of atoms exhibiting a secondary or residual valence, tend to produce regimentation of the molecules of hydrocarbon oil when added thereto. A metal immersed in a strongly polar compound will show a film of

the compound in which there is a regimentation of molecules oriented with respect to the surface of the metal by which they are adsorbed or absorbed.

One object of our invention is to provide a substantially noncorrosive lubricant for use with the newer, easily corroded bearing compositions. It is to be noted, however, that the improved lubricant here described is advantageously employed with all types of bearings, since it is less corrosive during use with any of the metals commonly encountered in practice.

Another object of the invention is to provide a lubricant inhibited against oxidation during use.

A further object is to provide a lubricant containing an addend capable of reacting with or otherwise rendering inert such corrosive products as may be formed during extended use.

Other objects of the invention will appear in the following description.

Our invention comprises the addition to all kinds of lubricants of salts or soaps of organic bases with sulfur bearing acids. These salts may be of diverse types and both the anionic and cationic parts of these soaps may be varied. Thus the cations may be derived from primary, secondary, or tertiary amines or quaternary ammonium bases. The organic radicals in these amines and ammonium bases may be aliphatic, aromatic or otherwise cyclic aralkyl or otherwise mixed in type and may contain halogen, oxygen, sulfur or other inorganic elements. The sulfur-bearing acidic radicals may contain sulfur in various forms. They may be thio-esters, mercaptans, sulfones, heterocyclic sulfur rings, or sulfurized unsaturated acids or sulfur-chloride treated unsaturated acids and the like. In the following examples, any of the cations may be used with any of the anions to form these soaps; and it is to be understood that each of these combinations when blended, suspended, or otherwise mixed with a lubricant is an example of the invention.

I. Anions

A. Sulfurized acids

1. Sulfurized oleic acid
2. Sulfurized linoleic acids
3. Sulfurized linolenic acids
4. Sulfurized elaidic acid
5. Sulfurized corn oil acids
6. Sulfurized soy oil acids
7. Sulfurized lard oil acids
8. Sulfurized tung oil acids
9. Sulfurized abietic acid

10. Sulfurized cholic acid
11. Sulfurized naphthenic acids
- B. Phosphorus sulfide-treated acids (containing phosphorus and sulfur)
 1. Phosphorus pentasulfide-treated corn oil acids 5
 2. Phosphorus trisulfide-treated corn oil acids
 3. Phosphorus pentasulfide-treated soy oil acids 10
 4. Phosphorus pentasulfide-treated oleic acid
 5. Phosphorus pentasulfide-treated linoleic acid
- C. Sulfur chloride-treated acids 15
 1. Sulfur chloride-treated oleic acid
 2. Sulfur chloride-treated linoleic acid
 3. Sulfur chloride-treated linolenic acids 20
 4. Sulfur chloride-treated elaidic acid
 5. Sulfur chloride-treated corn oil acids
 6. Sulfur chloride-treated soy oil acids 25
 7. Sulfur chloride-treated lard oil acids
 8. Sulfur chloride-treated tung oil acids 30
 9. Sulfur chloride-treated abietic acid
 10. Sulfur chloride-treated cholic acid
 11. Sulfur chloride-treated naphthenic acids 35
- D. Sulfur bearing acids of known constitution
 1. Mercapto acids
 - a. Mercapto-stearic acid 40
 - b. Mercapto-acetic acid
 - c. Thiophenol - 4 - carboxylic acid
 - d. Thiophenylacetic acid
 - e. Mercapto-chlorostearic acid 45
 2. Sulfido acids
 - a. Methylmercapto-stearic acid
 - b. Ethylmercaptophenyl acetic acid
 - c. Amylmercaptobenzene - 4 - carboxylic acid 50
 - d. Methylmercapto - chloro - stearic acid
 3. Sulfone acids
 - a. Ethylsulfone - beta-carboxylic acid 55
 - b. Phenylsulfone-4-carboxylic acid
 - c. Chlorophenylsulfone-2-carboxylic acid 60
 4. Disulfide acids
 - a. Ethyldisulfidobenzene - 2 - carboxylic acid
 - b. Amyldisulfidophenylacetic acid 65
 - c. Benzylidisulfidobenzylstearic acid
 5. Sulfonic acids
 - a. Benzene sulfonic acid
 - b. Tri - isopropyl naphthalene sulfonic acid 70
 - c. Chloronaphthalene sulfonic acid
 - d. Amyl sulfonic acid 75

6. Sulfinic acids
 - a. Benzene sulfinic acid
 - b. n-Butyl sulfinic acid
7. Sulfato acids
 - a. Acid sulfate of 12-hydroxystearic acid
 - b. Acid sulfate of ricinoleic acid
 - c. Neutral sulfate of 12-hydroxystearic acid
8. Sulfite acids
 - a. Sulfite of 12-hydroxystearic acid
 - b. Sulfite of ricinoleic acid
9. Xanthates
 - a. Ethylxanthate
 - b. Butylxanthate
 - c. Amylxanthate
 - d. Benzylxanthate

II. Cations

A. Primary amines

1. Aliphatic
 - Methyl amine, ethyl amine, amyl amine, dodecyl (lauryl) amine, octadecyl amine, oleyl amine, ethanolamine, methyl ester of glycine, chloroethylamine, and propylene diamine
2. Carbocyclic
 - a. Aromatic
 - Aniline, toluidine, aminodiphenyl, sulfanilic acid, picryl amine, alpha and beta naphthyl amines, and the phenylene diamines
 - b. Naphthenic
 - Cyclohexyl amine, methyl cyclopentyl amine, and hexahydrophenylene diamines
3. Heterocyclic
 - Aminopyridine and aminobenzofuran

B. Secondary amines

1. Aliphatic
 - Dimethylamine, diamylamine, ethyl amyl amine, and diethanolamine
2. Carbocyclic
 - a. Aromatic
 - Methyl aniline, diphenylamine, phenyl alpha-naphthylamine, amylaniline, and ditolylamine
 - b. Naphthenic
 - Dicyclohexylamine and methyl cyclohexylamine
3. Heterocyclic
 - Methylamino pyridine

C. Tertiary amines

1. Aliphatic
 - Trimethyl amine, triamylamine, and triethanolamine
2. Carbocyclic
 - a. Aromatic
 - Triphenylamine, dimethylaniline, and diamylaniline

b. Naphthenic

Tricyclohexylamine,
methyl dicyclohexyl-
amine, and dimethyl
cyclohexylamine

3. Heterocyclic

Pyridine, dimethyl aminoben-
zofuran

D. Quaternary ammonium bases

1. Aliphatic

Tetramethylammonium hy-
droxide, trimethylamylam-
monium hydroxide

2. Carbocyclic

Trimethylbenzyl ammonium
hydroxide, trimethylcyclo-
hexylammonium hydroxide

3. Heterocyclic

Methylpyridinium hydroxide

The soaps derived from these organic bases may contain in the organic radical an additional element or combination of elements including the halogens, sulfur, phosphorus, nitrogen, or oxygen.

Some of the combinations of the cations with the anions are listed below, but it is obvious that all the possible combinations serve as examples of the invention when admixed with lubricating oils or greases:

1. Methyl ammonium salts of sulfurized corn oil acids
2. Amyl ammonium salts of sulfurized soy bean oil acids
3. Octadecylammonium salts of sulfurized beta fat
4. Propylene diammonium salts of sulfurized linoleic acid
5. Alpha-naphthylammonium salts of sulfurized oleic acid
6. Cyclohexylammonium salts of sulfur-chloride treated corn oil acids
7. Benzofurylammonium salts of sulfur-chloride treated soy bean oil acids.
8. Diethanolammonium salts of sulfur-chloride treated beta fat
9. Methyl phenyl ammonium salts of sulfur-chloride treated linoleic acid
10. Dicyclohexylammonium salts of sulfur-chloride treated oleic acid
11. Triamylammonium mercaptostearate
12. Diamyl phenyl ammonium salts of sulfurized lard oil acids
13. Pyridinium salts of sulfur-chloride treated lard oil acids
14. Tetramethylammonium ethyl sulfone-beta-carboxylate
15. Trimethyl amyl ammonium amylsulfido-phenylacetate
16. Trimethyl benzyl ammonium amylxanthate
17. Trimethyl cyclohexyl ammonium salts of the reaction product of benzyl disulfide, dichlorostearic acid, and aluminum chloride.

The addends of this invention have a dual action in a lubricant. Our action involves increased load-carrying ability and/or oiliness, while another action is directed to the stability

of the lubricant. For load-carrying capacity, quantities ranging from 0.1 per cent to about 10.0 per cent must be added. As an anticorrosive agent and/or an antisludging agent, much smaller amounts must be used, ranging from approximately 0.001 to 0.1 per cent. The action of the sulfur-bearing organic soaps is specific but difficult to understand. These compounds may be added to any type of hydrocarbon lubricants, but show an unusual value in highly refined and solvent-treated lubricants.

The lubricating oil portion of the blends of our invention may be so-called mineral or hydrocarbon oils or may consist of wholly or contain only in part certain fatty oils including corn oil, soy bean oil, lard oil, and the like. The blends may contain voltolized oils or synthetic oils of lubricating viscosity. Soap thickened or otherwise thickened oils used as greases may be employed. Addends for other purposes such as pour point depressors may be present.

These compounds have varying degrees of solubility in hydrocarbon oil. In some cases, it is necessary to use a solvent for the compound or to form colloidal suspensions of the compound in oil.

The film strength and oxidation characteristics of solid and semisolid greases may be improved by the addition of small amounts of our sulfur-bearing organic soaps thereto. The chemical purity for use as extreme pressure addition agents is not critical. All that is important is that no corrosive contaminants be present. Mixtures of a number of these compounds may be employed.

It will be understood that certain features and sub-combinations are of utility and may be employed without reference to other features and sub-combinations. This is contemplated by and is within the scope of our claims. It is further obvious that various changes may be made in details within the scope of our claims without departing from the spirit of our invention. It is therefore to be understood that our invention is not to be limited to the specific details shown and described.

Having thus described our invention, we claim:

1. A lubricant comprising in combination a major proportion of an oil of lubricating viscosity and a minor proportion of a salt of a quaternary ammonium base and a sulfur-bearing organic acid.

2. A lubricant comprising in combination a major proportion of an oil of lubricating viscosity and a minor proportion of triamylammonium mercaptostearate.

3. A lubricant comprising in combination a major proportion of an oil of lubricating viscosity and a minor proportion of the cyclohexylammonium salts of sulfur-chloride treated soy bean oil acids.

4. A lubricant comprising in combination a major proportion of an oil of lubricating viscosity and a minor proportion of alpha-naphthylammonium salts of sulfurized oleic acid.

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