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RUST INHIBITING COMPOSITION

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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 the 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 valuable 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 with more volatile oil bases and in combination with fatty substances they may be applied to form protective coatings for metal surfaces which are exposed to humid air.

The corrosion preventing compositions of the present invention are formed by adding to a suitable oil base an additive consisting of a mixed carboxylic acid-sulfonic acid ester of a polyhydroxy alcohol, where the carboxylate portion of the ester is derived from an aliphatic or cycloaliphatic carboxylic acid having from 1 to 30 carbon atoms per molecule, and the sulfonate portion is derived from an alkane or cycloalkane sulfonic acid having 1 to 30 carbon atoms per molecule. Such a mixed ester is formed by esterifying at least one hydroxyl group of polyhydroxy alcohol with a carboxylic acid and at least one hydroxyl group with a sulfonic acid.

Where the polyhydroxy alcohol is a diol the resulting diester, in order to come within the scope of this invention, is formed partially by esterification of the diol with a monocarboxylic acid and partially by esterification with a sulfonic acid, employing well known esterification methods. It is generally preferable to first partially esterify the alcohol with a carboxylic acid, as this generally produces a liquid product which can be conveniently handled in the subsequent esterification with a sulfonic acid. In this process a small amount of diester may be formed by completely esterifying the diol with either the carboxylic acid or the sulfonic acid, but such by-products will be formed only in small quantities and will not appreciably effect the inhibiting properties of the primary product. Instead of employing a carboxylic acid or sulfonic acid as such, the anhydride or acid halide of the desired acid in each case may be employed in known esterification processes.

Where the polyhydroxy alcohol contains more

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than two hydroxyl groups the polyhydroxy alcohol may be partially or completely esterified. The resulting ester must contain at least one carboxylic acid radical and at least one sulfonic acid radical, and dicarboxylic acids may be employed instead of mono-carboxylic acids. In the latter case dicarboxylic acids containing 0 to 8 carbon atoms in the chain between the two carboxyl groups are preferred. In the preparation of these polyesters one or more than one carboxylic acid and one or more than one sulfonic acid may be employed. Where a polybasic carboxylic acid is employed either normal esterification or cross linkage esterification may occur, but in either case a satisfactory mixed ester will be formed.

In the preparation of the mixed esters of the present invention any alcohol may be employed containing at least two hydroxyl groups, where the hydrocarbon portion of the alcohol is an alkyl or cycloalkyl group. Such alcohols may contain an inert substituent in the molecule. A preferred group of alcohols comprises those containing four hydroxyl groups per molecule, among which pentaerythritol and sorbitan are especially suitable examples. As further illustrations of alcohols which may be conveniently employed in accordance with the present invention may be mentioned ethylene glycol, propylene glycol, 1,3-propanediol, glycerol, pentaglycerol, tris(hydroxymethyl) nitromethane, 2-methyl-2-nitro - 1,3 - propanediol, 2-ethyl-2-nitro-1,3-propanediol, sorbitol and inositol.

The carboxylic acids which are suitable for the preparation of the rust inhibiting compositions of the present invention include any aliphatic or cycloaliphatic carboxylic acids having 1 to 30 carbon atoms per molecule and these include saturated as well as unsaturated acids having one or two carboxyl groups. Among the more preferred examples of such acids may be mentioned acetic, butyric, valeric, lauric, palmitic, stearic, oleic, linoleic, ricinoleic, eleomargic, erucic, behenic, arachidic, lignoceric and similar fatty acids, also dicarboxylic acids, such as oxalic acid, succinic acid, maleic acid and fumaric acid, also the naphthenic acids, as well as carboxylic acids derived by the oxidation of petroleum products. Naturally occurring products containing any of the above or similar acids, such as tall oil, castor oil, soybean oil, linseed oil, olive oil, tung oil, rapeseed oil, menhaden oil and the like, or acids derived therefrom may be conveniently employed. The sulfonic acids which are to be employed in the preparation of the mixed esters include any sulfonic acid derived from a saturated aliphatic or cycloaliphatic hydrocarbon containing 1 to 30 carbon atoms per molecule. These may include pure acids, such as ethanesulfonic acid, as well as mixtures of sulfonic acids such as

those obtained in the sulfonation of petroleum oils or the oxidation of mercaptans.

Some specific examples of mixed esters derived from the alcohols and acids described above are pentaerythritol mono-oleate mono-ethanesulfonate, pentaerythritol di-oleate mono-petroleum-sulfonate mono-ethanesulfonate, pentaerythritol mono-laurate tri-ethanesulfonate, pentaerythritol mono-petroleum-sulfonate mono-acetate, pentaerythritol mono-maleate mono-petroleum-sulfonate mono-oleate, sorbitan mono-oleate mono-ethanesulfonate, sorbitan di-stearate di-petroleum-sulfonate, sorbitan mono-naphthenate mono-oleate mono-ethanesulfonate, glycerol mono-oleate mono-ethanesulfonate, glycerol mono-palmitate di-petroleum-sulfonate, glycerol mono-oleate mono-acetate mono-petroleum-sulfonate, ethylene glycol mono-oleate mono-ethanesulfonate, and homologs thereof.

The additives of the present invention may be advantageously employed with petroleum fractions of a wide variety, although their preferred use is in lubricating oil bases to form lubricant compositions which also act as corrosion preventives. The base stocks may be derived from various types of crude petroleum and may consist of distillates or blends of various kinds which have been refined by any of the conventional methods. Synthetic oils may also be used such as those obtained by the polymerization of olefins or by the hydrogenation of coal or its products. In the case of lubricants, the base stock chosen will normally be that oil which without the new additives gives the optimum performance in the service contemplated. These base oils may vary considerably in viscosity and other properties depending upon the particular uses for which they are desired. For crankcase use they usually range from about 40 to 130 seconds viscosity Saybolt at 210° F. The viscosity index may range from less than 0 to 100 or even higher. Turbine oils usually have a viscosity of 40 to 60 seconds Saybolt at 210° F. Corrosion preventing compositions other than lubricating oils may comprise base stocks of a wide variety with respect to viscosity and may consist of mixtures of base stocks, as in slushing oils, which may consist of a mixture of naphtha and lubricating oil and may contain small amounts of petroleum or a fatty compound such as degras.

In addition to the materials to be added to the base stock according to the present invention, other agents may be present in lubricating compositions and other corrosion preventing compositions, such as heat thickened fatty oils, sulfurized oils, organo-metallic compounds, metallic or other soaps, sludge dispersers, antioxidants, thickeners, viscosity index improvers, pour point depressors, oiliness agents, resins, olefin polymers and colloidal solids such as graphite or zinc oxides. Typical addition agents serving the purposes described are phenol sulfides and their metallic salts, metal salts of salicylic naphthenic, organo-substituted phosphoric, and petroleum sulfonic acids, and the like. Solvents and assisting agents such as esters, ketones, alcohols, aldehydes, halogenated and nitrated compounds and the like may also be employed.

For the purpose of the present invention, the esters described herein are added to the base stock in proportions preferably ranging from 0.01% to 10% by weight and in some cases larger proportions may be employed to advantage.

The following examples illustrate the application of the present invention to a lubricant suitable for use in an airplane engine, but these examples are not to be construed as limiting the scope of the invention in any way.

EXAMPLE 1

To 200.3 g. (½ mol) of pentaerythritol mono-oleate (prepared by esterifying equal molecular quantities of pentaerythritol and oleic acid) in a 1-liter 4-necked flask equipped with a stirrer, thermometer, separatory funnel, nitrogen inlet tube, and reflux condenser equipped with a water separator was added 250 g. of toluene. The solution was refluxed at 120° C. for ½ hour to remove a small amount of water (0.2 cc.) from the reagents. Additional refluxing produced no more water. To the refluxing solution 64.3 g. (0.58 mol) of ethanesulfonic acid was added dropwise over a period of 1 hour with the temperature of the solution at 116° C. Water was produced immediately on adding the ethanesulfonic acid. After refluxing for 3 hours 9 cc. of watery distillate (about ½ mol of water) had separated from the refluxing liquid. The material was then cooled and washed twice with a saturated aqueous sodium bicarbonate solution. When the second bicarbonate washing evolved no more carbon dioxide, the ester solution was washed with water to give a solution neutral to litmus paper. The toluene was removed by distillation under reduced pressure. The ester product was a dark amber colored viscous material weighing 220 grams. The following inspections were obtained:

	Found	Calculated
Saponification No. ..... mg. KOH/g.	218.5	227.3
Acidity ..... do	4.48	0
Sulfur ..... percent	4.11	6.50
Carbon ..... do	68.17	61.00
Hydrogen ..... do	10.77	9.82

The low sulfur content and high carbon and hydrogen values indicate that the mole ratio of the sulfonate to the oleate radical to the mole ester is slightly under 1:1. The yield based on ½ mol quantities was 91.3%.

This ester was then evaluated for its rust inhibiting properties by employing it in a 1% concentration by weight in a phenol treated Mid-Continent oil of 120 seconds viscosity Saybolt at 210° F. as a crankcase oil in a single cylinder air-cooled aviation type engine of 5.7 H. P., manufactured by the Wisconsin Motor Corporation. The engine was operated at a speed of 2400 R. P. M. on 91 grade aviation gasoline containing 4 cc. tetraethyl lead per gallon. After running the engine for 8 hours with this test oil, the stainless steel cylinder, which had the same composition as the cylinders of a full scale airplane engine such as a Pratt and Whitney R1340 engine, was removed from the engine and stored in a Tenney humidity cabinet in which the temperature was caused to vary between 72° and 90° F. and the relative humidity between 94% and 53% during each 24-hour period. Typical conditions in a tropical climate were thus simulated. After each 24-hour cycle the amount of rust present on the cylinder wall was observed and the storage period continued until a test period of 10 days had been completed. The amount of rust present at each observation was recorded as the percent of the total cylinder barrel area which had become rusted. A rating of 0.5% denotes a rusted area covering approximately ¼ sq. in., since the total

cylinder barrel area is about 56 sq. in. For comparative purposes the base oil with no inhibitor was evaluated to determine its rust producing properties in a similar manner. The observations made in the two tests are given in the following table:

Cylinder rusting test (percent of cylinder wall rusted)

	Days of Storage									
	1	2	3	4	5	6	7	8	9	10
Uninhibited Oil	5	10	15	22	30	35	39	42	44	45
Same+1% Ester	0	0	0	0	0.25	0.5	0.5	0.5	0.5	0.5

For comparison, it may be noted that other tests have shown that pentaerythritol mono-oleate without the ethanesulfonate radical permitted rusting to an extent of about 10% of the cylinder after 5 days' storage under the conditions of the test.

EXAMPLE 2

To 214.5 g. (½ mol) of sorbitan mono-oleate (prepared by esterifying equal molecular proportions of either sorbitan or sorbitol with oleic acid) in the same apparatus as that used in Example 1 was added 200 g. of toluene. The solution was then refluxed at 118° C. for 1 hour during which time about 0.5 cc. of watery distillate was collected. Additional refluxing produced no more water. To the refluxing solution 55.1 g. (½ mol) of ethanesulfonic acid was added dropwise over a period of 2¼ hours. Water was produced immediately. After 3 hours refluxing 8.6 cc. of water distillate (about ½ mol) had collected in the water separator. The solution was diluted with 400 g. of toluene, washed with a saturated aqueous sodium bicarbonate solution and then finally washed with water until neutral to litmus paper. The toluene was distilled off under reduced pressure to give a dark amber colored ester product weighing 203 g., which represented a yield of 78%.

This product was evaluated in the same manner as that described under Example 1, with the following observations of the condition of the cylinder after storing for various periods in the humidity cabinet:

Cylinder rusting test (percent of cylinder wall rusted)

	Days of Storage									
	1	2	3	4	5	6	7	8	9	10
Uninhibited Oil	5	10	15	22	30	35	39	42	44	45
Same+1% Ester	1.5	2	3	5	5	5	5	5	6	7

For comparison, it may be noted that with a blend containing 1% sorbitan mono-oleate 14% rusting was observed at the end of 5 days under the same test conditions.

EXAMPLE 2

To 133.5 g. (⅓ mol) of pentaerythritol mono-oleate in a 1-liter 4-necked flask equipped with a stirrer, thermometer, separatory funnel, nitrogen inlet tube, and reflux condenser was added 100 g. of toluene. To this mixture cooled to 3° C. was slowly added 42.9 g. (⅓ mol) of ethanesulfonyl chloride over a period of ½ hour. Stirring was continued for 2 hours, after which 52.5 g. (⅔ mol) of pyridine was added over a period of 1 hour (to absorb the HCl by-product), the temperature being maintained at 3° C. After stirring for 3 more hours the mixture was allowed to warm to room temperature. The pyridine hydrochloride was filtered off and washed with 300 g. of toluene. The toluene solution of the product was then thoroughly washed with dilute hydrochloric acid, aqueous sodium bicarbonate solution, and water, after which the toluene was stripped off at 30 mm. reduced pressure. The product weighing 153 g. (representing a yield of 93.2% based on the pentaerythritol mono-oleate) was a dark amber colored viscous liquid having the following inspections:

	Found	Calculated
Saponification No. mg. KOH/g.	237.5	227.3
Acidity mg. KOH/g.	13.17	0
Sulfur percent	4.26	6.50
Carbon do	67.05	61.00
Hydrogen do	10.25	9.82
Chlorine do	0.68	0

This product was evaluated in the manner described under Example 1, with the following observations of the condition of the cylinder after storing for various periods in the humidity cabinet:

Cylinder rusting test (percent of cylinder wall rusted)

	Days of Storage									
	1	2	3	4	5	6	7	8	9	10
Uninhibited Oil	5	10	15	22	30	35	39	42	44	45
Same+1% Ester	0	0	Trace	0.25	0.5	0.5	0.5	0.5	0.5	1

It will be recalled that tests have shown that pentaerythritol mono-oleate without the ethane-

sulfonate radical permitted rusting to an extent of about 10% of the cylinder after 5 days' storage under the conditions of the test.

From the results of the three examples described above, it will be seen that the addition of the ethanesulfonate group to the pentaerythritol mono-oleate and the sorbitan monooleate group markedly increased the rust inhibiting properties of the compound.

The invention is not to be considered as limited by any of the examples described or disclosed herein, which are given by way of illustration only, but is to be limited solely by the terms of the appended claims.

What is claimed is:

1. As a new composition of matter a mixed partial ester of a polyhydroxyl alcohol selected from the group which consists of sorbitan and pentaerythritol, the esterifying group being oleic acid and ethane sulfonate.

2. As a new composition of matter pentaerythritol monooleate containing an ethane sulfonic acid esterifying group.

3. The method which comprises reacting a polyhydroxyl alcohol selected from the group which consists of sorbitan and pentaerythritol with a sufficient amount of oleic acid to esterify one hydroxyl group of said alcohol, and subsequently reacting the product thus formed, with a sufficient amount of an acidic material selected from the group which consists of ethane sulfonic acid and ethane sulfonyl chloride to esterify an additional hydroxyl group of said alcohol.

4. The method which comprises reacting pentaerythritol with a sufficient amount of oleic acid to esterify one hydroxyl group of said pentaerythritol and subsequently reacting the product thus formed with a sufficient amount of ethanesulfonic acid to esterify an additional hydroxyl group of said pentaerythritol.

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