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PARTIAL FATTY ACID ESTERS OF ALKITOL ANHYDRIDES AND A DIMERIC ACID, AS CORROSION INHIBITORS

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This invention relates to chemical compounds and mineral oil compositions containing the same. More particularly, the invention relates to the class of acid esters of dimers of dienoic and trienoic acids with partial fatty acid esters of alkitol anhydrides. The compounds of this invention have been found to possess unusually outstanding corrosion inhibiting properties, and they may be advantageously employed in mineral oil compositions without imparting undesirable water emulsification tendencies thereto.

As is well known in the art, "straight" or "uncompounded" mineral oils are often deficient in one or more respects for the particular use to which they are put. For example, a high resistance to rust or corrosion is important for fuels or lubricants which contact metal surfaces in the presence of water. Fuels or lubricants for internal combustion engines and for gas or steam turbines are examples of materials which may desirably have incorporated therein additives or improvement agents which impart corrosion inhibiting properties thereto.

Failure to provide sufficient resistance to rust or corrosion by a particular mineral oil, fuel or lubricant may result in extensive wear or damage to costly, finely-machined moving parts. In addition, the damaging effects of rust or corrosion are not necessarily limited to moving parts themselves, since rust particles may flake off and form deposits elsewhere, thereby causing clogging of conduits, valves, filters, screens, etc. To overcome this and other deficiencies of uncompounded mineral oils, various agents known as "addition agents," "additives" or "improvement agents" are commonly incorporated in the particular mineral oil to be used.

The compounds of the present invention form extraordinary effective corrosion inhibitors which may be used as improvement agents or additives for mineral oils and particularly for lubricating oils such as turbine oils, which are required to function in the presence of water without excessive emulsification. The compounds included by the invention are the acid esters of dimeric acids derived from unsaturated fatty acids containing from 6 to 22 carbon atoms and having from 2 to 3 ethylenic linkages per molecule with partial esters of fatty acids containing from 12 to 24 carbon atoms and alkitol anhydrides. Methods of making the foregoing compounds and mineral oil compositions containing these compounds are also included by the invention.

The acid esters of this invention are the reaction products resulting from the esterification of a dimerized unsaturated fatty acid of the indicated class with the desired partial fatty acid ester of an alkitol anhydride. The ratio of reactants may range from one mol of dimerized acid per mol of partial fatty acid ester up to the number of mols of dimerized acid that is equal to the number of free hydroxyl groups in the partial fatty acid ester, per mol of partial fatty acid ester.

The esterification reaction is effected in conventional manner and under conventional conditions. Thus, while

esterification may proceed slowly at room temperature, the reaction is normally advantageously accelerated by heating the reactants, usually with refluxing, and/or by the use of conventional esterification catalysts, such as hydrogen chloride, sulfuric acid, or an aromatic sulfonic acid, such as p-toluenesulfonic acid. The reaction may be driven to substantial completion by removing one of the products of reaction. Since the herein disclosed dimeric unsaturated fatty acids, partial esters of alkitol anhydrides, and their reaction products boil at a temperature substantially above the boiling point of water, the reaction conveniently may be driven to completion by removal of the water of esterification by distillation. The removal of water from the reaction mixture may be facilitated by mechanical agitation, or by bubbling an inert gas, such as nitrogen, through the reaction mixture.

By way of illustrating the foregoing process, one, two or three mols of dimerized acid may be esterified with one mol of a partial fatty acid ester containing three free hydroxyl groups, under conventional reaction conditions, with the elimination, respectively, of one, two or three mols of water of esterification, to form, respectively, a mono-, di- or tri-acid or a mono-, di-, or tri-carboxylic ester of the dimerized acid and the partial fatty acid ester.

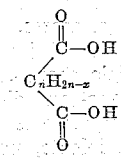
If desired, the reaction products of this invention may be prepared by effecting esterification of the reactants in mineral oil solution. This expedient is advantageous in that it prevents localized overheating of the reactants. Moreover, the resulting reaction products are in the form of mineral oil concentrates, the use of which often facilitates solution of the additives in their ultimate vehicles.

The dimerized acids referred to above are dimers, i. e., bimolecular addition products of conjugated or unconjugated dienoic or trienoic fatty acids having from 6 to 22 carbon atoms before dimerization. Dimeric acids derived from dienoic and trienoic fatty acids are well-known and can be prepared by conventional methods which form no part of this invention.

More particularly, dimerized acids capable of forming the compounds of this invention are prepared from di- or trienoic fatty acids having the generic formula

$$C_nH_{2n-x}COOH$$

where n is an integer of from 5 to 21 and x is 3 or 5. As will be evident, such monomeric acids contain from 6 to 22 carbon atoms and may contain 2 or 3 ethylenic linkages as the ratio of carbon to hydrogen increases, i. e., as x increases from 3 to 5. Dimerized acids corresponding to the addition products of the foregoing acids therefore may be defined by the generic formula:



where n is an integer of from 10 to 42 and where x is an even integer of from 6 to 10. These dimeric acids are therefore dibasic or dicarboxylic acids having from 12 to 44 carbon atoms.

Representative members of the class of dimerized acids capable of forming the compounds of this invention are dimers of dienoic acids such as sorbic (hexadienoic), linoleic (octadecadienoic), humoceric (nonadecadienoic) and eicosinic (eicosadienoic) acids. Dimers of trienoic acids, for example, linolenic and eleostearic (octadecatrienoic) acids also may be used.

It is not necessary that both of the unsaturated fatty acid molecules of the bimolecular addition product be

identical. Dimers of mixed composition such as those obtained by dimerizing mixed dienoic, mixed trienoic or mixed dienoic and trienoic acids such as may be derived from certain naturally occurring drying oils, e. g., linseed oil and soybean oil, are quite satisfactory.

Dienoic and trienoic acids having 18 carbon atoms, especially those having conjugated olefinic linkages, are preferred for reasons of economy of procurement, ease of reaction and the general excellence of the additives prepared therefrom.

The partial esters of alkitol anhydrides and fatty acids adapted for use in the formation of the reaction products of this invention are the reaction products resulting from esterification with the desired fatty acid of at least one, but less than all, of the available hydroxyl groups of an alkitol anhydride. By alkitol anhydride is meant an intramolecular, mono- or di-anhydride of a polyhydric alcohol which contains at least 4 carbon atoms and at least 4 hydroxyl groups, or mixtures of said anhydrides. Representative of the class of alkitols are erythritol; pentitols, such as arabitol, xylitol and adonitil; and hexitols such as mannitol, dulcitol and sorbitol, just as the xylitans and sorbitans are representative of the alkitol anhydrides, or alkitans.

Fatty acids capable of forming partial esters of alkitol anhydrides suited to the preparation of the additives of this invention are the fatty acids containing from 12 to 24 carbon atoms. These acids may be saturated or unsaturated, and they may be substituted with groups which do not adversely affect the oil-solubility or corrosion inhibiting properties of the final reaction product. Representative of this group of acids are lauric acid, oleic acid, ricinoleic acid, stearic acid and lignostearic acid.

Partial esters capable of reacting to form the reaction products of this invention include those formed by reacting a fatty acid of the foregoing kind with the desired alkitol anhydride in a molar ratio of at least 1:1, but less than that which would result in neutralization of all of the hydroxyl groups of the alkitol anhydride. The use of mixtures of partial fatty acid esters of alkitol anhydrides is also included within the scope of the invention. Specific examples of partial esters of alkitol anhydrides capable of reacting with dimeric unsaturated fatty acids to form acid esters included within the scope of the invention are xylitan and sorbitan mono-, sesqui-, di- and trioleates and stearates. Partial esters of hexitol anhydrides, i. e., anhydrides of polyhydric alcohols containing 6 carbon atoms and 6 hydroxyl groups, are preferred.

The partial esters of alkitol anhydrides disclosed herein as well as the method of preparing the same are conventional and form no part of the present invention. Accordingly, they need not be described in detail.

Representative specific examples of acid esters of dimeric acids with partial fatty acid esters of alkitans included in this invention are the mono- and polycarboxylic acid esters of dimerized linoleic, linolenic and eleostearic acids with sorbitan and xylitan mono-, sesqui-, di- and tri-oleates and stearates. Included within the foregoing representative class of compounds are mono-, di-, and tri-acid dilinoleic mono-, di- and tri-esters of sorbitan monooleate, mono- and di-acid dilinoleic mono- and di-esters of sorbitan dioleate, mono-acid dilinoleic mono-esters of sorbitan trioleate, mono- and di-acid dilinoleic mono- and di-esters of xylitan monooleate, mono-acid dilinoleic mono-esters of xylitan dioleate, and corresponding acid esters made from dimerized linolenic and eleostearic acids, as well as those made from partial esters of stearic acid.

The preparation of the class of compounds included by the invention can be further illustrated by the following specific example:

EXAMPLE I

An acid ester of a dimeric unsaturated fatty acid and a partial fatty acid ester of an alkitol anhydride was prepared by admixture and reaction of 428 parts by weight of sorbitan monooleate (manufactured by the Atlas Powder Company of Wilmington, Delaware, and marketed under the name "Span 80") with 560 parts by weight of dimerized linoleic acid (manufactured by Emery Industries, Inc. of Cincinnati, Ohio, and marketed under the name of Emery 955 Dimer Acid). The reaction mixture was heated under reflux, until 18 parts by weight of water had been trapped off, the maximum temperature reached by the reaction mixture being 500° F. The dimerized linoleic acid of this example had the following characteristics:

Physical state:	Straw-colored, viscous liquid
Molecular weight (approx.)	564
Gravity, ° API	13.0
Viscosity, SUV, 200° F	597
Flash, OC, ° F	510
Fire, OC, ° F	575
Color, NPA	+10
Iodine No., Mod Hanus	83.3
Saponification No	186
Neutralization No	182
Dimer content (approx.) ---percent--	85
Trimer and higher (approx.) ---do---	12
Monomer (approx.) ---do---	3

The properties of the sorbitan monooleate were as follows:

Molecular weight (approx.)	428
Gravity, °API	10.1
Sp. gr., 60°/60° F	0.999
Lb./gal., 60° F	8.32
Viscosity, SUV, Sec.:	
100° F	1827
210	108.3
Flash, P-M, °F	400
Flash, OC, °F	410
Fire, OC, °F	450
Pour, °F	+10
Physical state, room temp	Viscous liquid
Color, ASTM Union	4.5
Water by dist'n, percent	Nil
Carbon residue, Conradson, percent	2.94
Neutralization value:	
ASTM D 974–51 T—	
Total acid No	6.15
pH value, glass-calomel electrodes	7.0
Saponification No.:	
ASTM D 94–48 T	149.0
Acetyl value, Gulf 433	142
Ash, percent	0.212

The product obtained in the above-described reaction was a clear, viscous liquid containing predominantly mono-acid esters of dimerized linoleic acid and sorbitan monooleate, having the following physical properties:

Gravity, °API	13.4
Sp. gr., 60°/60° F	0.977
Lb./gal., 60° F	8.13
Viscosity, SUV, Sec.:	
100° F	9,936
210	498
Flash, P-M, °F	425
Pour, °F	0
Physical state, room temp	Viscous liquid
Color, ASTM Union	6.0
Neutralization Value:	
ASTM D 974–51 T—	
Total acid No	70
pH value, glass-calomel electrodes	4.6

The acid esters of other dimerized unsaturated fatty acids and other partial fatty acid esters of alkitol anhydrides are similarly prepared.

To facilitate handling, blending and the like, it is often desirable to utilize a mineral oil solution of the

acid esters. Typical concentrates of the above-prepared acid esters in a lubricating oil had the following properties:

Properties	Sorbitan Monooleate-Dilinoleic-Acid Esters (75% Concentration)	
	Sample No. 1	Sample No. 2
Gravity, °API (wide range in gravity)	18.0	17.5
Viscosity, SUV, Sec.:		
100° F	3,026	5,729
210° F	206	362
Flash, P-M, ° F	360	430
Pour, ° F	+5	+5
Color, ASTM Union	3.75	6.5
Water by Dist'n, percent	trace	trace
Water, p. p. m., Karl Fischer Method	1,513	
Neutralization Value, ASTM D974-52T, Total Acid No.	51.53	48.95
pH Value, Glass-Calomel Electrodes	4.5	5.1

The reaction products resulting from the above-described procedure, either alone or in the form of a mineral oil concentrate, may be incorporated in the desired vehicle in any conventional manner. Where the vehicle is a mineral lubricating oil, e. g., a turbine oil, the reaction products are employed in a minor proportion, sufficient to confer corrosion inhibiting properties upon the latter. Normally from about 0.1 to about 1.0 percent of the additive by weight of the composition is sufficient for this purpose, although greater proportions, i. e., up to 2 or 3 percent by weight, are sometimes desirable and can be used. Examples of various mineral oils which can be benefited by the additives of this invention are gasoline, kerosene, distillate and residual fuel oils, motor oils, lubricating greases and turbine oils. The invention further includes mineral oil compositions wherein the solvent constituent is not employed as a fuel or a lubricant, but merely as a solvent vehicle. Exemplary of this type of composition are light naphtha and similar solvents containing the novel compounds of this invention. In such instances the compositions find use in the coating art, whereby metallic articles subject to rust or corrosion are brushed, dipped or sprayed with a composition comprising the solvent vehicle and the additive. Subsequent evaporation of the solvent leaves an adherent, corrosion-resisting coating of the additive on the article.

As indicated above, the herein disclosed compounds are highly effective corrosion inhibitors. This property of the compounds of this invention has been demonstrated by subjecting lubricating oil compositions containing small concentrations of these additives to standard test procedures ASTM D 665–52 T and ASTM D 943–47 T. These tests are described in detail in the ASTM Standards of Petroleum Products and Lubricants of 1952 and 1947, respectively. Briefly, Procedure A of ASTM test D 665–52 T involves immersion of a standard steel test rod for 24 hours in an agitated mixture of distilled water and test oil maintained at a temperature of 140° F. The corrosion inhibiting properties of the oil can be evaluated by examination of the steel rod for corrosion or rust upon completion of the test. ASTM D 943–47 T involves the passage of oxygen at a measured rate of 3 liters per hour into an oil-water mixture maintained at 203° F., and having an iron coil immersed therein. The test is carried out for a predetermined number of hours or until the oil has reached a neutralization number of 2.0. The corrosion inhibiting properties of the oil can be determined during the test by examination of the iron coil for rust or corrosion.

The corrosion inhibiting properties of the additives of the present invention were markedly superior to those of either of the parent compounds as indicated by the data set forth in the following example:

EXAMPLE II

To separate samples of a highly refined, highly paraffinic turbine oil base inhibited against oxidation and having an API gravity of between 30.5° and 32.5° and a viscosity of 150 SUS at 100° F. were added respectively 0.05 percent by weight of dimerized linoleic acid, sorbitan monooleate, and the reaction product prepared in accordance with Example I. These samples together with a sample of the unimproved turbine oil base were subjected to the above-described ASTM tests as indicated. The results of these tests are set forth in the following table:

Table A

Additive	Conc., percent by Wt.	ASTM D665-52T, Distilled Water, 24 Hrs., Steel Rod, Area Rusted, percent	ASTM D943-47T, 500 Hrs., Iron Coil, Appearance
None		100	Severe Rust.
Dimerized Linoleic Acid	0.05	70	Light Rust.
Sorbitan Monooleate	0.05	5	Do.
Dimerized Linoleic Acid-Sorbitan Monooleate Acid Ester Reaction Product of Example I.	0.05	0	Bright.

The compounds of the present invention achieve their beneficial results without at the same time imparting to the oils the undesirable emulsion-forming tendencies which normally would be expected from a knowledge of the emulsification tendencies conferred upon oils by alkitol anhydrides. This advantage has been demonstrated by subjecting lubricating oils containing small concentrations of the additives of this invention to the standard procedure of Federal Emulsification Test Fed. 320.1.5, described in Federal Specifications VV–L–791d, amended 20 June, 1950, and to the standard steam emulsion test procedure, ASTM D 157–51 T. Briefly, the Federal Emulsification Test is carried out by agitating a mixture of 40 ml. of the tested oil and 40 ml. of distilled water or a standard aqueous salt solution for 5 minutes. The tendency toward emulsion formation is determined by measuring the number of ml. in the water layer, in the oil layer and in the emulsion layer, if any, and/or by observing the time required for the emulsion to break. The ASTM steam emulsion test is carried out by passing live steam through a measured sample of the test oil until the volume of the condensed steam and oil is double that of the original oil sample. The oil and water mixture is then allowed to settle at a temperature of 200–203° F. The number of seconds required for the separation of the original volume of oil is reported as the Steam Emulsion number.

The water emulsification properties of the additives of this invention are illustrated by the following example:

EXAMPLE III

To separate samples of a turbine oil base of the same type as that described in Example II were added respectively 0.05 percent by weight sorbitan monooleate and the reaction product prepared according to Example I. The oil samples were then subjected to the standard emulsification test procedures described above. The results of these tests are indicated in the following table:

Table B

	Turbine Oil plus 0.05% by Wt. Sorbitan Monooleate	Turbine Oil plus 0.05% by Wt. Reaction Product of Example I
Federal Emulsification Test Fed. 320.1.5:		
Distilled Water—		
Oil Layer, ml	40	40
Water Layer, ml	40	40
Emulsion, ml	0	0
Time to Break, min	38	2
Salt Water—		
Oil Layer, ml	40	40
Water Layer, ml	40	40
Emulsion, ml	0	0
Time to Break, min	30	3
Steam Emulsion No., ASTM D157-51T, Time to Break, sec	165	111

Accordingly, examination of Table A indicates that the compounds of the present invention possess decidedly superior corrosion inhibiting properties as compared with either of the materials reacted to form said compounds. Examination of the results set forth in Table B indicates that the compounds of this invention overcome to a large extent the undesirable emulsion-forming tendencies of the partial fatty acid esters of alkitol anhydrides. Similar desirable properties have been demonstrated for various representative acid esters within the disclosed class of compounds, including, for example, di-acid and tri-acid dilinoleic di- and tri-esters of sorbitan monooleate.

It is to be understood that the improved mineral oil compositions of this invention can be additionally improved by incorporation therein of other known additives in order to confer thereon other desirable properties, such as increased resistance to oxidation, increased stability, etc. Thus, there can be added viscosity index improvers, thickeners, bearing corrosion inhibitors, antioxidants, extreme pressure agents, foam inhibitors, detergents, dyes, sludge inhibitors, etc.

The reaction products included by the invention also find utility as corrosion-inhibiting additives for various paints, varnishes, automobile undercoatings and the like. In the use of the agents of this invention in the above-described coating compositions, it may be desirable to employ these agents in substantially greater concentrations than are normally utilized in fuels and lubricants.

It will be understood by those skilled in the art that numerous modifications may be resorted to without departing from the spirit of the invention or the scope of the appended claims.

We claim:

1. An acid ester of (1) a dimeric acid derived from an unsaturated fatty acid containing from 6 to 22 carbon atoms and having from 2 to 3 ethylenic linkages per molecule and (2) a partial ester of a fatty acid containing from 12 to 24 carbon atoms and an alkitol anhydride containing 4 to 6 carbon atoms, said acid ester containing at least 1 unreacted carboxyl group per molecule.

2. An acid ester of (1) a dimeric acid derived from an unsaturated fatty acid containing 18 carbon atoms and having from 2 to 3 ethylenic linkages per molecule and (2) a partial ester of a fatty acid containing 18 carbon atoms and a hexitol anhydride, said acid ester containing at least 1 unreacted carboxyl group per molecule.

3. An acid ester selected from the group consisting of mono-, di-, and tri-acid esters of a dimer of linoleic acid and sorbitan monooleate.

4. A mono-acid ester of dilinoleic acid and sorbitan monooleate.

5. A di-acid ester of dilinoleic acid and sorbitan monooleate.

6. A tri-acid ester of dilinoleic acid and sorbitan monooleate.

7. A method of preparing an acid ester of a dimerized unsaturated fatty acid and a partial ester of an alkitol anhydride, which acid ester contains at least 1 unreacted carboxyl group per molecule, said method comprising esterifying a dimeric acid derived from an unsaturated fatty acid containing from 6 to 22 carbon atoms and having from 2 to 3 ethylenic linkages per molecule with a partial ester of a fatty acid containing from 12 to 24 carbon atoms and an alkitol anhydride containing 4 to 6 carbon atoms, in a mol ratio of at least one mol of dimeric acid per mol of partial ester, and continuing the reaction until approximately 1 mol of water of esterification per mol of reacted dimeric acid has been produced.

8. A mineral oil composition comprising a major amount of a mineral oil and a minor amount, sufficient to impart corrosion inhibiting properties to the composition, of an acid ester of (1) a dimeric acid derived from an unsaturated fatty acid containing from 6 to 22 carbon atoms and having from 2 to 3 ethylenic linkages per molecule and (2) a partial ester of a fatty acid containing from 12 to 24 carbon atoms and an alkitol anhydride containing 4 to 6 carbon atoms, said acid ester containing at least 1 unreacted carboxyl group per molecule.

9. The composition of claim 8 wherein the mineral oil is a lubricating oil.

10. The composition of claim 8 wherein the mineral oil is a turbine oil.

11. A lubricating oil composition comprising a major amount of a mineral lubricating oil and a minor amount, sufficient to impart corrosion inhibiting properties to the composition, of an acid ester of (1) a dimeric acid derived from an unsaturated fatty acid containing 18 carbon atoms and having from 2 to 3 ethylenic linkages per molecule and (2) a partial ester of a fatty acid containing 18 carbon atoms and a hexitol anhydride, said acid ester containing at least 1 unreacted carboxyl group per molecule.

12. A lubricating oil composition comprising a major amount of a mineral lubricating oil and a minor amount, sufficient to impart corrosion inhibiting properties to the composition, of an acid ester selected from the group consisting of mono-, di-, and tri-acid esters of a dimer of linoleic acid and sorbitan monooleate.

13. The composition of claim 12 wherein said acid ester is present in the composition in an amount of from about 0.01 to about 1.0 per cent by weight of the composition.

14. The composition of claim 12 where the acid ester is a mono-acid ester of dilinoleic acid and sorbitan monooleate.

15. The composition of claim 12 where the acid ester is a di-acid ester of dilinoleic acid and sorbitan monooleate.

16. The composition of claim 12 where the acid ester is a tri-acid ester of dilinoleic acid and sorbitan monooleate.

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