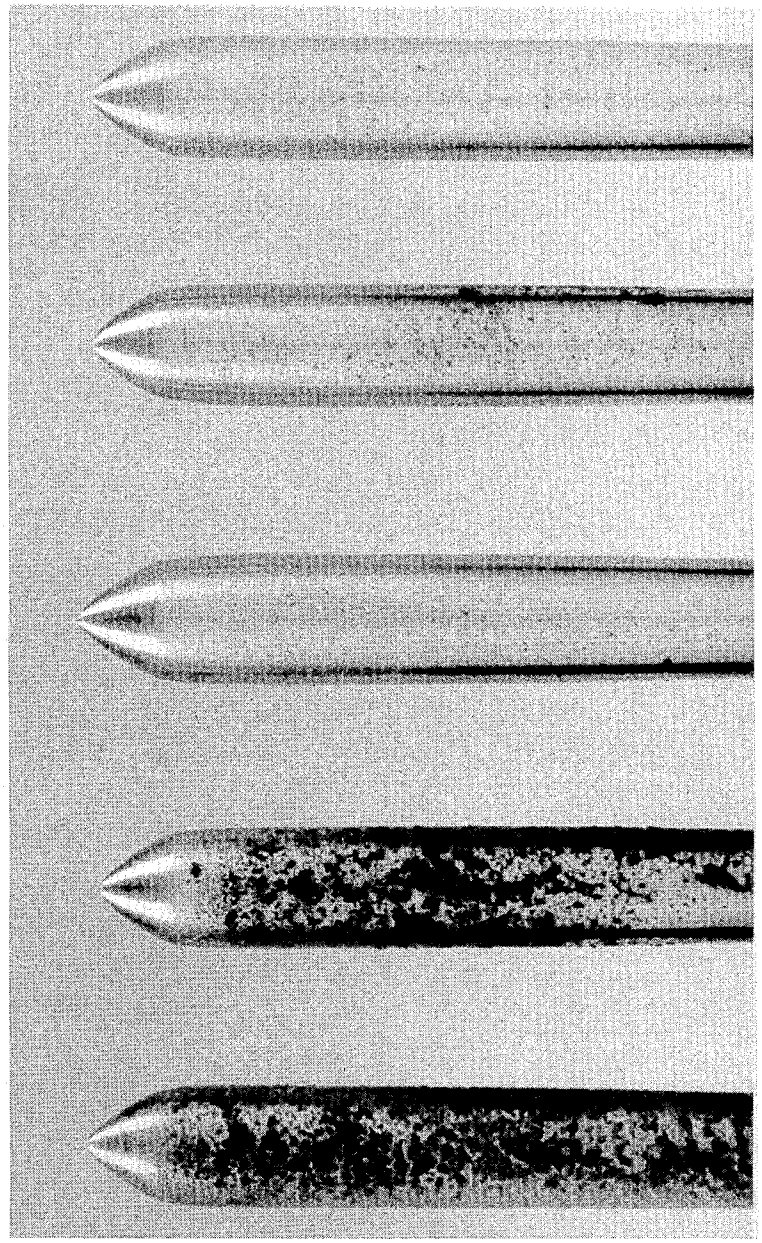
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CORROSION INHIBITORS

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CORROSION INHIBITORS

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ABSTRACT OF THE DISCLOSURE

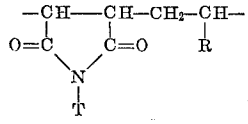
The phosphate salts of amine nitrogen containing low order copolymers of maleimide and hydrocarbon 1-olefins find use in providing corrosion inhibition, particularly rust inhibition, in hydrocarbon media such as fuels.

This invention concerns novel organic corrosion inhibitors used in conjunction with hydrocarbon liquids. More particularly, this invention concerns novel organic phosphate salts which find use as corrosion inhibitors, particularly for rust inhibition, in conjunction with hydrocarbon liquids.

In the handling of hydrocarbon liquids, it is frequently necessary to transport and/or store the liquids in steel or iron containers or pipelines. Almost invariably, the hydrocarbon liquids contain traces or more of water which reacts with the container, resulting in rusting and contamination of the hydrocarbon liquid. This problem is especially serious when handling gasoline, kerosene, fuel oil, diesel fuel, etc.

Moreover, it is found that to varying degrees less highly refined oils and fuels have materials which act as corrosion or rust inhibitors. The greater the purification during refining—removal of nitrogen, oxygen and sulfur-containing materials—the more difficult becomes the corrosion problem.

It has now been found that excellent corrosion inhibition, particularly rust inhibition, can be obtained even with hydrofined fuels, by adding to the hydrocarbon medium the phosphate salt of a relatively low order copolymer of maleimide and hydrocarbon 1-olefins, wherein the polymer has the following recurring unit:

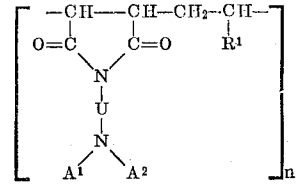


wherein R is hydrogen or alkyl of from 1 to 20 carbon atoms, T is an aliphatic monoamino hydrocarbon radical (an aliphatic hydrocarbon radical having 1 amino nitrogen, either primary, secondary or tertiary) of from 3 to 30 carbon atoms and the sum of the carbon atoms of R+T is at least 12 and generally less than about 50. The number of the above units in the polymer will generally be from 4 to 20, more usually from 6 to 16. The alkyl ester of phosphoric acid which is used will generally be a mono- or diester having at least one alkyl group of from about 8 to 30 carbon atoms. At least about 0.5 of the amino nitrogen present in the polymer will be neutralized by the phosphoric acid to form the ammonium salt.

The figure depicts the results of the rust inhibition test ASTM D 665 involving the compositions of this invention in comparison to a standard and a commercial rust inhibitor.

Considering the maleimide olefin copolymer first, the molecular weight of the polymer will generally be from about 2,000 to 15,000, more usually from about 4,000 to 10,000.

For the most part, the polymer will have the following formula:



wherein n is an integer of from 4 to 20, more usually of from 6 to 16, R^1 is hydrogen or alkyl of from 1 to 20 carbon atoms, more usually of from 8 to 18 carbon atoms, U is alkylene of from 2 to 6 carbon atoms, usually of from 2 to 3 carbon atoms, A^1 and A^2 are the same or different and are hydrogen or alkyl of from 1 to 20 carbon atoms, preferably one of A^1 and A^2 is other than hydrogen, and the sum of the carbon atoms of R^1, U, A^1 and A^2 is in the range of 12 to 50, preferably 16 to 40. When A^1 is hydrogen, A^2 is preferably alkyl of from 8 to 20 carbon atoms.

Illustrative of various aliphatic aminohydrocarbon radicals are aminohexyl, aminodecyl, aminooctadecyl, N-hexylaminohexyl, N-decylaminopropyl, N-tetradecylaminopropyl, N-hexadecylaminopropyl, N,N - dimethylaminoethyl, N,N-dimethylaminopropyl, N,N-diethylaminopropyl, etc.

The compounds of this invention are readily prepared by copolymerizing an aliphatic 1-olefin of from 2 to 30 carbon atoms, preferably of from 8 to 20 carbon atoms with maleic anhydride by means of free radical catalysis, and then combining the resulting polymer with the desired amine at elevated temperatures to form the alternating N-substituted polysuccinimide.

The end groups of the polymer will be derived from the catalyst or be derived according to the various methods of termination in free radical polymerization. The polymeric chain may terminate by transfer, coupling or disproportionation, resulting in alkyl groups, alkenyl groups, succinimidyl groups, maleimidyl groups or radicals derived from the initiator.

The copolymerization of maleic anhydride with aliphatic 1-olefins is well known in the art. See for example U.S. Patent No. 3,051,562. Therefore, the polymerization conditions will be discussed only briefly.

The olefins which find use include ethylene, propylene, butene-1, 4-methylpentene-1, decene, dodecene, tetradecene, pentadecene, hexadecene, octadecene, nonadecene, eicosene, tetrapropylene, tetraisobutylene, hexapropylene, etc. Generally, a mixture of olefins will be used rather than a single olefin. When using mixed olefins, superior solubility in hydrocarbons is obtained. The mixture will generally have not more than about 50 percent of any single olefin and preferably not more than about 30 mole percent of any single olefin.

The free radical catalyst used for the polymerization may be any organic compound which at a temperature in the range of 50° to 150° C. decomposes to form free radicals which may then initiate the polymeric chain, although temperatures outside this range may be used advantageously under some conditions. Various azo, hydroperoxide or peroxidic catalyst may be used having the desired decomposition rate at the chosen temperature of polymerization.

In carrying out the polymerizations, a solvent, such as inert hydrocarbons or halohydrocarbons, may be used to advantage. Illustrative of such solvents are benzene, toluene, chlorobenzene, etc.

Usually, the solvent will be from 20 to 80 weight percent of the total reaction mixture, more usually about 30 to 70 weight percent.

The mole ratio of α-olefin to maleic anhydride will generally be about 0.9–1.2:1.2–0.9, more usually about 1:1. The ratio of olefin to catalyst will generally be about 1:0.005–0.1 mole ratio.

Turning now to a consideration of the phosphoric acid ester. As already indicated, mono- and dibasic phosphoric acid esters or mixtures thereof will be used. The phosphates will have the following formula:

$$(R^2O)_{3-m}\overset{O}{\overset{\|}{P}}(OH)_m$$

wherein m is an integer or fractional number of from 1 to 2, preferably about 1.5, and R^2 is an alkyl group of at least 8 carbon atoms and generally fewer than 30 carbon atoms, usually in the range of about 10 to 18 carbon atoms.

Illustrative of the various phosphate esters include monodecyl phosphate, didecyl phosphate, didodecyl phosphate, monotridecyl phosphate, ditridecyl phosphate, octyl,decyl phosphate, decyl,dodecyl phosphate, etc As indicated by the formulae, the diester alkyl groups may be the same or different.

The ratio of the phosphate esters to maleimide groups, i.e., the number of basic amino nitrogens present in the polymer, will generally be in the range of at least about 0.4 to 0.8, more usually from about 0.5 to 0.70. While higher ratios of phosphate to amino nitrogen might be achieved in particular instances, it is generally found that less than about 80 percent of the available amino groups are tritratable with phosphoric acid. Therefore, it is usually difficult to obtain a greater ratio of phosphate to amino nitrogen than about 0.80.

The maleimide copolymer may be readily prepared as its phosphate salt by combining the copolymer with the requisitie amount of phosphate ester in the absence of solvent. However, a solvent may be used which can be a suitable hydrocarbon, preparing the maleimide phosphate salt as a concentrate in the hydrocarbon, which may subsequently be diluted to the necessary concentration for use as a corrosion inhibitor.

The composition of this invention can be used in a variety of hydrocarbon fluids, such as oils, fuels, etc., wherever the presence of small amounts of water creates corrosion problems. It is found that as little as 2.5 parts per million (p.p.m.) of the phosphate salt composition provides some corrosion inhibition, although generally at least from about 5 and not more than about 50 parts per million will be used. More usually, from about 5 to 25 parts per million will provide satisfactory corrosion inhibition.

The following examples are offered by way of illustration and not by way of limitation.

EXAMPLE A

Preparation of maleic anhydride-α-olefin copolymer

Into a reaction flask was introduced 243 g. (1.0 mole) of C_{15-20} cracked wax 1-olefins, 98 g. (1.0 mole) of maleic anhydride and 341 g. of benzene. The mixture was stirred at a temperature of 140° F. and 9.7 g. (0.04 mole) of benzoyl peroxide in a minimum of benzene added. The solution was then heated at 185° F. for 12 hours. The product was characterized by its infrared spectrum and viscosity (minimum $V_{100° F.}$=75 SSU).

EXAMPLE I

(A) Into a reaction flask was introduced 682 g. (1.0 mole) of a 50 weight percent solution of copolymer prepared in Example A in benzene, 324 g. (1.0 mole) of N-octadecenyl propylene diamine, and 306 g. of xylene. The mixture was stirred at a temperature of 356° F. for 6 hours at which time approximately 18 g. of water was collected in a trap. The mixture was then filtered through Celite. The yield was 582 g. (90 percent). The product was characterized by its infrared spectrum, showing the characteristic succinimide absorption. Molecular weight (Thermo-NAM-Differential Diffusion Technique)=6,140.

(B) The phosphate salt was prepared by combining 426 g. of the above polymer with 85 g. of an approximately 1:1 mole mixture of mono- and di(tridecyl) phosphate and diluting the resulting salt with 85 g. of xylene.

EXAMPLE II

(A) Into a reaction flask was introduced 126.7 g. of a copolymer prepared as described in Example A as a 27 percent solution in benzene, 9.2 g. of N,N-dimethyl propylenediamine and 44.1 g. of xylene and the mixture heated to 80° C., azeotroping the water with benzene. The temperature was then raised to 110° C. and maintained for 2 hours. An infrared spectrum substantiated the presence of imide.

(B) The phosphate salt was prepared by combining 94.1 g. of the polymer above with 34.4 g. of a 1:1 mole mixture of mono- and di(tridecyl) phosphoric acid, the temperature rising because of the exothermicity of the reaction. After cooling, the product was diluted with 34.4 g. of xylene.

In order to demonstrate the excellent effectiveness of the compositions of this invention as rust inhibitors, a number of fuels of varying purity, that is, the degree of hydrofining or purification, were tested according to the rusting test ASTM D 665–60, using synthetic sea water. The following table indicates the various oils or fuels used, the test conditions and the results, the rating being from 1 to 7. 7 being completely rusted and 1 being no rust.

TABLE I

	Test conditions		Additive (p.p.m.) Ex. I		
Base fuel [1]	Time (hr.)	Temp., °F.	0	10	25
Straight run distillate	20	82	5	3	[2] 2
Do	22	82	6	------	1
Kerosine	20	82	7	2	[2] 1
Do	20	82	6	------	1
Straight run distillate	20	82	6	------	1
Do	20	82	3	------	1
Straight run distillate cat-cracked distillate blend	5	140	7	------	1

[1] The different kerosines and straight run distillates are from different sources and different samples.
[2] At 20 p.p.m.

From the results of an ASTM D 665–60 test made with synthetic sea water for 20 hours at 80° F., a photograph of the resulting spindles was made, appearing as the figure. The first spindle (to the extreme left) is the base fuel; straight run cat-cracked distillate; the second spindle employed 20 p.p.m. of a commercial rust inhibitor; the third and fourth spindles employed 10 and 5 p.p.m. of the composition of Example I; and the fifth spindle employed 10 p.p.m. of the composition of Example II. The photograph graphically demonstrates the excellent protection from rust provided by the compositions of this invention.

A preferred embodiment of this invention is to use in fuel from 5 to 25 p.p.m. of the compositions of this invention, with from about 80 to 200 p.p.m. of the parent polysuccinimide. These polysuccinimides are found to be excellent liquid fuel additives, acting as dispersants and detergents. The combination of the parent polysuccinimide and its phosphate salt provides an excellent package for improving the properties of liquid fuels.

Using a 70 percent catalytically cracked light cycle oil plus 30 percent vacuum top-cut straight run fuel, the polysuccinimide of Example IA was tested, as well as combinations of the compositions of Example IA and IB according to known tests for determining detergency and disperancy effectiveness in fuels.

The first test comprises heating a sample fuel for 90 minutes at 300° F., cooling at ambient temperatures for 90 minutes, and then filtering through a Whatman No. 1 filter paper. The appearance of the deposits on the filter is rated by a reflectometer on a rating scale of 100% re-

flectance for a new white filter and 0% reflectance for a completely black filter.

The second test comprises heating the fuel for 20 hours at 200° F. The fuel was then cooled at ambient temperature for 24 hours and filtered through a tared 5-micron pore size millipore membrane filter. The filter is then weighed and the results are shown as parts per million of filter residue.

The following table indicates the results.

TABLE II

Additive	Conc., p.p.m.	First test [1]	Second test
		43	27
Example IA	100	78	1
Examples IA/IB	90/10	79	1
Examples IA/IB	80/20	74	2

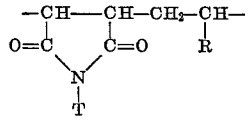
[1] A passing value is above 73.

It is evident from the above results that at extremely low concentrations, excellent protection from rusting and corrosion is obtained by employing the compositions of this invention. Even with the hydrofined fuels, which are notoriously troublesome as far as rusting of iron or steel containers, at extremely low concentrations, namely 25 p.p.m., complete protection from rusting is obtained.

As will be evident to those skilled in the art, various modifications on this invention can be made or followed, in the light of the foregoing disclosure and discussion, without departing from the spirit or scope of the disclosure or from the scope of the following claims.

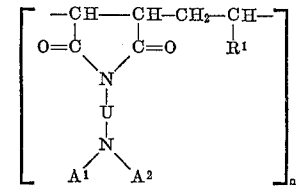
What is claimed is:

1. A hydrocarbon distillate fuel composition having in an amount sufficient to provide corrosion inhibition, a composition consisting of the phosphate salt of a polymer of from 4 to 20 recurring units of the formula:



wherein R is hydrogen or alkyl of from 1 to 20 carbon atoms, T is an aliphatic monoamino hydrocarbon radical of from 3 to 30 carbon atoms and the sum of the carbon atoms of $R+T$ is in the range of from about 12 to 50, wherein at least about 0.5 of the amino nitrogen present in the polymer is neutralized by phosphoric acid ester having from 1 to 2 alkyl groups of from about 8 to 30 carbon atoms.

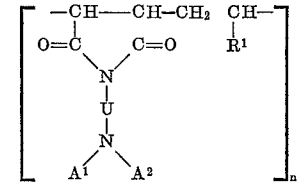
2. A hydrocarbon distillate fuel composition having in an amount sufficient to provide corrosion inhibition, a composition consisting of the phosphate salt of a polymer of a polymer of the formula:



wherein n is of from 4 to 20, R^1 is hydrogen or alkyl of from 1 to 20 carbon atoms, U is alkylene of from 2 to 6 carbon atoms and A^1 and A^2 are hydrogen or alkyl of from 1 to 20 carbon atoms, and the sum of the carbon atoms of R^1, U, A^1 and A^2 is in the range of 12 to 50, and at least 0.5 of the amino nitrogen present in the polymer is neutralized with a phosphate acid ester having from 1 to 2 alkyl groups of from about 8 to 30 carbon atoms.

3. A hydrocarbon distillate fuel composition having in an amount sufficient to provide corrosion inhibition, a composition according to claim 2, wherein the alkyl groups of said phosphoric acid ester are of from 10 to 20 carbon atoms.

4. A hydrocarbon distillate fuel composition having in an amount sufficient to provide corrosion inhibition a composition according to claim 2 and in an amount sufficient to provide detergency and dispersancy a polymer of the formula:



wherein n is of from 4 to 20, R^1 is alkyl of from 8 to 18 carbon atoms, U is alkylene of from 2 to 6 carbon atoms and A^1 and A^2 are hydrogen or alkyl of from 1 to 20 carbon atoms, and the sum of the carbon atoms of R^1, U, A^1 and A^2 is in the range of 12 to 50.

References Cited

UNITED STATES PATENTS

3,012,055	12/1961	Pollitzer	44—62
3,051,562	8/1962	Gee et al.	44—62
3,197,409	7/1965	De Vries	44—62
3,216,940	11/1965	Stuart et al.	44—62
3,216,941	11/1965	De Vries	44—62
3,231,498	11/1966	De Vries	44—62
3,235,503	2/1966	De Vries	44—62

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