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2,976,245

ESTERS OF 1,4-BUTANEDIOL AND 1,2,4-BUTANETRIOL AS RUST INHIBITORS

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The inventions here presented are new rust inhibitors in the form of esters of 1,4-butanediol or 1,2,4-butanetriol which are outstandingly effective as rust inhibitors and which in addition are free from gum forming and ash forming residues.

Because of the tendency of iron objects to rust when exposed to the weather, many attempts have been made to provide protective coatings. When the article is stationary in all its parts, a heavy layer of paint will preserve the surface and prevent rusting for long periods of time. When however there are moving parts in the article, especially when they are nicely fitted and require lubricant protection, many difficulties appear. They cannot be covered with heavy coats of paint since such a covering interferes with the movement of the respective parts, and in addition rapidly wears away, causes undesirable dimension changes, and is very difficult to prepare without pinholes therein which, when present, largely destroy the rust protection. Accordingly a coating of some sort which is both a lubricant and a rust preventer is highly desirable. Many substances have been tried of which perhaps the best previous one is a mixture of sulfonated corn oil in a petroleum product such as lubricating oil or vaseline or paraffin or the like. Many other rust preventers have also been proposed including various salts and esters of many organic acids; various of the amines; various esters and many other chemical compounds, which may in addition require cosolvents, synergists, auxiliaries, and the like. None of the substances previously known are, however, fully satisfactory since they tend to yield gummy deposits or provide insufficient protection or contain heavy metal substances which cause precipitation and which when heated yield troublesome ash residues and the like. Some of the others are expensive, or are in short supply, or decompose too easily through hydrolysis or through thermal effects or undesirably alter the system.

According to the present invention it is now found that the esters of butanediol and triol, especially if the esterifying acid is of relatively high molecular weight; that is, has more than 8 or 10 carbon atoms per molecule and particularly if there is a unit of unsaturation in the esterifying organic acid, yield outstandingly good rust inhibitors, which are, in addition, good lubricants, are compatible with other lubricants in general; yield no ash upon combustion and are sufficiently adhesive and film forming to stay in place for substantial periods of time without draining, rubbing or wearing off.

Accordingly these esters are highly desirable as lubricant additives especially in internal combustion engine oils since they do not gum when heated, do show an adequate heat resistance, show a substantial lubricating effect, do not substantially alter the viscosity index, do not decompose unduly in the presence of water, and in addition do not deposit ash or other incrustations which may lead to the fouling of spark plugs, piston rings, valves, and the like, nor do they build up residues in the engine cylinders.

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Other objects and details of the invention will be apparent from the following description.

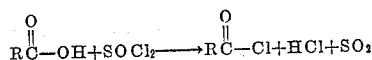
The primary reactant to form the compositions of matter of the present invention is found in 1,4-butanediol or 1,2,4-butanetriol. These compounds are prepared, as is well known in the art, by the condensation of acetylene and formaldehyde to yield 2-butyne-1,4-diol when passed over a copper acetylide catalyst at moderately elevated temperature and pressure. The resulting 2-butyne-1,4-diol which results from this primary reaction may then be hydrogenated to 1,4-butanediol by any convenient reducing or hydrogenating procedure, hydrogen under pressure in the presence of a nickel catalyst being the preferred procedure. Alternatively the hydrogenation may be accomplished by hydrolysis with water in the presence of mercury salt catalyst to yield 1,4-dihydroxy-2-butanone and subsequent hydrogenation to yield the 1,2,4-butanetriol.

These methods of producing the butanediol and butanetriol are well known and well reported in the literature both in patents, textbooks, PB Report 60574, FIAT 1003, and other places.

These two compounds are readily esterified by any desired acid, esterification by organic acids having more than about 12 carbon atoms per molecule then yields the new rust inhibitor of the present invention. The preferred method of esterification is through the use of acid chlorides of the desired esterifying acid. The preferred organic acid is found in the oleyl group.

In practicing the invention the butanediol or triol may first be prepared by the above processes well known in the art. These processes are outlined broadly above, and the details are well known to those skilled in the art and need not be repeated here.

The butanediol and triol having been procured are then esterified. This may be done by forming the acid chloride of the desired organic acid by reaction with phosphorus trichloride, phosphorus pentachloride, thionyl chloride, and the like. These reactions are well known in the art. An illustration is:



The acid chloride and the alcohol are then heated together in a reaction vessel, or one may be added to the other, preference usually being, especially in the case of the partial esters, to add the acid chloride to the alcohol. The reaction proceeds with the evolution of hydrogen chloride. It is usual in the laboratory to add an acid acceptor such as pyridine, to the reaction mixture. This absorbs the hydrogen chloride and allows the reaction to proceed. When the reaction is completed, the ester may be removed from the slurry by taking advantage of the diverse solubilities, the esters having but slight solubility in water. Various other techniques may also be employed. It is not necessary to distill the product.

The resulting mono or di esters of the diol, and mono, di and tri esters of the triol then form the rust inhibitor to be added to the various lubricants or diluents in small amounts. Depending upon the size of the molecule of the esterifying acid, these esters are mobile liquids, relatively viscous liquids, highly viscous liquids, waxes or solids. It does however appear that the molecular weight is of importance in the rust inhibiting action, the higher molecular weight acids at least above C₁₂ being best, the lower acids such as C₄, C₆ being relatively less effective. The solids may be preferred for the application of slush coats on stored machinery although excellent protection in this type application is also afforded by the liquids. The esters prepared from most organic acids are fluids at ordinary temperatures which are readily soluble in lubricat-

ing oils and other hydrocarbons and when so dissolved yield excellent rust protection.

It may be noted that "dimer acid" usually has 36 carbon atoms and 2 carboxyl groups, that is 18 carbon atoms per carboxyl and there is usually present a certain amount of "trimer acid" containing 54 carbon atoms which, in turn, has 3 carboxyl groups; again 18 carbon atoms per carboxyl group. Esters of acids having less than about 6 carbon atoms per carboxyl group are relatively less effective than esters of higher molecular weight acids but they are useful under very mild conditions, even the acetate showing at least the beginning of rust inhibition. However for heavy commercial service, it is usually desirable that the esterifying acid contain 6 or more carbon atoms per carboxyl. No upper limit for the carbon atom number per carboxyl group has as yet been found but it certainly lies well above 30, probably 60, and may well include all of the higher, stable organic acids.

The following examples are offered as showing the characteristics and preferred method of use of the invention but are not intended to limit the scope of the claims in any way.

EXAMPLE 1

A rust test was carried out as follows: Various solutions of inhibitors were prepared either in a petroleum hydrocarbon (B.P. 90-100° C.) or in a crankcase type petroleum hydrocarbon lubricant (540 cps. at 25° C., initial boiling point 375° C.). A mild steel bar was turned in a lathe and the chips, as formed, were allowed to fall into the solutions. The solutions were then drained away from the chips, which were then placed in shallow Petri dishes and subjected to the corrosive environment of a humidity chamber which was maintained at about 55° C. and the relative humidity was cycled through 100% periodically, about every two hours. The chips were inspected frequently, usually daily, and the time was counted until 10% of the chips had visible signs of rust. In the following table are recorded these times for various solutions.

Duration of 10% rusty chips

	Glyceryl oleate (Prior Art)	Butanediol monooleate, weeks	Butanetriol monooleate, days	Butanediol dioleate, days	Butanediol dimer acids diester, days	Butanediol distearate, days	Butanediol Dilaurate, days
Percentage inhibitor in low boiling hydrocarbon (90-100° C.):							
0.25.....	<18 hrs.						
0.5.....	1 day.....	1	>9	4	>6		<1
1.....	3 days.....			3		3	
2.....	4 days.....	4	>9	4	>6		<1
Percentage inhibitor in high boiling hydrocarbon (375° C.):							
0.5.....			>9	7	>6	>1	<1
2.....		>4	>9	3	4-6		<1

In the above table the symbols more than (>) indicate that the test was discontinued before the required rust developed. All of the above systems were in solution at room temperature. The glyceryl oleate was, however, dark colored and gummy on the chips, especially in the higher concentrations. Possibly this is due, in part, to hydrolysis, followed by oxidation or polymerization.

The table indicates a large factor of superiority of esters of butanediol and butanetriol over glyceryl oleate. Various other glycerides such as the stearates, palmitates, and mixtures were found to be inferior, as were their intermediates (e.g. glycerol, oleic acid, stearic acid). The table also shows that short chain acid esters are not as efficient inhibitors as the longer chains; in addition to the dilaurate shown in the table, the dibutyrate, diacetate and the like exhibited less inhibition under the severe conditions of the test.

The table indicates the superiority of the esters of many unsaturated acids over corresponding saturated

acids. In the case of dimer acid, the structure has not yet been completely elucidated. It is known that some of the molecules may contain unsaturation. Dimer acid is well known, its preparation is described in J. Am. Soc. Oil Chemists 24, 65 (March 1947) and it is referred to often as in U.S. Patent 2,464,399. It is essentially polymerized linoleic acid having, typically, an average molecular weight of about 600, an acid value of 180 mg. KOH per gram, dimer content 75%, trimer content 25%, monomer content of 3%, sp. gr. 15° C.=0.95. This type compound is available in several slight modifications.

In addition, the preferred esters of the C₄ alcohols have the superiority over esters of other polyhydroxy alcohols such as glycerol, sorbitol, pentaerythritol in that there is complete solubility without additives, and chemical stability, and the inhibition is outstanding, no synergists, tars, residues and the like being necessary.

EXAMPLE 2

As further evidence of excellence, 0.5% and 2% solutions of inhibitors were prepared in the high boiling hydrocarbon of Example 1 and subjected to the static drop test of Baker, Jones and Zisman (Ind. Eng. Chem. 41, 137 (1949) for 2 days at 60° C. with the following results.

	butanetriol monooleate	glyceryl monooleate (Prior Art)	butanediol monooleate	butanediol diester of dimer acid	butanediol dioleate
2%.....	passes ¹	fails ²	passes.....	passes.....	fails.....
0.5%.....	do.....	do. ²	do.....	fails.....	Do.....

¹ Slight hydrolysis.

² Pronounced hydrolysis.

This indicates that the preferred inhibitors pass a severe standard test and are stable. Dilaurate, dibutyrate, diacetate, of butanediol were less effective, longer chains being desirable for good inhibition. This also indicates basis for preferring monoesters to diesters, the

monoesters being more effective, and at lower concentrations.

In addition, the preferred inhibitors and related compounds are convenient to use, being liquids at usual temperatures. For example, the monooleate of butanetriol is a mobile liquid at room temperature, becoming somewhat viscous but easily manipulated at 5° C. and when frozen completely melts at 0° C.

Examples of other esters which may be employed for the inhibition of rust in various environments are butanetriol dioleate, butanetriol trioleate, butanetriol monoester, diester and triester of dimer acid, as well as the ricinoleates, the linoleates, the linolenates, palmitates, and the like of both polyhydric alcohols.

These compounds may be dissolved in various liquids such as petroleum hydrocarbons, gasolines, kerosenes, diesel fuels, motor oils, crankcase oils, greases, petrolatums and the like, alcohols, fats, solvents such as dry cleaning solvents, degreasing solvents, paints, coatings, synthetic liquids, such as lubricants and greases, hydraulic

fluids and the like, and when so compounded impart protection to the ferrous metals contacted by these fluids from the deleterious effects of rust, the choice of ester being governed by such factors as the severity of the corrosive environment, the specific liquid to be inhibited and so forth.

The inhibitors, in addition to protecting containers such as tanks, pipelines, machinery, processing equipment, conduits, may also be used in the manner of slushing compounds when a metal to be protected is dipped into a solution of the inhibitor, or the solution is applied as a film, using such implements as spraying apparatus, paint brushes, rags, or the like.

Various other uses will suggest themselves. The agents may be introduced into oil wells for the prevention of rust to the metal parts, and certain of them may be of use in the acidization process.

These inhibitors are easily removed when their services are no longer required. They deposit no residue when ignited which adds to their utility in that, for example, when used in crankcase oils, there is no fouling of spark plugs, piston rings, no preignition-causing residues are deposited.

Thus the compositions of matter of the present invention provide new and useful rust inhibitors in the form of an ester of butane polyalcohols with acids, preferably organic of substantial molecular weight as indicated, such as from 12 to 20 or 25 or more carbon atoms per carboxyl group.

While there are above disclosed but a limited number of embodiments of the compositions of matter of the present invention, it is possible to provide still other embodiments without departing from the inventive concept herein disclosed, and it is therefore desired that only such limitations be imposed upon the appended claims as are stated therein or required by the prior art.

The invention claimed is:

1. A corrosion inhibited petroleum hydrocarbon com-

position consisting essentially of a major amount of a petroleum hydrocarbon and a minor effective corrosion inhibiting amount of a compound selected from the group consisting of oleic acid esters of 1,4-butanediol and 1,2,4-butanetriol and dimerized linoleic acid esters of 1,4-butanediol and 1,2,4-butanetriol.

2. A corrosion inhibited petroleum hydrocarbon composition consisting essentially of a major amount of a petroleum hydrocarbon and a minor effective corrosion inhibiting amount of 1,4-butanediol monooleate.

3. A corrosion inhibited petroleum hydrocarbon composition consisting essentially of a major amount of a petroleum hydrocarbon and a minor effective corrosion inhibiting amount of 1,2,4-butanetriol monooleate.

4. A corrosion inhibited petroleum hydrocarbon composition consisting essentially of a major amount of a petroleum hydrocarbon and a minor effective corrosion inhibiting amount of 1,4-butanediol dioleate.

5. A corrosion inhibited petroleum hydrocarbon composition consisting essentially of a major amount of a petroleum hydrocarbon and a minor effective corrosion inhibiting amount of the diester of dimerized linoleic acid and 1,4-butanediol.

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