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REACTION PRODUCTS OF DICYCLIC TERPENES AND SULFONIC ACIDS

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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.

This application is a continuation-in-part of U. S. Serial No. 195,140, filed on November 10, 1950, and now abandoned.

The rust preventing additives of the present invention are particularly valuable when incorporated in the lubricating oils of internal combustion engines, but they may also be employed in turbine oils and in 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 materials of the present invention which are employed as corrosion preventing additives for mineral oils are addition products obtained by reacting together a dicyclic terpene and an essentially hydrocarbon sulfonic acid, e. g., a petroleum sulfonic acid. The addition products may be prepared for example by reacting substantially equimolar quantities of the two reactants at ordinary temperatures, but somewhat elevated temperatures, of the order of about 50° to 100° C., are preferred to accelerate the reaction. The reaction is normally completed within a period of about 1 to 3 hours at the higher temperatures. Solvents such as alcohol, alcohol-water, and oil may be employed if desired. The ratio of sulfonic acid to terpene is not critical and a molar excess of either compound may be used. Generally about one mol of terpene per mol of sulfonic acid radical is used.

Typical examples of dicyclic terpenes which may be employed are α-pinene, β-pinene, camphene, fenchene, sabinene, carene, bornylene, and natural products rich in such terpenes, such as turpentine oil.

The sulfonic acid employed to react with the dicyclic terpene may be any sulfonic acid, whether aliphatic or aromatic. Typical examples of suitable aliphatic sulfonic acids include methane-sulfonic acid, ethanesulfonic acid, n-butanesulfonic acid, n-hexanesulfonic acid, wax sulfonic acids, and the like. Typical aromatic acids include petroleum sulfonic acids, benzenesulfonic acid, m-chlorbenzenesulfonic acid, p-toluenesulfonic acid, 2,4-xylenesulfonic acid, phenolsulfonic acids, m-benzenedisulfonic acid, toluene-2,4-disulfonic acid, mixtures of C_{10}–C_{18} alkylbenzene sulfonic acids, and the like. Aromatic sulfonic acids, particularly petroleum sulfonic acids, are preferred.

The additives of the present invention may be advantageously employed as the active rust preventing ingredient in any mineral oil solvent, 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 other rust inhibitors. When employed in motor fuels they minimize oil deterioration and reduce engine deposits. In the preparation of plastic type products, cut-back asphalts, microcrystalline waxes, synthetic waxes, and the like are included in the formulations. Concentrations of the additive in mineral oil solvents may vary from 0.025 to 5%, although concentrations of 1 to 2% are more generally preferred, especially when the composition is a mineral lubricating oil. When used in aviation gasoline and in turbo-fuel for aircraft they are also effective for retarding the formation of ice crystals from water accidentally introduced in the fuel tank or in fuel-feed systems and thereby they prevent the clogging of filters. In such compositions, as little as 0.005% of the additives can be used satisfactorily.

In the examples given below there are given detailed descriptions of the preparation and testing of typical additives of this invention, but it is to be understood that these examples are given merely as illustrations and are not to be construed as limiting the scope of the invention in any way.

Example 1

A mixture of 25 g. of α-pinene and 1000 ml. of a sulfonic acid extract (containing about 500 mol. wt. petroleum sulfonic acid),[1] representing about equimolar quantities of the reactants, was refluxed with stirring for 3 hours at 83° C. The product was then poured into an evaporating dish and placed on the steam bath to remove alcohol and water. A dark, viscous, pleasant smelling material was obtained which contained 4.4% sulfur.

Example 2

1500 ml. of a sulfonic acid extract[1] (376 mol. wt. acid) was concentrated on the steam bath with nitrogen blowing to about half its volume. This concentrate and an equimolar proportion of α-pinene (49.0 g.) were refluxed with stirring for 3 hours at 88° C. The product was then poured into an evaporating dish and placed on the steam bath to remove alcohol and water. A viscous, dark colored, pleasant smelling liquid was obtained which contained 7.0% sulfur.

Example 3

A mixture of C_{12}–C_{16} alkyl benzenes was obtained by conventional alkylation of benzene with a mixture of C_{12}–C_{16} polypropenes and polybutenes. The alkyl benzenes contained an average of about 18 carbon atoms in the alkyl groups on each benzene ring. This mixture was sulfonated with sulfuric acid to form mixed sulfonic acids having an average molecular weight of about 400. A solution was prepared containing 25.2 weight percent of these sulfonic acids in mineral lubricating oil. 291 grams of the oil-sulfonic acid solution (0.2 mol sulfonic acid) and 27.2 grams (0.2 mol) of camphene were then stirred together for one hour at room temperature and then for three hours at 85° C. A clear, dark red, viscous liquid having a pleasant odor was obtained at the reaction product.

Example 4

22.0 g. (0.2 mol) of ethane sulfonic acid was added dropwise at room temperature over a 30 minute period with rapid stirring, to a solution of 27.2 g. (0.2 mol) of camphene in 50 g. of a mineral lubricating oil. A temperature rise to 50° C. was observed during this period. The reaction mixture was stirred at 85° C. for three

[1] The sulfonic acid extract contains typical predominantly aromatic petroleum sulfonic acids and is obtained by treating a petroleum lubricating oil fraction with fuming sulfuric acid, settling the sludge, and extracting the oil with isopropanol-water (50–50% vol. ratio).

hours after which a viscous dark-red liquid product was recovered.

Example 5

A mixture of 16.7 g. (0.04 mol) of wax sulfonic acid (418 average molecular weight), 5.4 g. (0.04 mol) of α-pinene, and 33.3 g. of mineral lubricating oil was heated at 85° C. for three hours. A clear, dark-red liquid product possessing a sweet odor was obtained.

Example 6

Oil compositions were prepared by dissolving 1% and 2% by weight of the products prepared as described above in Examples 1–3 in acid treated Coastal lubricating oils of 100 seconds viscosity (Saybolt) at 100° F. and 1200 seconds viscosity (Saybolt) at 100° F., respectively. These blends and samples of the unblended base stocks were submitted to a humidity cabinet test to determine the degree to which the oils prevent the rusting of a steel surface in a warm humid atmosphere. This test was conducted by dipping panels of 1020 cold rolled steel, 2" x 4" in size, in the oil samples and hanging them in an AN–H–31 humidity cabinet maintained at a temperature of 120±2° F., the panels being surrounded by air of 100% humidity. Failure under this test is considered to take place when rusting occurs to an extent greater than 3 rust spots, no one of which is greater than 1 mm. in diameter. Results are shown in the following table:

Composition:	Hours to rust
Acid treated Coastal stock, 100 SUS/100° F.	2
Acid treated Coastal stock, 100 SUS/100° F. plus 1%* of Example 1 reaction product	196
Acid treated Coastal stock, 100 SUS/100° F. plus 2%* of Example 1 reaction product	312+
Acid treated Coastal stock, 100 SUS/100° F. plus 1%* of Example 2 reaction product	156
Acid treated Coastal stock, 100 SUS/100° F. plus 2%* of Example 2 reaction product	312
Acid treated Coastal stock, 100 SUS/100° F. plus 1%* of Example 3 reaction product	50
Acid treated Coastal stock, 1200 SUS/100° F.	2
Acid treated Coastal stock, 100 SUS/100° F. plus 2%* of Example 2 reaction product	288

*Active ingredient.

What is claimed is:

1. As a composition of matter an addition product formed by reacting together a dicyclic terpene and a sulfonic acid selected from the group consisting of aliphatic and aromatic sulfonic acids.

2. As a composition of matter an addition product formed by reacting together a dicyclic terpene and an aromatic sulfonic acid.

3. As a composition of matter an addition product formed by reacting together a dicyclic terpene and a petroleum sulfonic acid.

4. As a composition of matter a reaction product formed by reacting together equimolar quantities of α-pinene and an aromatic sulfonic acid at a temperature of about 50° to 100° C.

5. As a composition of matter a reaction product formed by reacting together camphene and an aromatic sulfonic acid in substantially equimolar amounts at a temperature of about 50° to 100° C.

6. The process which comprises reacting equimolar quantities of a dicyclic terpene and a sulfonic acid selected from the group consisting of aliphatic and aromatic sulfonic acids at a temperature in the range of about 50° to 100° C.

7. A process which comprises reacting equimolar amounts of a dicyclic terpene and an aromatic sulfonic acid at about 50° to 100° C.

8. A process which comprises reacting equimolar amounts of α-pinene and a petroleum sulfonic acid for a period of about 1 to 3 hours at a temperature in the range of about 50° to 100° C.

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