Patented June 3, 1947

2,421,631

UNITED STATES PATENT OFFICE

2,421,631

LUBRICATING OIL

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No Drawing. Original application August 2, 1941, Serial No. 405,213. Divided and this application May 16, 1945, Serial No. 594,162

15 Claims. (Cl. 252—33.6)

1

Our invention relates to lubricating oils and more particularly to improved lubricating oils of high film strength which are non-corrosive toward easily corroded bearing materials.

This is a division of our copending application Serial No. 405,213, filed August 2, 1941, now Patent No. 2,395,889, issued March 5, 1946, which, in turn is a continuation-in-part of our application Serial No. 275,488, filed May 24, 1939 (now Patent No. 2,257,750, issued October 7, 1941.)

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 to be added 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 begins to occur and also decrease the rate of 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 predicted from a simply additive effect.

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.

2

One object of our invention is to provide a substantially non-corrosive 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 of our invention 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 consists of the addition to lubricants of all kinds of salts or soaps of certain 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 purely organic or purely metallic or organometallic. In introducing sulfur into the acid radical of our salts, we have found that certain compounds rich in sulfur react with unsaturated acids to yield peculiarly effective addends for lubricating oils. By compounds rich in sulfur, we mean those containing more than 50 per cent of sulfur in their molecular composition. Examples of these reagents are phosphorus pentasulfide, phosphorus pentasulfide, phosphorus trisulfide, and alkali metal polysulfides (sodium disulfide, potassium trisulfide, and higher sulfides). These particular sulfurizing agents yield particularly effectively bound sulfur in the molecule of the sulfurized acid. The herein described salts of such sulfurized acids are extraordinary detergents and inhibitors of oxidation when added to lubricants of all kinds. They contain no corrosive halogen and are more effective inhibitors than salts of acids containing sulfur in known structures such as sulfonic acids, sulfones, thioethers, heterocyclic sulfur, 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. Alkali metal polysulfide-treated acids
  1. Sodium pentasulfide - treated oleic acid
  2. Sodium tetrasulfide - treated linoleic acid
  3. Sodium trisulfide-treated linolenic acid
  4. Sodium disulfide-treated elaidic acid
  5. Potassium pentasulfide-treated corn oil acids
  6. Potassium trisulfide - treated soy oil acids
  7. Potassium tetrasulfide-treated lard oil acids
  8. Lithium pentasulfide-treated tung oil acids
  9. Lithium tetrasulfide - treated abietic acid
  10. Lithium trisulfide - treated cholic acid
  11. Ammonium pentasulfide-treated naphthenic acids
- B. Phosphorus sulfide treated acids (containing phosphorus and sulfur)
  1. Phosphorus pentasulfide-treated corn oil acids
  2. Phosphorus trisulfide-treated corn oil acids
  3. Phosphorus pentasulfide-treated soy oil acids
  4. Phosphorus pentasulfide-treated oleic acid
  5. Phosphorus pentasulfide-treated linoleic acid

II. Cations
- A. Metallic
  1. Group 1
     Lithium, sodium, potassium, rubidium, cesium, copper
  2. Group 2
     Calcium, strontium, barium, beryllium, magnesium, zinc, cadmium, mercury
  3. Group 3
     Aluminum, gallium, indidium, thallium
  4. Group 4
     Titanium, zirconium, tin, lead
  5. Group 5
     Arsenic, antimony, bismuth
  6. Group 6
     Chromium, molybdenum, tungsten
  7. Group 7
     Manganese
  8. Group 8
     Iron, cobalt, nickel
- B. Organo-Metallic

These organo-metallic soaps may have, in the organo-metallic cation, an organic radical or radicals of the aliphatic or carbocyclic or heterocyclic series. The metallic element of the compound may be any one of a number of which the following are representative. For convenience, we shall list them in accordance with their occurrence in the periodic table:

Group II
- Magnesium
- Zinc
- Cadmium
- Mercury

Group III
- Boron
- Aluminum
- Thallium

Group IV
- Silicon
- Tin
- Lead

Group V
- Arsenic
- Bismuth
- Antimony

Group VI
- Tellurium
- Selenium

Some of the organo-metallic radicals which may act as cations in forming the soaps to be used are:

Group II
- Phenylmagnesium
- Propyl magnesium
- Methylzinc
- Cresylzinc
- Xylylcadmium
- Iso-Amylcadmium
- Butylmercury
- Mesitylmercury
- Nitrophenylmercury
- Naphthylmercury

Group III
- Phenylboron (II)
- Diphenylboron (I)
- o-Xylylboron (II)
- Dipropylaluminum
- Diethylthallium
- Diphenylthallium
- Di-p-tolylthallium

Group IV
- Triphenylsilicon
- Triphenylgermanium
- Di-isoamyltin
- Di-alpha-naphthyltin
- Diphenyltin
- Ethylphenyltin
- iso-Propyltin
- Triethyltin
- Triphenyltin
- Di-isobutyllead
- Diethyllead
- Diphenyllead
- Triphenyllead

Group V
- Ethylarsenic
- Diphenylantimony
- Di-alphanaphthylbismuth
- Diphenylbismuth

Group VI
- Phenyltellurium
- Diphenyltellurium
- Triphenyltellurium
- Phenylselenium

The soaps derived from these organo-metallic radicals may contain in the organic radical or attached to the metal or in the anion of the soap 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. Sodium salts of sulfurized corn oil acids
2. Aluminum salts of sulfurized beta fat
3. Stannous salts of sulfurized corn oil acids
4. Stannic salts of sulfurized corn oil acids
5. Ammonium salts of sulfurized soy oil acids
6. Triphenyltin salts of sulfurized corn oil acids
7. Diethylthallium salts of sulfurized corn oil acids
8. Phenylmagnesium salt of sulfurized oleic acid
9. Nitrophenylmercuric salt of sulfurized lard oil acids
10. Diphenylthallium salts of sulfurized soybean oil acids
11. Triamylammonium salts of sulfurized lard oil acids
12. Calcium salts of sulfurized corn oil acids
13. Lead salts of sulfurized beta fat
14. Barium salt of sulfurized oleic acid, sulfurized with sodium pentasulfide
15. Triphenyltin salt of sulfurized oleic acid
16. Benzyltrimethylammonium salt of sulfurized oleic acid, sulfurized with phosphorus pentasulfide
17. Calcium salt of sulfurized oleic acid, sulfurized with sodium pentasulfide
18. Calcium salt of sulfurized oleic acid, sulfurized with sodium trisulfide
19. Benzyltrimethylammonium salts of sulfurized corn oil acids, sulfurized with sodium pentasulfide
20. Triphenyltin salts of sulfurized soybean oil acids, sulfurized with phosphorus pentasulfide

While all of the above examples give the unusual results described, we have found that particular emphasis should be placed on the organo-metallic salts of sulfur-bearing acids because they are especially effective antioxidants and corrosion inhibitors; furthermore the tin salts (metallic or organo-metallic) deserve notice as exhibiting these properties to a high degree.

The addends of this invention have a dual action in a lubricant. One 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 organo-metallic compounds 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, soybean 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 metallic 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 subcombinations are of utility and may be employed without reference to other features and subcombinations. 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.

We claim:

1. A lubricant comprising in combination a major proportion of oil of lubricating viscosity and a minor proportion, sufficient to stabilize said oil against oxidation, of a salt of a sulfurized relatively high molecular weight carboxylic acid, said carboxylic acid being unsaturated and being sulfurized by reaction with sodium pentasulfide.

2. A lubricant comprising in combination a major proportion of oil of lubricating viscosity and a minor proportion, sufficient to stabilize said oil against oxidation, of a metallic salt of a sulfurized relatively high molecular weight carboxylic acid, said carboxylic acid being unsaturated and being sulfurized by reaction with sodium pentasulfide.

3. A lubricant comprising in combination a major proportion of oil of lubricating viscosity and a minor proportion, sufficient to stabilize said oil against oxidation, of an organo-metallic salt of a sulfurized relatively high molecular weight carboxylic acid, said carboxylic acid being unsaturated and being sulfurized by reaction with sodium pentasulfide.

4. A lubricant comprising in combination a major proportion of oil of lubricating viscosity and a minor proportion, sufficient to stabilize said oil against oxidation, of a salt of an organic base and a sulfurized relatively high molecular weight caboxylic acid, said carboxylic acid being unsaturated and being sulfurized by reaction with sodium pentasulfide.

5. A lubricant comprising in combination a major proportion of oil of lubricating viscosity and a minor proportion, sufficient to stabilize said oil against oxidation, of a salt of a sulfurized relatively high molecular weight aliphatic carboxylic acid, said aliphatic carboxylic acid being unsaturated and being sulfurized by reaction with sodium pentasulfide.

6. A lubricant comprising in combination a major proportion of oil of lubricating viscosity and a minor proportion, sufficient to stabilize said oil against oxidation, of a metallic salt of a sulfurized relatively high molecular weight aliphatic carboxylic acid, said aliphatic carboxylic acid being unsaturated and being sulfurized by reaction with sodium pentasulfide.

7. A lubricant comprising in combination a major proportion of oil of lubricating viscosity and a minor proportion, sufficient to stabilize said oil against oxidation, of an organo-metallic salt of a sulfurized relatively high molecular weight aliphatic carboxylic acid, said aliphatic carbox-

ylic acid being unsaturated and being sulfurized by reaction with sodium pentasulfide.

8. A lubricant comprising in combination a major proportion of oil of lubricating viscosity and a minor proportion, sufficient to stabilize said oil against oxidation, of a salt of an organic base and a sulfurized relatively high molecular weight aliphatic carboxylic acid, said aliphatic carboxylic acid being unsaturated and being sulfurized by reaction with sodium pentasulfide.

9. A lubricant comprising in combination a major proportion of oil of lubricating viscosity and a minor proportion, sufficient to stabilize said oil against oxidation, of a salt of sulfurized soybean oil acids, said soybean oil acids being sulfurized by reaction with sodium pentasulfide.

10. A lubricant comprising in combination a major proportion of oil of lubricating viscosity and a minor proportion, sufficient to stabilize said oil against oxidation, of a salt of sulfurized corn oil acids, said corn oil acids being sulfurized by reaction with sodium pentasulfide.

11. A lubricant comprising in combination a major proportion of oil of lubricating viscosity and a minor proportion, sufficient to stabilize said oil against oxidation, of a salt of sulfurized oleic acid, said oleic acid being sulfurized by reaction with sodium pentasulfide.

12. A lubricant comprising in combination a major proportion of oil of lubricating viscosity and a minor proportion, sufficient to stabilize said oil against oxidation, of benzyltrimethyl ammonium salts of sulfurized corn oil acids, said corn oil acids being sulfurized by reaction with sodium pentasulfide.

13. A lubricant comprising in combination a major proportion of oil of lubricating viscosity and a minor proportion, sufficient to stabilize said oil against oxidation, of the calcium salt of sulfurized oleic acid, said oleic acid being sulfurized by reaction with sodium pentasulfide.

14. A lubricant comprising in combination a major proportion of oil of lubricating viscosity and a minor proportion, sufficient to stabilize said oil against oxidation, of triphenyltin salts of sulfurized soybean oil acids, said soybean oil acids being sulfurized by reaction with sodium pentasulfide.

15. A lubricant comprising in combination a major proportion of oil of lubricating viscosity and from 0.001 to 10 per cent of a salt of a sulfurized relatively high molecular weight carboxylic acid, said carboxylic acid being unsaturated and being sulfurized by reaction with sodium pentasulfide.

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