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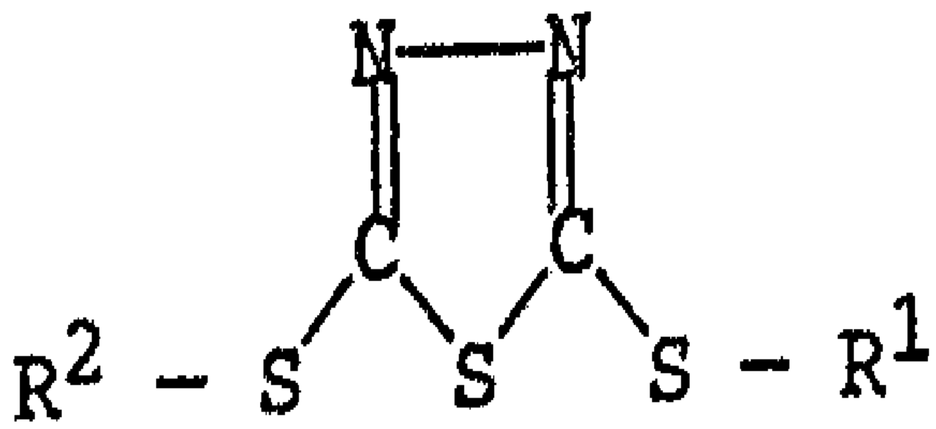
(54) **COMPOSITION DE MAZOUT LEGER CONTENANT UNE COMBINAISON D'INHIBITEURS DE CORROSION DU CUIVRE**

(54) **DISTILLATE FUEL COMPOSITON CONTAINING COMBINATION OF COPPER CORROSION INHIBITORS**

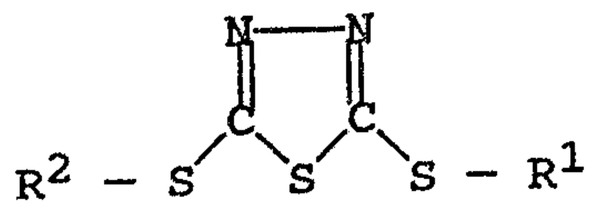


(57) A distillate fuel composition for reducing copper corrosion in fuel delivery systems and internal combustion engines which comprises a synergistic combination of (a) a 2,5-dihydrocarbyldithio-1,3,4-thiadiazole of the formula (see formula above) wherein R^1 and R^2 are independently R^3S or H where R^3 is a hydrocarbyl group containing from I to 16 carbon atoms with the proviso that at Least one of R^1 and R^2 is not hydrogen, and (b) an adduct of tolyltriazole and a basic nitrogen compound selected from the group consisting of polyamines, akoxyamines, aryloxyamines and monoalkyleneamines.

ABSTRACT OF THE DISCLOSURE

A distillate fuel composition for reducing copper corrosion in fuel delivery systems and internal combustion engines which comprises a synergistic combination of

(a) a 2,5-dihydrocarbyldithio-1,3,4-thiadiazole of the formula



wherein R^1 and R^2 are independently R^3S or H where R^3 is a hydrocarbyl group containing from 1 to 16 carbon atoms with the proviso that at least one of R^1 and R^2 is not hydrogen, and

(b) an adduct of tolyltriazole and a basic nitrogen compound selected from the group consisting of polyamines, alkoxyamines, aryloxyamines and monoalkyleneamines.

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BACKGROUND OF THE INVENTION

1. Field Of The Invention

This invention relates to a distillate fuel composition containing a thiadiazole and a tolyltriazole adduct as copper corrosion inhibitors, and its use to reduce copper corrosion in fuel delivery systems and internal combustion engines.

2. Description Of The Related Art

It is well known that elemental sulfur, hydrogen sulfide and other sulfur compounds, contained in hydrocarbon streams are corrosive and damaging to metal equipment, particularly copper and copper alloys. Sulfur and sulfur compounds may be present in varying concentrations in the refined fuel and additional contamination may take place as a consequence of transporting the refined fuel through pipelines containing sulfur contaminants. Sulfur has a particularly corrosive effect on equipment such as brass valves, gauges and in-tank fuel pump copper commutators.

A commonly used technique for inhibiting corrosion of copper, steel or copper alloys in fuel systems is by the use of corrosion inhibitors. These additives are either sulfur scavengers or metal deactivators that coat metal surfaces preventing sulfur components to react with the metal. Many such corrosion inhibitors are known. For example, U.S. Patent 3,663,561 discloses 2-hydrocarbylthio-5-mercapto-1,3,4-thiadiazoles which are stated to be useful as sulfur scavengers and U.S. Patent 5,035,720 relates to a corrosion inhibiting composition comprising an oil-soluble adduct of a triazole and a basic nitrogen compound.

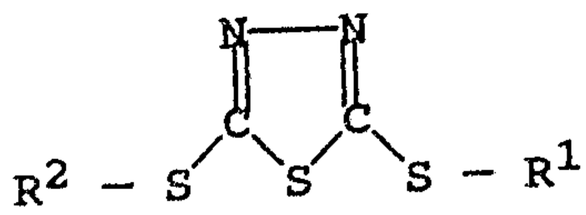
It would be desirable to have a copper corrosion inhibitor which would protect copper at low treat rates when exposed to a variety of fuels under different conditions and which would not produce high levels of insolubles or cause injector sticking in diesel engines.

2118618

SUMMARY OF THE INVENTION

This invention relates to a distillate fuel composition having improved copper corrosion properties which comprises a major amount of distillate fuel and an amount effective to provide copper corrosion protection of a synergistic additive combination of

(a) a 2,5-dihydrocarbyldithio-1,3,4-thiadiazole of the formula



where R^1 and R^2 are independently hydrogen or R^3S where R^3 is a hydrocarbyl group containing 1 to 16 carbon atoms with the proviso that at least one of R^1 and R^2 is not hydrogen, and

(b) an adduct of tolyltriazole and a basic nitrogen compound selected from the group consisting of polyamines, alkoxyamines, aryloxyamines and monoalkyleneamines.

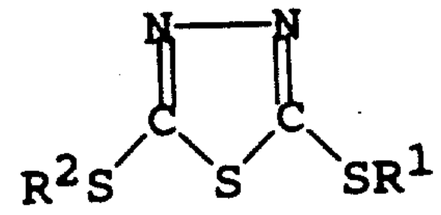
In another embodiment, this invention concerns a method for reducing copper corrosion in a fuel delivery system or internal combustion engine by operating the fuel delivery system or internal combustion engine with the composition described above. Yet another embodiment involves a fuel additive concentrate containing the above additive combination.

Detailed Description Of The Invention

This invention concerns the discovery that a distillate fuel containing a major amount of distillate fuel and a minor amount of a synergistic combination of (a) 2,5-hydrocarbyldithio-1,3,4-thiadiazole and (b) an adduct of tolyltriazole and basic nitrogen compound can reduce copper corrosion in fuel delivery systems and internal combustion engines. The combination of components (a) and (b) unexpectedly

provides better protection from copper corrosion than either of the components alone.

In the additive combination noted above, component (a) is a thiadiazole of the formula



where R^1 and R^2 are hydrogen or R^3S, R^3 is preferably a C_1 to C_{10} hydrocarbyl group. The hydrocarbyl groups include aliphatic (alkyl or alkenyl) and alicylic groups which may be substituted with hydroxy, amino, nitro and the like. Examples of preferred R^3 groups include methyl, ethyl, n- and iso-propyl, n-, sec- and tert-butyl, hexyl, cyclohexyl, octyl and decyl.

Preferred tolyltriazole adducts include the 1:1 adducts of tolyltriazole with fatty amines. Especially preferred fatty amines have the formula $R^4R^5NR^6$ where R^4 and R^5 are C_1 to C_4 hydrocarbyl groups which may be substituted with hydroxy, particularly C_2 alkyl substituted with hydroxy and R^6 is a C_8 to C_{20} hydrocarbyl group, especially C_{12} to C_{18} alkyl or alkenyl. Examples of preferred adducts include the 1:1 adduct between tolyltriazole and bis(2-hydroxyethyl) oleylamine and between tolyltriazole and bis (2-hydroxyethyl) coco-amine.

The tolyltriazole adducts with polyamines, alkoxyamines, aryloxyamines and monoalkyleneamines may be prepared by the methods described in U.S. Patent 5,035,720. In general, the amine is heated to between 70°C and 100°C and tolytriazole added slowly to the heated amine with stirring. Tolyltriazole is added to amine in an approximate 1:1 mole ratio. Upon completion of the reaction, the reaction mixture is cooled and may be used without further purification.

The distillate fuels of this invention will, in general, comprise a major amount of gasoline and a minor synergistic amount of the thiadiazole and the tolytriazole adduct. However, the precise

amount and ratio of the thiadiazole and tolytriazole adduct can vary broadly. As such, only an amount effective or sufficient to reduce the formation of engine intake system deposits need be used. Typically, however, the amount of the thiadiazole component will range from about 2 to about 30 ppmw, although greater amounts could be used. Preferably, from about 2 to about 10 ppmw of the thiadiazole component will be present in the fuel. The amount of tolyltriazole adduct will generally range from about 8 to about 90 ppmw, preferably from about 8 to about 40 ppmw, based on fuel.

Other additives may be included in the fuel. Examples of such additives include antiknock agents (e.g., tetraethyl lead), detergents or dispersants, demulsifiers, antioxidants and the like.

Although the tolyltriazole adducts and thiadiazoles used herein will generally be added to a distillate fuel, they may be formulated as a concentrate using an organic solvent (e.g., a hydrocarbon solvent, an alcohol solvent, or mixtures thereof) boiling in the range of about 165°C to about 400°C. Preferably, an aromatic hydrocarbon solvent (such as benzene, toluene, xylene, or higher boiling aromatics or aromatic thinners, and the like) is used. Aliphatic alcohols containing from 3 to 8 carbon atoms (such as isopropanol, isobutylcarbinol, n-butanol, and the like), alone or in combination with hydrocarbon solvents, can also be used. The amount of thiadiazole in the concentrate will ordinarily be at least 10 wt% and, generally, will not exceed about 50 wt%. The amount of adduct of tolyltriazole and basic nitrogen compound will generally be between 30 wt% and 70 wt%. The amount of solvent will make up the balance of the concentrate.

This invention will be further understood by reference to the following examples, which include a preferred embodiment of this invention.

Example 1

This example shows a comparison of copper corrosion between a typical metal deactivator and the synergistic combination according to this invention. The corrosion test is ASTM D-130 which is described as follows.

A polished copper strip is immersed in 30 ml of sample contained in a clean, dry 25 by 150 mm test tube and placed into a controlled temperature bath at 100±1°C. After 3 hours, the copper strip is removed, washed, and compared with the ASTM Copper Strip Corrosion Standards.

The ratings correspond to the following descriptions of the appearance of the copper strip:

Rating	Description
1a	Slight tarnish. Light orange, almost the same as a freshly polished strip.
1b	Slight tarnish. Dar orange.
2a	Moderate tarnish. Claret red.
2b	Moderate tarnish. Lavender.
2c	Moderate tarnish. Multicoloured with lavender blue or silver, or both, overlaid on claret red.
2d	Moderate tarnish. Silvery.
2e	Moderate tarnish. Brassy or gold.
3a	Dark tarnish. Magenta overcast on brassy strip.
3b	Dark tarnish. Multicoloured with red and green showing (peacock), but no gray.
4a	Corrosion. Transparent black, dark grey or brown with peacock green barely showing.
4b	Corrosion. Graphite or lusterless black.
4c	Corrosion. Glossy or jet black.

Various samples of diesel fuels, including sour diesel fuels were treated with Reomet® 39 which is believed to be a 1-(dioctyl-amino) methyl tolyltriazole manufactured by Ciba-Geigy Corp. and a combination of 30 wt% Elco® 461 which is believed to be a dioctyldi-thio-1,3,4-thiadiazole manufactured by Elco Corp. and 70 wt% Petrolite® 91-57676 which is believed to be a 1:1 adduct of tolyl-triazole and bis(2-hydroxyethyl)cocoamine manufactured by Petrolite

Corp., and tested for copper corrosion using ASTMD-130. The results are shown in Table 1.

TABLE 1

		Copper Corrosion Rating (D-130)			
Additive	Treat rate, mg/l	Diesel 506	Diesel 506 +9 mg/l S°	Diesel 434	Diesel 434 +9 mg/l S°
--	0	3a	4a	3b	4a
Reomet 39	10	3a	3b	3b	3b
	20	3a	3b	3b	3b
	30	3a	3b	3b	3b
	40	3a	3b	3b	3b
	50	3a	3b	3b	4a
	80	3a	3b	3b	3b
Elco 461 +91-57676	10	3a	3b	3b	3b
	20		3b	3a	3b
	30	1b	3b	3a	4a
	40	1b	1b	1b	1b

This data demonstrates that the combination of Elco® 461 plus Petrolite® 91-57676 is capable of achieving a corrosion rating of 1a/1b at the 30 to 40 mg/l treat rate whereas Reomet 39 cannot even at twice the treat rate.

Example 2

This example demonstrates the synergistic action of a thiadiazole plus tolyltriazole adduct versus either component acting alone. Table 2 is a comparison of Petrolite® 91-57676 alone, Elco® alone and a combination of 30 wt% Elco® 461 plus 70 wt% Petrolite®

1-57676 using the copper corrosion test ASTM D-130 described in Example 1.

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TABLE 2

Additive	Copper Corrosion Rating (D-130) Treat Rate mg/l	Diesel 295 +9 mg/l S°
--	0	4a
91-57676	10	4a
	20	4a
	30	4a
	40	4a
Elco 461	5	4a
	10	4a
	15	2d
	20	1b
	25	1b
30 wt% Elco 461 70 wt% 91-57676	10	4a
	20	4a
	30	1b
	40	1b

Petrolite® 91-57676 alone cannot achieve a 1a/1b rating over the treat rate studied. Elco® 461 is capable of achieving a 1a/1b rating at a treat rate of 20 mg/l. The combination according to invention shown in Table 2 can achieve a 1a/1b rating at a total 30 mg/l treat rate. This 30 mg/l treat rate is made up of 9 mg/l of Elco® 461 and 21 mg/l of Petrolite® 91-57676. Thus, the combination achieves a comparable rating at a treat rate which is less than one-half the treat rate of either component alone.

Example 3

This example shows that the synergistic combination of the invention produces less insolubles when compared to a single component alone. The test used to determine insolubles is ASTM D-2274 which is described as follows. A 350 ml volume of filtered middle distillate fuel is aged at 95°C for 16 hours while oxygen is bubbled through the sample at a rate of 3 L/h. After aging, the sample is cooled to approximately room temperature before filtering to obtain the filterable insolubles quantity. Adherent insolubles are then removed from

the oxidation cell and associated glassware with trisolvent. The trisolvent is evaporated to obtain the quantity of adherent insolubles. The sum of the filterable and adherent insolubles, expressed as milligrams per 100 ml, is reported as total insolubles.

The results are summarized in Table 3.

TABLE 3

Properties	Diesel Base	Diesel Base +100 mg/l Elco 461	Diesel Base +30 mg/l Elco 461 +70 mg/l 91-57676
Filt Insol, mg/100 ml	0.68	1.3	0.54
Adh Insol, mg/100 ml	0.09	0.2	0.11
Total Insol, mg/100 ml	0.77	1.5	0.65
Colour Initial	< 2.0	< 2.0	< 2.0
Colour Final	< 2.5	< 3.0	< 3.0

As shown in Table 3, the combination of Elco® 461/Petrolite® 91-57676 produces less insolubles than Elco® 461 alone at equivalent treat rate.

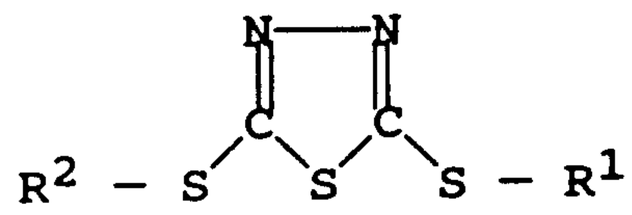
Example 4

An important test for fuel performance in diesel engines is an injector sticking test. This is a qualitative test which evaluates fuel performance in a diesel engine under a given set of engine operating conditions with the only variable being the fuel under evaluation. Each diesel injector is visually inspected for stickiness after each 20 hr. cycle of a four cycle test protocol. The combination of 30 wt% Elco® 461/70 wt% Petrolite® 91-57676 passed this test at 100 mg/l treat rate whereas Elco® 461 at the same treat rate failed.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A distillate fuel composition which comprises a major amount of distillate fuel and an amount effective to provide copper corrosion protection of a synergistic additive combination of

(a) a 2,5-dihydrocarbyldithio-1,3,4-thiadiazole of the formula



wherein R^1 and R^2 are independently R^3S or H where R^3 is a hydrocarbyl group containing from 1 to 16 carbon atoms with the proviso that at least one of R^1 and R^2 is not hydrogen, and

(b) a 1:1 adduct of tolyltriazole and a fatty amine of the formula $R^4R^5NR^6$ where R^4 and R^5 are C_1 to C_4 hydrocarbyl groups or said groups substituted by OH and R^6 is a hydrocarbyl group of from 8 to 20 carbon atoms.

2. The composition of claim 1 wherein R^3 is a hydrocarbyl group of from 1 to 10 carbon atoms.

3. The composition of claim 1 wherein R^4 and R^5 are hydroxyethyl groups.

4. The composition of claim 1 wherein the tolyltriazole adduct is a 1:1 adduct of tolyltriazole with bis(2-hydroxyethyl) oleylamine or with bis(2-hydroxyethyl)cocoamine.

5. The composition of claim 1 wherein the amount of component (a) is from 2 to 30 ppmw and the amount of component (b) is from 8 to 90 ppmw.

6. A method for reducing copper corrosion in a fuel delivery system or internal combustion engine which comprises operating the

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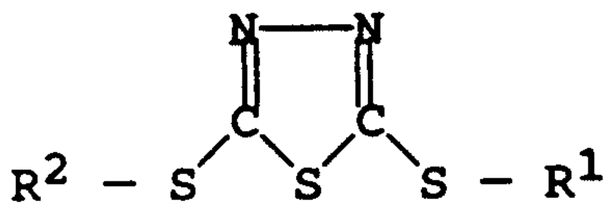
fuel delivery system or internal combustion engine with a fuel containing an effective amount to reduce copper corrosion of the synergistic combination of any one of claims 1 to 5.

7. An additive concentrate suitable for blending with a distillate fuel to provide copper corrosion protection which comprises a solvent and from 10 wt% to 50 wt% based on solvent of a 2,5-dihydrocarbyldithio-1,3,4-thiadiazole of the formula



wherein R^1 and R^2 are independently R^3S or H where R^3 is a hydrocarbyl group containing from 1 to 16 carbon atoms with the proviso that at least one of R^1 and R^2 is not hydrogen, and from 30 wt% to 70 wt% based on solvent of a 1:1 adduct of tolyltriazole and a fatty amine of the formula $R^4R^5NR^6$ where R^4 and R^5 are C_1 and C_4 hydrocarbyl groups and R^6 is a hydrocarbyl group of from 8 to 20 carbon atoms.

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