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CORROSION PROTECTIVE COMPOSITION

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This invention relates to non-gaseous hydrocarbon compositions possessing corrosion-protecting properties, and more particularly is concerned with such compositions containing dissolved small amounts of high molecular weight carboxylic acids having anti-corrosive properties.

It is already known that the addition of small amounts of certain oil-soluble polycarboxylic acids or hydroxy aromatic carboxylic acids impart to lubricating oils and other non-gaseous hydrocarbons, such as gasoline, Diesel fuels, kerosene, gas oil, lubricating oils, petrolatum, petroleum plastics, etc., strong corrosion-protective properties. Acids possessing this property are those having at least 12, and preferably 20 or more carbon atoms, and it is desirable that their active radicals, i. e., the several carboxylic radicals, or carboxylic and hydroxyl radicals, as the case may be, be as close to each other as possible and be separated from each other by not more than 4, and preferably by not more than 2, intervening atoms. Stability of the acids under conditions to which the compositions are exposed is an added requirement.

Among the polycarboxylic acids which are particularly useful for preventing corrosion are the following: polymerized and hydrogenated fatty acids, e. g., voltolized and hydrogenated lauric, palmitic, stearic, oleic, ricinoleic, etc., acids, unsaturated fatty acids polymerized with a halide polymerization catalyst such as BF_3 and subsequently hydrogenated; alkyl phthalic acids, alkylated naphthalene dicarboxylic acids, such as alkyl naphthalic acids; various alkylated aliphatic polycarboxylic acids such as succinic, glutaric, adipic, pimelic, suberic, azelaic, tricarballic, etc., acids. If desired, these acids may contain various substitution radicals as hydroxyl, ether, amino, nitro, hydrosulfide, sulfide, halide, etc., radicals, the most important limiting factor being the necessary stability. In general, it is preferred to use a saturated aliphatic dicarboxylic acid having the carboxyl radicals as close to each other as possible and as is consistent with the requirement for stability. Particularly effective are alkyl succinic acids having at least 16, and preferably 20 to 40 carbon atoms. Malonic acid and its alkyl derivatives are known to be unstable and, therefore, cannot be used.

Of the hydroxy carboxylic acids, hydroxy aromatic carboxylic acids in which the hydroxy radical is directly attached to the aromatic nucleus are most useful; for example, various alkyl phenol or naphthol carboxylic acids wherein the carboxylic acid radical is attached to the nucleus di-

rectly or through a carbon linkage, e. g., alkyl salicylic acids, preferably those whose alkyl radicals contain 12 or more carbon atoms, hydroxy naphthoic acids or hydroxy aromatic fatty acids such as may be produced by coupling a phenol or a naphthol, etc., with oleic or other unsaturated fatty acid or with rosin acid, etc., in the presence of aluminum chloride.

It has been found in the past that the mechanism by which the above acids protect materials from corrosion is one of formation of a protective film which adheres to the metal more or less tenaciously. However, this film formation, and more particularly the anchoring of the film on the metal surface, appears to be a very slow process, often requiring 24 hours or longer. It was then discovered that the presence of water would greatly accelerate the rate of formation as well as the tenacity of the protective film. It was therefore thought that the presence of at least small amounts of water was essential for the formation of the film.

It is an object of this invention to produce corrosion-inhibiting hydrocarbon compositions which deposit on metals a protective film within a reasonably short time. It is another purpose to produce this film with the aid of certain carboxylic acids without the aid of water; and it is a purpose to produce with these acids and without water such a protective film which has a tenacity greater than that obtained heretofore even in the presence of water.

I have discovered that the rate of formation of the protective film can be accelerated and its tenacity be materially increased by the presence of certain auxiliary compounds other than water. More particularly I have found that this improvement can be achieved either by using a mixture of the above two types of corrosion-inhibiting acids or else by employing in conjunction with either certain oil-soluble, substantially water-insoluble monocarboxylic acids or esters of monocarboxylic acids which by themselves have little, if any, corrosion-protective powers and which preferably are free from ether-forming hydroxyl radicals positioned in close proximity to the acid radical. Suitable acids of the latter type are, for example, fatty acids having at least 7, and preferably from 10 to 30, carbon atoms, e. g., lauric, stearic, oleic, arachic, behenic, ricinoleic, etc., acids, wool fat acids, carboxylic acids produced by oxidation of paraffin wax, naphthenic acids, rosin acids such as abietic acid, hydrogenated abietic acids, acids derived from tall-oil, benzoic acid, alkyl benzoic acids, naphthoic

acids, phenyl acetic acid, aromatic fatty acids, etc. Esters suitable for our purpose are particularly those combining monohydric alcohols with monocarboxylic acids, which esters possess at least 6 carbon atoms, for example, butyl, hexyl, octyl, decyl, oleyl, stearyl, etc., acetates, propionates, butyrates, valerates, laurates, palmitates, oleates, stearates, rosinates, abietates, naphthenates, benzoates, naphthoates, etc., corresponding methyl, ethyl, propyl, isopropyl esters having 6 or more carbon atoms, etc.

The enhancing effect of the monocarboxylic acids and their esters seems to be quite specific in that acids other than carboxylic acids such as various organic phosphorus acids, sulfonic acids, etc., have an effect just opposite, that is, decreasing the protective effect of the primary corrosion inhibitors and in many cases causing rapid corrosion in spite of the presence of the inhibitor.

The useful amounts of the corrosion-inhibiting polycarboxylic acids or hydroxy aromatic carboxylic acids used in various hydrocarbon compositions are known to vary between fairly wide limits, depending not only on the particular use to which the composition is to be put, but also depending on the susceptibility of the hydrocarbon composition toward these acids. In general, the presence of large amounts of petroleum resins, gums, etc., has a retarding effect. Thus, in distillate oils as gasoline, kerosene, diesel fuel oils, gas oil, light lubricating oils, etc., amounts of the active corrosion-inhibiting acids between .001%–1%, are normally ample. In bright stocks amounts from .1% to about 1% may be required, and in petroleum plastics, such as albino asphalts, or in petrolatums, suitable amounts may range from below .1% to above 1% and may be as high as 5%–10%.

The amounts of the auxiliary acids or esters which I add may be of an order similar to those of the corrosion-inhibiting acids. Thus the amount of auxiliary compounds may be about the same as, or smaller or higher than, that of the main inhibitor. In general, however, I prefer to use quantities below 1%.

The importance of rapidly forming a tenacious corrosion-protecting film is, of course, manifest. For example, when machining metal parts to very accurate dimensions, the machined surface must be immediately protected against rusting as soon as it is finished. Thus, simple dipping of the object into a suitable oil should have a complete protective effect so that subsequent handling does not cause local rusting.

Likewise, under many circumstances it is very desirable that water be absent, for water being substantially insoluble in hydrocarbons tends to form a separate phase which requires strong agitation in order to make it effective as an accelerator for the active corrosion-inhibiting acids. This may lead to emulsion troubles. The presence of mutual solvent for oil and water does not always solve this difficulty, inasmuch as the mutual solvent may be extracted from the hydrocarbon compounds in contact with large amounts of water, as a result of which two separate layers are formed again.

The following examples illustrate my invention:

A light lubricating oil was divided into several portions, to some of which small amounts of a saturated alkyl succinic acid (molecular weight about 650) or mixtures of this acid with fatty acids were added. The resulting oils were then

tested by two tests, a corrosion test and a film tenacity test as follows:

Corrosion test.—A clean steel strip is immersed in the well stirred oil kept at 167° F. After 30 minutes, 10% based on the volume of the oil, of an aqueous 2% NaCl solution is added. The steel strip is removed from the stirred mixture after 48 hours, inspected visually and the extent of rusting recorded.

Film tenacity test.—Two clean steel strips are immersed in the oil for 30 minutes. They are transferred then to beakers holding stirred distilled water; one kept at room temperature, the other at 167° F. The number of hours elapsed until rusting starts are recorded.

Results were as follows:

Alkyl succinic acid	Fatty acid	Corrosion test in 2% NaCl solution	Film tenacity test	
			At room temperature hrs.	At 167° F. hrs.
Per cent				
0.1	None	10% rusted	5	34
0.1	0.2% stearic acid	Clean	20	2
0.1	0.2% oleic acid	do	48	10
0.01	None	Completely rusted. ¹		
0.01	.02% stearic acid	10% rusted		
0.01	.01% naphthenic acid ²	25% rusted		

¹ Rusting started in less than 1 hr.

² Equivalent weight=342.

The addition of the auxiliary acids or esters to hydrocarbon oils containing the primary anti-corrosives is of greatest importance when dealing with well-refined hydrocarbon compositions. Conventional refining methods, such as acid and alkil treatment, solvent extraction, hydrogenation, etc., raise the susceptibility of the hydrocarbons to the protective action of the primary anti-corrosives on the one hand, but on the other hand, remove naphthenic and other monocarboxylic acids which may naturally be contained in the hydrocarbons in small amounts and which enhance the action of the primary anti-corrosives. However, even if small amounts of naphthenic and similar acids are naturally present, in general the addition of further amounts of the auxiliary acids or esters of the type described is beneficial.

I claim as my invention:

1. A corrosion-inhibiting composition comprising non-gaseous hydrocarbons containing amounts sufficient to inhibit corrosion each of a polycarboxylic acid having corrosion-inhibiting properties, and of an auxiliary oil-soluble, water-insoluble compound having but little corrosion inhibiting power selected from the group consisting of hydrocarbon monocarboxylic acids free from ether-forming hydroxyl radicals and esters thereof with monohydric alcohols.

2. The composition of claim 1 wherein said polycarboxylic acid is an alkyl succinic acid having at least 16 carbon atoms.

3. The composition of claim 1 wherein said polycarboxylic acid is an alkyl succinic acid having between 20–40 carbon atoms.

4. The composition of claim 1 wherein said hydrocarbon is a lubricating oil.

5. A corrosion-inhibiting composition comprising non-gaseous hydrocarbons containing amounts sufficient to inhibit corrosion each of a corrosion-inhibiting acid selected from the group consisting of polycarboxylic acids and hydroxy

aromatic carboxylic acids having at least 12 carbon atoms, and of an oil-soluble, water-insoluble, hydrocarbon monocarboxylic acid free from ether-forming hydroxyl radicals.

6. A corrosion-inhibiting composition comprising non-gaseous hydrocarbons containing amounts sufficient to inhibit corrosion each of a corrosion-inhibiting acid selected from the group consisting of polycarboxylic acids and hydroxy aromatic carboxylic acids, whose active radicals are separated from each other by not more than 4 carbon atoms, having at least 12 carbon atoms and of a fatty acid having at least 7 carbon atoms.

7. A corrosion-inhibiting composition comprising non-gaseous hydrocarbons containing amounts sufficient to inhibit corrosion each of a corrosion-inhibiting acid selected from the group consisting of polycarboxylic acids and hydroxy aromatic carboxylic acids, whose active radicals

are separated from each other by not more than 4 carbon atoms, having at least 12 carbon atoms and of a naphthenic acid having at least 7 carbon atoms.

8. A corrosion-inhibiting composition comprising non-gaseous hydrocarbons normally free from carboxylic acids to which have been added amounts sufficient to inhibit corrosion each of a polycarboxylic acid having corrosion-inhibiting properties, and of an auxiliary oil-soluble, water-insoluble compound having but little corrosion inhibiting power selected from the group consisting of hydrocarbon monocarboxylic acids free from ether-forming hydroxyl radicals and esters thereof with monohydric alcohols.

9. The composition of claim 1 wherein said small amounts of the added compounds range from about .001% to 1%.

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