Patented July 7, 1953

2,644,793

UNITED STATES PATENT OFFICE

2,644,793

RUST INHIBITING COMPOSITION

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No Drawing. Application August 30, 1950, Serial No. 182,421

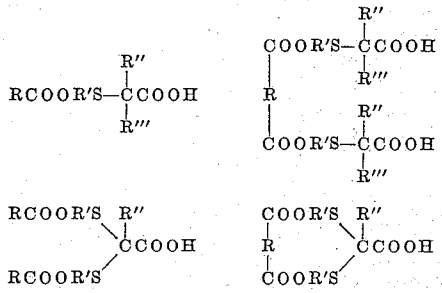
9 Claims. (Cl. 252—48.6)

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This invention relates to rust preventing oil compositions and more particularly to mineral lubricating oil compositions which tend to inhibit rusting and corrosion of metal parts which are exposed to moisture.

A primary object of the present invention is the preparation of compositions which may be employed as internal combustion engine lubricants and which will also serve for protection of exposed surfaces of such engines when the same are not in use. When operating engines in climates having a high humidity, rusting begins within a very short period of time after the engine is shut down. The compositions of the present invention are particularly valuable in preventing such rusting, and they are useful not only in the lubrication of internal combustion engines but with oil bases of suitable viscosity they may be employed as turbine oils or as lubricants for fire arms, ordnance equipment, industrial machinery, etc., and for any lubricating purposes where metal surfaces are exposed to humid air. The compounds may also be added to other mineral oil bases and employed in motor fuels, emulsions, hydrocarbon polymers, polishes, paints, sprays, and the like.

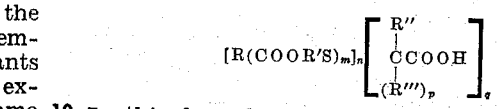
The compositions of the present invention consist essentially of a hydrocarbon oil solvent containing dissolved therein a compound which may be described as a carboxyalkylthioalkyl ester of an aliphatic carboxylic acid. Compounds of this type may be formed by first esterifying a carboxylic acid with a mercaptoalkanol and then reacting the ester thus formed with a fatty acid which contains one or two chlorine atoms substituted in the alpha position, or the ester may be reacted with an alkali metal salt of such chlorinated acid and the resulting reaction product converted into the free acid. The mercaptoalkyl esters may be formed from either monocarboxylic or dicarboxylic acids, but compounds containing two or more dicarboxylic acid radicals per molecule are not contemplated in connection with this invention. With this limitation, the following types of reaction products are possible:



In the above formulas, R is an alkyl, alkenyl or cycloaliphatic group containing 2 to 21 carbon atoms, R' is an alkylene group containing 2 to 6

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carbon atoms, R'' and R''' are hydrogen or alkyl groups, the total number of carbon atoms in both R'' and R''' being not greater than 21. These formulas may be summarized in a single general formula as follows:



In this formula, R, R' R'' and R''' have the meanings given above; m and n are integers from 1 to 2, n being 1 when m is 2; p is a number from 0 to 1 representing the presence or absence of the group R'''; and q is an integer from 1 to 2, but is 2 only when m equals 2, n equals 1 and p equals 1.

A preferred group of compounds, on account of their special suitability for the purpose of the invention and the availability of ingredients in their preparation, is represented by the formula—

$$RCOOCH_2CH_2SCH_2COOH$$

where R has the meaning given above.

The above described compounds may be prepared by first esterifying a suitable aliphatic acid with a mercaptoalkanol, e. g., mercaptoethanol, by the usual esterification processes, using a conventional esterification catalyst, such as p-toluene sulfonic acid or sulfosalicylic acid, and using a suitable solvent as required. In the second step of the process, it is desirable to convert the mercaptoalkyl ester thus formed into an alkali metal mercaptide and to react this compound with an alkali metal salt of the chlorinated fatty acid. This may be done by first reacting the mercaptoethyl ester and the chlorinated acid with a metallic base to form the metallic salt separately, or the mercaptoalkyl ester and chlorinated acid may be dissolved together in a suitable solvent and the required amount of the metallic base added. Suitable solvents for this reaction are isopropyl alcohol, ethyl alcohol, acetone, methylethyl ketone, and the like, with or without the addition of water, depending upon the solubility characteristics of the reactants. The reaction is exothermic and the temperature should normally be maintained within the range of 10° to 90° C. The reaction will normally be completed in about one to two hours. After completion of the reaction, the reaction mixture is acidified, e. g., with hydrochloric acid. The nonaqueous product is separated, washed with water to remove excessive acid, dried by heating under reduced pressure, and filtered.

The aliphatic acids which are employed to form the mercaptoalkyl ester are monobasic or dibasic aliphatic or cycloaliphatic acids, either saturated or unsaturated, containing 2 to 21 carbon atoms exclusive of the carboxyl groups. Typical examples of suitable acids include propionic acid, butyric acid, caproic acid, nonanoic acid, lauric

acid, stearic acid, teracrylic acid, oleic acid, succinic acid, adipic acid, sebacic acid, erucic acid, and the like.

Among the mercaptoalkanols which may be employed to esterify the aliphatic acids above described may be mentioned mercaptoethanol, mercapto-n-propanol, mercaptoisopropanol, mercapto-n-butanol, mercapto-n-hexanol, and similar compounds, either straight chain or branched, containing 2 to 6 carbon atoms.

The chlorinated fatty acids which may be employed in the reaction described above include all mono- or di-alpha-chlorinated acids containing not more than 21 carbon atoms. Such acids will include α-monochloroacetic acid, α,α'-di-chloroacetic acid, α-chloropropionic acid, α-chloro-n-butyric acid, α-chloroisobutyric acid, α-chlorolauric acid, and the like.

The additives of the present invention may be advantageously employed as the active rust preventing ingredient in any hydrocarbon solvent, especially of the petroleum hydrocarbon type, and such solvent oils may, for example, be naphthas, spindle oils, light and heavy lubricating oil fractions, etc., and may be used when other ingredients are present such as in greases, sprays, paints, etc., and in lubricating oils containing other additives such as detergents, pour depressants, thickeners, extreme pressure agents, and the like. Plastic type products, cut-back asphalts, microcrystalline waxes, synthetic waxes, and the like, may be included in the formulations. Concentrations of the additive in hydrocarbon solvents may vary from 0.001 to 5%, although concentrations of 0.01 to 0.5% are more generally preferred, especially when the composition is a mineral lubricating oil. For commercial purposes, when the additives are to be employed in mineral lubricating oils, it is convenient to prepare concentrated oil solutions in which the amount of additives in the compositions ranges from 25 to 50% by weight and to transport and store them in such form. In preparing lubricating oil compositions the additive concentrate is merely blended with the base oil in the required amount.

Below are given detailed descriptions of preparations of three examples of additives of the type described above as well as the results of the laboratory tests which were applied to determine their effectiveness when employed in a lubricating oil composition. It is to be understood that these examples are given to illustrate the present invention and are not to be construed as limiting the scope thereof in any way.

Example 1.—Acetic acid derivative of mercaptoethyl oleate

78 g. (1 mol) of mercaptoethanol and 282 g. (1 mol) of oleic acid were esterified by refluxing in 250 cc. of toluene in the presence of 3 g. of sulfosalicylic acid as catalyst. Water was continuously removed by azeotropic distillation until the reaction was complete. The reaction mixture was filtered and the toluene removed by vacuum distillation.

171 g. (0.5 mol) of the mercaptoethyloleate prepared as described above was dissolved in 300 cc. of isopropyl alcohol and reacted with a solution of 20 g. (0.5 mol) of sodium hydroxide dissolved in 50 cc. of water, maintaining the temperature below 25° C. by external cooling. A solution of sodium chloroacetate, prepared by neutralizing a solution of 47.5 g. (0.5 mol) of chloroacetic acid in 100 cc. of water with a solution of 20 g. (0.5 mol) of sodium hydroxide dissolved in 50 cc. of water, was then added to the above mercaptide solution, maintaining the reaction temperature below 25° C. by means of external cooling. The reaction temperature was maintained for one hour at room temperature and one hour at 60° C. The mixture was then cooled, acidified with hydrochloric acid, and the product separated and washed three times with water. The product was dried by heating under reduced pressure and then filtered. 145 g. of the product was obtained having a neutralization number of 143 mg. KOH per gram and containing 6.62 weight per cent of sulfur.

Example 2.—Acetic acid derivative of mercaptoethyl laurate

78 g. (1.0 mol) of mercaptoethanol and 200 g. (1.0 mol) of lauric acid were esterified as described in Example 1 in a solution of 250 cc. of toluene containing 3 g. of sulfosalicylic acid as catalyst. 255 g. of mercaptoethyl laurate was obtained after filtering and removing the toluene by vacuum distillation.

244 g. (0.94 mol) of the mercaptoethyl laurate and 98 g. (1.03 mols) of monochloroacetic acid were dissolved in 350 cc. of isopropyl alcohol and the mixture cooled in an ice bath. A solution of 79 g. (1.98 mol) of NaOH dissolved in 200 cc. of water was added slowly with stirring, maintaining the reaction temperature at about 10° C. by means of external cooling. The reaction mixture was stirred for one hour at room temperature and 30 minutes at 60° C. It was then cooled and acidified with hydrochloric acid. The product was separated, washed with water, dried by nitrogen blowing, and filtered. 288 g. of product having a neutralization number of 168 mg. KOH per gram was obtained.

Example 3.—Acetic acid derivative of mercaptoethyl nonanoate

216 g. (0.99 mol) of mercaptoethyl nonanoate was obtained by esterifying 153 g. (1.0 mol) of nonanoic acid (obtained by the oxidation of the "Oxo" aldehyde) with 78 g. (1.0 mol) of mercaptoethanol by the procedure of Example 1.

203 g. (0.93 mol) of the ester and 97 g. (1.03 mols) of monochloroacetic acid were dissolved in 350 cc. of isopropyl alcohol and 79 g. (1.98 mols) of sodium hydroxide dissolved in 200 cc. of water was added, maintaining the reaction temperature at about 10° C. by external cooling. The temperature of the mixture was kept at about 30° C. for 30 minutes and at 60° C. for 15 minutes, after which it was cooled and acidified with HCl. 186 g. of the product having a neutralization number of 210 mg. KOH per gram was isolated and purified by the procedure of Example 2.

Example 4.—Laboratory rusting test

Turbine oil compositions were prepared by dissolving small proportions of each of the products of Examples 1 to 3 in a solvent extracted Mid-continent lubricating oil base of 150 S. S. U. viscosity at 100° F., each of the samples containing also 0.4% by weight of di-tert.-butyl-p-cresol as an oxidation inhibitor. Samples of these compositions and of the base oil containing only the oxidation inhibitor were submitted to the standard ASTM turbine oil rust test, designation D665–47T, using the procedure (Procedure B) prescribed for synthetic sea water. The procedure, in brief, is carried out as follows:

350 cc. of the oil sample is placed in a beaker and held at a temperature of 140±2° F. A cylin-

drical steel specimen 0.50 inch in diameter and 5.5 inches long, made of 1020 cold rolled steel, is suspended in the sample and the oil stirred for 30 minutes to insure complete wetting of the steel specimen. 50 cc. of the oil sample is then pipetted out and 30 cc. of synthetic sea water added. The beaker is covered and the oil sample is stirred at a temperature of 140°±2° F. for a 24 hour period. At the end of this period the steel specimen is removed, washed with naphtha, and examined for rusting.

Results of the tests carried out as described above were as follows:

Rust Inhibitor	Concentration (Weight Percent)	Degree of Rusting
None		Very heavy.
Product of Example 1	0.05	Trace.
Product of Example 2	0.03	None.
Product of Example 3	0.05	Do.
Product of Example 3	0.03	Trace.

What is claimed is:

1. As a new composition of matter a compound of the formula—

$$RCOOCH_2CH_2SCH_2COOH$$

where R is a hydrocarbon radical selected from the group consisting of aliphatic and cycloaliphatic radicals and containing 2 to 21 carbon atoms.

2. As a new composition of matter a compound according to claim 1 in which R is the radical $CH_3(CH_2)_7CH{=}CH(CH_2)_7$.

3. A composition according to claim 1 in which R is the radical $CH_3(CH_2)_{10}$.

4. A composition according to claim 1 in which R is the radical $CH_3(CH_2)_7$.

5. A mineral lubricating oil containing dissolved therein 0.001 to 5% of the compound of the formula

$$RCOOCH_2CH_2SCH_2COOH$$

where R is a hydrocarbon radical selected from the group consisting of aliphatic and cycloaliphatic radicals and containing 2 to 21 carbon atoms.

6. A composition according to claim 5 in which R is the radical $CH_3(CH_2)_7CH{=}CH(CH_2)_7$.

7. A composition according to claim 5 in which R is the radical $CH_3(CH_2)_{10}$.

8. A composition according to claim 5 in which R is the radical $CH_3(CH_2)_7$.

9. A composition consisting essentially of a mineral lubricating oil and an additive as defined in claim 5, the amount of the additive in the composition being 25 to 50% by weight.

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