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LUBRICANTS

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This invention relates to improved lubricants. More particularly it relates to compounded oils which have, in addition to valuable lubricating properties, the property of preventing corrosion on metal surfaces.

Engines which are exposed without operation to the atmosphere for considerable periods of time develop considerable corrosion, so that frequently they become inoperable or operate with greatly reduced efficiency for a shorter useful operating life.

The above observations apply with particular force to engines exposed to severely corrosive atmospheres, such as are encountered, for example, on shipboard, in coastal areas, and in many industrial areas. Engines in military equipment are often subjected to storage in corrosive atmospheres for long periods of time, for example in transoceanic shipping. Furthermore, the operation of internal combustion engines, especially spark ignition engines, results in the production of gases which corrode various metal engine parts with which they come in contact. Particularly corrosive gases are generated in the operation of internal combustion engines upon fuels containing ethyl fluid.

Heretofore it has been proposed to protect metal surfaces from corrosion by the use of readily removable protective coatings, known as slushing compounds. Slushing compounds are petroleum rust preventives and are usually classified as oils and greases, from the standpoints of appearance, handling and service properties.

Lubricating oils which can also be used as a rust preventive for internal combustion engines, in addition to meeting the usual specifications concerning viscosity, volatility and pour point, must have four main properties:

- (1) Ability to protect against high humidity and moisture condensation;
- (2) A minimum effect on all metals which may be included in an engine assembly;
- (3) Ability to be readily applied to and removed from an engine assembly;
- (4) Ability to neutralize acidic products of combustion in the engine.

It will be apparent that practical specifications based on the above properties can hardly be absolute in nature, but relative standards, represented by certain tests, have been offered and widely accepted. These tests will be described briefly. Unless otherwise indicated, all tests are carried out upon cold rolled, sandblasted S. A. E. 1020 steel panels, 2" x 4" x $\frac{1}{16}$ ".

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In the humidity test, the steel panels are suspended in an atmosphere of 100% humidity at 100° F. in a special cabinet and the time of initial corrosion of the panels is noted. The humidity cabinet is provided with heating units and thermal regulators for automatic temperature control. A water level of two to three inches is maintained in the bottom of the cabinet to give approximately 100% humidity at all times. The steel panels are coated by dipping into the rust preventive material and are suspended by glass hooks from a glass rod running across the top of the humidity cabinet. To insure that no moisture of condensation comes in contact with the steel panels, stainless steel shields are placed above the panels in such a position that no moisture from the shields can drip on the panels. From 1 to 1.5 complete changes of saturated air per hour are provided in the cabinet. A satisfactory rust preventive should give a minimum of 200 hours protection to the steel panels in the humidity test.

In the test designed to evaluate the effects of the rust preventive composition on metals, cleaned lead, copper, magnesium and steel panels, respectively, are immersed to the extent of three-quarters of their area in 160 grams of the rust preventive composition to which 1% of water has been added. After seven days storage at 160° F. the change in weight of each panel is determined.

In this test, coupled lead-steel panels also are tightly clamped together at an angle of approximately 30 degrees and immersed as described above. Panels of lead, copper and magnesium 2" x 4" x $\frac{1}{16}$ " should not show more than 25 mg. change in weight. Likewise coupled panels of lead-steel should not show more than 35 mg. change in weight.

The salt water immersion test is designed to measure the ability of rust preventives to protect metal parts against salt air or sea water. In this test the steel panel is dipped in the rust preventive oil, allowed to drain for 24 hours at room temperature, and is then placed in a 3.5% salt solution for twenty hours. At the conclusion of this time the panel must show no evidence of corrosion, staining, or rust.

The hydrobromic acid test is designed to measure the ability of the rust preventive oil to neutralize the acidic products of combustion of an internal combustion engine. In this test, the steel panel is dipped in 0.1% aqueous hydrobromic acid solution momentarily and is then slushed with the rust preventive oil for one minute. The panel is then hung in the laboratory atmosphere for four hours and allowed to drain.

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At the conclusion of this time the panel must show no corrosion, staining or rust.

Hydrocarbon lubricating oils produced by conventional petroleum refining methods do not possess the combination of properties necessary for service both as lubricants and rust preventives. The observation is common that rusting can occur on steel surfaces which have been coated with the usual straight mineral oils or petrolatums. In order to obtain the desired combination of properties, there has been a trend toward hydrocarbon oils compounded with various chemical agents, with more or less indifferent success.

Experience has shown that often the addition of a given reagent to a hydrocarbon lubricant results in the improvement of one desired property of the lubricant but exerts a deleterious effect on one or more of the other desired properties, so that the net result is that it is disadvantageous to add the reagent in question to the lubricant.

Although compounded oils satisfactorily exhibiting the first three properties described above have been produced, they have generally failed in the fourth property.

My copending application Serial No. 500,277, filed August 27, 1943, of which the present application is a continuation-in-part, relates to improved lubricant compositions having valuable lubricating properties as well as atmospheric corrosion inhibiting properties. However, it has been found that while the lubricant described in my copending application is an effective corrosion inhibiting lubricant, under some conditions it does not provide the desired corrosion inhibiting properties particularly with respect to the corrosion of special alloy bearings, for example those of the copper-lead or cadmium-silver type, under operating conditions.

Accordingly, it is an object of the present invention to provide a lubricant which is effective in preventing atmospheric corrosion as well as corrosion to internal parts of engines, particularly bearings of the hard metal alloy type, under operating conditions. Another object of this invention is to provide a corrosion preventive lubricating composition for internal combustion engines, particularly spark ignition engines. Still another object of this invention is to provide a corrosion preventive lubricating composition characterized by the ability to neutralize acidic engine combustion products while retaining the other desirable properties of corrosion preventive lubricants. Additional objects will become apparent as the description of this invention proceeds.

I have found that compositions comprising a small proportion of a castor compound, a sulfurized terpene, a preferentially oil-soluble petroleum sulfonate and a hydrocarbon lubricating oil possess the combination of properties desired in corrosion preventive lubricants.

By a castor compound I means castor oil or its derivatives. Suitable castor compounds include castor oil, castor amide and glycerol mono-ricinoleate. Although many castor compounds can be used successfully in my corrosion preventive lubricating composition, it is not intended to imply that they are all exactly equivalent in efficacy. In general, about 1% to about 10% of castor compound can be used, although somewhat smaller or larger proportions can also be used.

In general from about 0.1% to about 2% sulfurized terpene can be used. Suitable sulfurized

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terpenes are sulfurized dipentene, sulfurized pine oil, sulfurized turpentine, sulfurized pinene, sulfurized terpenol, sulfurized camphene and the like or mixtures of terpenes. I prefer to use sulfurized terpenes comprising a major part of dipentenes.

The sulfurized terpenes can be prepared by sulfurizing the desired terpene by any one of various sulfurization processes. Among the sulfurization processes which can suitably be employed is that of treating the terpene with sulfur and hydrogen sulfide in the presence of water or steam at temperatures within the range of about 250° F. to 450° F. and at pressures up to about 1500 pounds per square inch for a period of 1 to 10 hours. The sulfurized terpene can also be prepared by treating the desired terpene with a sulfur chloride, such as S_2Cl_2 or SCl_2 , at a temperature within the range of about 60° F. to about 250° F. When the terpene is sulfurized with a sulfur chloride, the chlorine present in the sulfurized material can be removed by treating the sulfurized material in a bomb at a temperature of about 300° F. to about 400° F. with ammonia or other aqueous or alcoholic alkalies, alkali metal sulfides and polysulfides, such as a sodium sulfide, or other bases. The sulfurized terpenes which are best suited for the herein-described purpose are those which have a sulfur content of from about 5% to about 45% or more and which show slight sulfur activity, as defined below, at 210° F. with increasing activity at higher temperatures, and show a decided activity at temperatures of the order of about 300° F. or higher.

The sulfurized terpenes may be characterized by their activity toward copper at various temperatures. This may be empirically evaluated by immersing a polished copper strip in a mineral oil containing the sulfurized terpene and examining the strip periodically. The more desirable sulfurized terpenes show little activity toward copper at 210° F. when used in relatively low concentrations, e. g. up to 2% in oil, but quickly darken a copper strip at 300° F. when used in the same concentrations. The sulfurized terpenes containing active sulfur, as measured by rapid darkening of the copper strip at 300° F. are effective corrosion inhibitors in the engine when used in concentrations as low as 0.5%. Sulfurized terpenes containing less active sulfur are also effective corrosion inhibitors in the engine but ordinarily higher concentrations are required. The sulfur activity of the sulfurized terpenes may be increased by heating the sulfurized material to temperatures of from about 300° F. to about 450° F. Sulfur activity of the sulfurized terpenes can also be increased by distilling the sulfurized terpene under conditions whereby the high sulfur-bearing fractions are concentrated in a 40% to about 95% bottoms. The sulfurized terpenes can also be concentrated by blowing the same with a gas at temperatures of about 150° F. to about 350° F. Sulfurized terpenes having a sulfur content above about 25% and preferably about 30% to about 40% or higher are most suitable when it is desired to employ low concentrations of the sulfurized terpenes in the finished lubricant.

Petroleum sulfonates are soaps of sulfonic acids obtained by the treatment of petroleum oils with strong sulfuric acid, usually fuming sulfuric acid. The preferentially oil-soluble sulfonic acids remain dissolved in the acid treated oil; they are commonly known as mahogany acids. Although a wide variety of mahogany soaps can be used for the purposes of this invention, I have found

that they exhibit some variation in efficacy in my corrosion preventive lubricating compositions, depending on their method of preparation.

I have found that superior mahogany acids and soaps therefrom, for the purpose of this invention, can be produced by treating distillates of from about 50 seconds to about 1000 seconds or higher, and preferably from about 200 to about 850 seconds Saybolt Universal viscosity at 100° F. with from about 6 to about 9 pounds, and preferably from about 7 to about 8 pounds of concentrated sulfuric acid, preferably fuming sulfuric acid, per gallon of oil.

The method of obtaining these desirable soaps of preferentially oil-soluble sulfonic acids derived from petroleum oils is illustrated by the following example, which describes the preparation of a sodium soap.

A petroleum oil distillate having a Saybolt Universal viscosity at 100° F. of from about 200 seconds to about 850 seconds is treated with from about 7 to about 8 pounds of fuming sulfuric acid per gallon of oil in one-half pound increments or "dumps." After the acid sludge from each one-half pound acid "dump" is settled and withdrawn, the next one-half pound of fuming sulfuric acid is added to the oil. The temperature of the oil before the fuming acid is added thereto is maintained below about 60° F. but due to the heat of reaction upon the addition of the sulfuric acid, the temperature of the oil may rise to from about 90° F. to about 100° F. After the required total amount of fuming sulfuric acid has been added to the oil and the oil freed of acid sludge, the acid treated oil containing oil-soluble sulfonic acids dissolved therein, is neutralized with a solution of sodium hydroxide. The aqueous alkali solution is then separated from the oil solution containing dissolved therein sodium soap of sulfonic acids and the latter then separated from the oil by extraction with alcohol of about 60% strength. The alcohol layer containing dissolved sodium sulfonates is then separated from the oil and subsequently distilled to recover the alcohol and remove water. The crude sulfonic soap obtained in this manner contains from about 30% to about 60% sodium sulfonate, from about 30% to about 60% oil, from about 1% to about 10% water, and up to 10% of inorganic salts which may be removed by the procedure hereinafter described.

The above procedure may be modified after the acid sludge is removed from the acid treated oil. The oil containing dissolved sulfonic acids is extracted with about 60% alcohol to remove the sulfonic acids which may then be neutralized with sodium hydroxide and subsequently freed of the alcohol by distillation.

The crude soaps of these preferentially oil-soluble sulfonic acids obtained by the procedure described above may be freed of inorganic salts by purification. This purification is preferably accomplished by dilution of the crude soap with from about ½ to about 10 parts, preferably 1 to 2 parts of 50% or higher strength alcohol, preferably alcohol of 60 to 70% strength, and allowing the salts to settle while maintaining the mixture within the temperature range of 130 to 175° F., preferably 155 to 165° F. When the salts have settled the supernatant alcohol-soap layer is separated and the alcohol is recovered by conventional distillation procedure. By this method of purification the salt content of the crude sulfonic soap can be readily reduced to 5% or less, e. g., to about 3.5%.

Suitable soaps of preferentially oil-soluble petroleum sulfonic acids include those of metals in groups I, II, III, IV, VI and VIII of the periodic table. Thus, for example, I can employ the sodium, potassium, lithium, calcium, barium, tin, lead, aluminum, chromium, cobalt and nickel soaps of preferentially oil-soluble petroleum sulfonic acids. I can also employ the ammonium, alkylammonium and alkylamine soaps of preferentially oil-soluble petroleum sulfonic acids. It is not intended to imply that the wide variety of sulfonates mentioned above are exactly equivalent for the purpose of my corrosion preventive lubricating compositions. Because of their relative cheapness and high efficacy I prefer to use the sodium soaps, especially the sodium soaps of the preferred mahogany acids whose preparation has been described above.

The exact proportion of petroleum sulfonate to be used in my corrosion preventive lubricating compositions will vary with the particular sulfonate chosen for use and upon the severity of the service conditions which are anticipated. In general, I have found that a useful range of petroleum sulfonate is about 20% to about 40%, the actual sulfonate soap content being in the range of about 8 to about 20%.

I can use any one of a wide variety of hydrocarbon lubricating oils. The hydrocarbon lubricating oil can be a pure or relatively pure individual hydrocarbon or a definite hydrocarbon mixture, or the complex mixture of hydrocarbons which constitute the lubricating oils produced in conventional petroleum refining operations. The choice of the particular oil to be used will depend on the viscosity desired and the lubricating qualities of the oil and the viscosity desired in the corrosion preventive lubricating composition. In general, I can satisfactorily use petroleum lubricating oils having a viscosity in the range of about 50 to about 80 seconds Saybolt Universal at 210° F.

Although slushing compounds which have previously been prepared by compounding mahogany sulfonates with mineral oils affords some measure of protection against corrosion on metal surfaces and exhibit the first three of the four properties mainly desired in corrosion preventive lubricating compositions, as described above, they fail completely to neutralize acid products, such as acidic products of combination in internal combustion engines, and fail to prevent substantial corrosion to the bearings of the hard metal alloy type.

Illustrative of lubricant compositions of the herein-described invention are the following:

	Example I	Example II
	Per cent	Per cent
Castor oil.....	2.0	2.0
Sodium mahogany soap.....	30.0	30.0
Sulfurized terpene.....	0.5	0.75
Hydrocarbon oil.....	67.5	67.25

The above compositions are completely satisfactory when tested by the humidity, salt solution, effect on metals, and hydrobromic acid tests previously described.

When tested in the engine, the composition illustrated by Example I gave a bearing loss of about 0.44 gram per whole bearing while the composition illustrated by Example II gave a bearing loss of about 0.21 gram per whole bearing. A satisfactory lubricant composition is one

which will prevent a bearing loss of more than 0.5 gram per full bearing.

The bearing loss is determined by subjecting the lubricant to a modified so-called "36 hour Chevrolet test," made in accordance with the Cooperative Research Council Test Procedure "C. R. C. Designation L-4-243" of February, 1943. The test is made in a six cylinder spark-ignition internal combustion engine equipped with two copper-lead alloy bearings and operating at about 3150 R. P. M. with an oil temperature of $250^{\circ}\text{F.} \pm 2^{\circ}\text{F.}$, for 10 grade oils, and $265^{\circ}\text{F.} \pm 2^{\circ}\text{F.}$ for 30 grade oils. The copper-lead alloy bearings are weighed before the test and at the end of the test period and the amount of corrosion expressed in grams per full bearing loss during the test period.

In addition to the hereinbefore-mentioned additives, the lubricant compositions can include polymeric thickeners, viscosity index improvers, oiliness agents, pour point depressants, antioxidants for castor oil compounds, antioxidants for hydrocarbon oils, etc.

The herein-described lubricant compositions are not only applicable to the protection of the interiors of internal combustion engines but are also applicable generally to the protection of metal surfaces as in gun barrels, metal containers, idle machinery, finished machine parts and accessories in storage, stand-by or emergency equipment, etc.

While I have described my invention by reference to certain preferred embodiments thereof, the same has been given by way of illustration only and is not intended to be a limitation of the scope of the invention except in so far as the same is defined by the appended claims.

I claim:

1. A lubricant composition having corrosion inhibiting properties comprising from about 1% to about 10% of a castor compound, selected from the group consisting of castor oil, castor amide and glycerol monoricinoleate, from about 0.1% to about 2% of a sulfurized terpene, small but corrosion inhibiting amounts of a soap of a preferentially oil-soluble petroleum sulfonic acid, and a major proportion of a hydrocarbon lubricating oil.

2. A composition of matter comprising from about 8% to about 20% of a soap of a preferentially oil-soluble petroleum sulfonic acid, from about 1% to about 10% of a castor compound selected from the group consisting of castor oil, castor amide, and glycerol monoricinoleate, from about 0.1% to about 2% of a sulfurized terpene and a major proportion of a hydrocarbon lubricating oil.

3. A composition of matter comprising from about 8% to about 20% of a soap of a preferentially oil-soluble petroleum sulfonic acid, from about 1% to about 10% castor oil, from about 0.1% to about 2% of a sulfurized terpene and a major proportion of a hydrocarbon lubricating oil.

4. A composition of matter comprising from about 8% to about 20% of a soap of a preferentially oil-soluble petroleum sulfonic acid, from about 1% to about 10% castor amide, from about 0.1% to about 2% of a sulfurized terpene and a major proportion of a hydrocarbon lubricating oil.

5. A composition of matter comprising from 8% to about 20% of a soap of a preferentially oil-soluble petroleum sulfonic acid, from about 1% to about 10% glycerol monoricinoleate, from about

0.1% to about 2% of a sulfurized terpene and a major proportion of a hydrocarbon lubricating oil.

6. A composition of matter comprising about 20% to about 40% of a soap of a preferentially oil-soluble sulfonic acid produced by treating a petroleum distillate having a viscosity in the range of about 50 to about 1000 seconds Saybolt Universal at 100°F. with from about 6 to about 9 pounds of strong sulfuric acid, and about 1% to about 10% of a castor compound selected from the group consisting of castor oil, castor amide and glycerol monoricinoleate, about 0.1% to about 2% of a sulfurized terpene, and a major proportion of a hydrocarbon lubricating oil.

7. A composition of matter comprising about 20% to about 40% of a soap of a preferentially oil-soluble sulfonic acid produced by treating a petroleum distillate having a viscosity in the range of about 50 to about 1000 seconds Saybolt Universal at 100°F. with from about 6 to about 9 pounds of strong sulfuric acid, about 1% to about 10% of castor oil, about 0.1% to about 2% of a sulfurized terpene, and a major proportion of a hydrocarbon lubricating oil.

8. A composition of matter comprising about 20% to about 40% of a soap of a preferentially oil-soluble sulfonic acid produced by treating a petroleum distillate having a viscosity in the range of about 50 to about 1000 seconds Saybolt Universal at 100°F. with from about 6 to about 9 pounds of strong sulfuric acid, about 1% to about 10% of a castor amide, about 0.1% to about 2% of a sulfurized terpene, and a major proportion of a hydrocarbon lubricating oil.

9. A composition of matter comprising about 20% to about 40% of a soap of a preferentially oil-soluble sulfonic acid produced by treating a petroleum distillate having a viscosity in the range of about 50 to about 1000 seconds Saybolt Universal at 100°F. with from about 6 to about 9 pounds of strong sulfuric acid, about 1% to about 10% of glycerol monoricinoleate, about 0.1% to about 2% of a sulfurized terpene exhibiting high sulfur activity at a temperature of about 300°F. and higher, and a major proportion of a hydrocarbon lubricating oil.

10. A composition of matter comprising about 20% to about 40% of a sodium soap of a preferentially oil-soluble sulfonic acid produced by treating a petroleum distillate having a viscosity in the range of about 50 to about 1000 seconds Saybolt Universal at 100°F. with from about 6 to about 9 pounds of strong sulfuric acid, about 1% to about 10% of a castor compound selected from the group consisting of castor oil, castor amide and glycerol monoricinoleate, about 0.1% to about 2% of a sulfurized terpene exhibiting high sulfur activity at a temperature of about 300°F. and higher, and a major proportion of a hydrocarbon lubricating oil.

11. A composition of matter comprising about 20% to about 40% of a sodium soap of a preferentially oil-soluble sulfonic acid produced by treating a petroleum distillate having a viscosity in the range of about 50 to about 1000 seconds Saybolt Universal at 100°F. with from about 6 to about 9 pounds of strong sulfuric acid, about 1% to about 10% of castor oil, about 0.1% to about 2% of a sulfurized terpene exhibiting high sulfur activity at a temperature of about 300°F. and higher, and a major proportion of a hydrocarbon lubricating oil.

12. A composition of matter comprising about 20% to about 40% of a sodium soap of a prefer-

entially oil-soluble sulfonic acid produced by treating a petroleum distillate having a viscosity in the range of about 50 to about 1000 seconds Saybolt Universal at 100° F. with from about 6 to about 9 pounds of strong sulfuric acid, about 1% to about 10% of castor amide, about 0.1% to about 2% of a sulfurized terpene exhibiting high sulfur activity at a temperature of about 300° F. and higher, and a major proportion of a hydrocarbon lubricating oil.

13. A composition of matter comprising about 20% to about 40% of a sodium soap of a preferentially oil-soluble sulfonic acid produced by treating a petroleum distillate having a viscosity in the range of about 50 to about 1000 seconds Saybolt Universal at 100° F. with from about 6

to about 9 pounds of strong sulfuric acid, about 1% to about 10% of glycerol monoricinoleate, about 0.1% to about 2% of a sulfurized terpene exhibiting high sulfur activity at a temperature of about 300° F. and higher, and a major proportion of a hydrocarbon lubricating oil.

14. A lubricant composition as described in claim 1 in which the soap of a preferentially oil-soluble petroleum sulfonic acid is a sodium soap of a preferentially oil-soluble petroleum sulfonic acid.

15. A composition as described in claim 2, in which the soap of a preferentially oil-soluble petroleum sulfonic acid is a sodium soap of a preferentially oil-soluble petroleum sulfonic acid.

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