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DIMERCAPTOTHIADIAZOLE-MERCAPTAN COUPLED COMPOUNDS
AS MULTIFUNCTIONAL ADDITIVES FOR LUBRICANTS AND FUELS

This invention is directed to combinations of
dimercaptiothiadiazole-mercaptan coupled dithio compounds
5 with amines which have proven to be highly effective
multifunctional antiwear/extreme pressure additives for
lubricants and fuels.

Dimercaptiothiadiazole derivatives, such as
2,5-dimercapto-1,3,4-thiadiazole, disodium
10 2,5-dimercaptiothiadiazole and 2, 5-bis(t-nonyl-dithio)
thiadiazole, are well known for their antioxidancy,
anticorrosion, and metal passivation properties in a
variety of lubricant applications, as disclosed in U.S.
Patent Nos. 4,661,273, 4,678,592 and 4,584,114.

15 Furthermore, U. S. 5,186,850 discloses that the
incorporation of the heterocyclic dimercaptiothiadiazole
functionality into succinimide structures provides ashless
dispersants with multifunctional antiwear, antioxidant and
corrosion inhibitor properties in lubricant compositions.
20 Additionally, various reaction products of mercapto- and
dimercaptiothiadiazoles have been known to possess extreme
pressure/antiwear properties, in a variety of lubricant
formulations, as exemplified in U.S. Pat. No. 4,661,273;
4,382,869; and 4,678,592.

25 The use of amines in lubricants and the detergent
industry has been well known for their alkalinity, surface
activity, and neutralization capability. Amine phosphate
is one class of additives used extensively in industrial
oils, and polyamine-derived succinimides are key components
30 in ashless dispersants of engine oils.

Reaction products of dimercaptiothiadiazole derived
alcohols and alkenyl succinic anhydrides and their
subsequent amine reaction products have been found to be
effective antiwear/antioxidant additives for lubricants;
35 see U.S. 4,908,144. U.S. 5,188,746 discloses antiwear/
antioxidant additives for lubricants based on

dimercaptothiadiazone derivatives of acrylate and methacrylate polymers and amine reaction products thereof.

It has now been found that the use of these combinations of thiadiazone-derived dithio additives with
5 amine derivatives, in accordance with the present invention, provide exceptional antiwear/EP activity with significantly enhanced metal passivating/corrosion inhibiting properties for lubricants and fuels.

Lubricant and fuel compositions in accordance with the
10 invention containing small additive concentration of a combination of a dimercaptothiadiazone-mercaptan coupled compound with an amine product possess excellent antiwear properties coupled with good extreme pressure activities. Additional antioxidation, cleanliness, antifatigue, high
15 temperature stabilizing, and friction modifying properties are likely. Both the thiadiazone-dithio moiety and the amine/ammonium salt moiety are believed to provide the basis for the synergistic antiwear and EP property of these novel additives.

20 All of these beneficial properties are believed to be enhanced as a result of this novel internal synergism. This unique internal synergism concept is believed to be applicable to similar structures containing (a) thiadiazone groups, (b) dithio linking groups, (c) amine groups within
25 the same component. The products of this invention show good stability and compatibility when used in the presence of other commonly used additives in fuel or lubricant compositions.

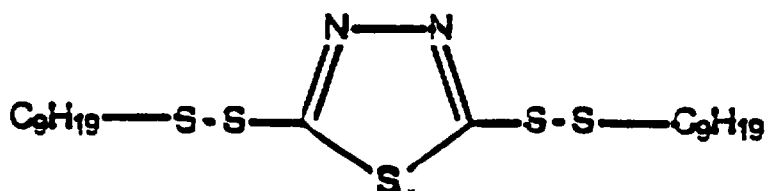
These remarkable benefits are also expected for a
30 variety of synthetic and mineral oil based lubricants and fuels particularly light distillate fuels containing these additives. The compositions of matter and the lubricant and fuel compositions are believed to be novel. To the best of our knowledge, these compositions have not been
35 previously used as antiwear/extreme pressure additives in lubricating oils, greases, or fuel applications.



More specifically this invention is directed to improved lubricant or fuel compositions comprising a major proportion of an oil of lubricating viscosity or a grease prepared therefrom, or a major proportion of a liquid hydrocarbyl or hydrocarboxy fuel and a minor proportion of a multifunctional antiwear/extreme pressure additive product of reaction consisting of combinations of dimercaptothiadiazole-mercaptan coupled dithio compounds with hydrocarbyl amines.

10 Preparation

2,5-dimercapto-1,3,4-thiadiazole (DMTD), made by the reaction of hydrazine with carbon disulfide, oxidatively coupled with alkyl mercaptans, such as nonyl, to form thiadiazole-derived dithio compounds (Structure A). These dithio adducts were then blended with various amines to form a new group of additive blends.



(Structure A)

However, applicants do not wish to be bound by a particular structure(s) or formula for the additive reaction products in accordance with the invention [Structure(s) B] i.e., the combination of the dithio adducts blended with the various amines.

The mercaptothiadiazoles may be prepared as above or made in any convenient manner or obtained as an article of commerce. Any suitable mercaptothiadiazole such as 2,5-dimercapto-1,3,4-thiadiazole; 3,5-dimercapto-1,2,4-thiadiazole; 4,5-dimercapto-1,2,5-thiadiazole; etc. can be used. Accordingly, the hydrocarbyl groups need not be alkyl or limited to C₉H₁₉ but may be R as in the below generalized structure:



(Structure B)

where R and R₁ can be the same or different and are hydrogen or C₁ to about C₃₀ hydrocarbonyl selected from alkyl, aryl, aralkyl, alkaryl and may optionally contain
 5 additional O, S, or N or mixtures thereof. Preferably R is C_nH_{2n+1}, where n is 1 to about 30.

Mercaptobenzothiazoles such as 6,7-dimercaptobenzo-2,1,3-thiadiazole are also believed to be suitable.

Generally, the amines used in this invention are
 10 aliphatic and can be primary, secondary, or tertiary and preferably alkylamines or arylamines.

Non-limiting examples of primary amines are methylamine; ethylamine; n-propylamine; isopropylamine; n-butylamine; dodecylamine; triacontylamine; allylamine; 2-
 15 propynylamine; cyclohexylamine; propargylamine; isobutylamine; sec-butylamine; 2-ethylhexylamine; cyclopropylmethylamine; t-butylamine; 1,1-dimethyl-2-propynylamine; 1,1-diethyl-2-propynylamine, 1-ethynylcyclohexylamine and benzylamine.

20 Non-limiting examples of secondary amines are dimethylamine, diethylamine, dibutylamine, diethylamine, ditetradecylamine, diallylamine, di-2-hexenylamine, dicyclohexylamine, methylethylamine, methylcyclohexylamine, diisopropylamine, diisopentylamine, ethyl
 25 cyclohexylamine, (3-amine-propyl)alkenylamine wherein the alkenyl group has 16 to 18 carbon atoms; (3-aminopropyl)alkenylamine wherein the alkenyl group has 18, 20, and 22 carbon atoms; and dihydrogenated tallow amine (e.g. Armeen 2HT).

Non-limiting examples of tertiary amines are trimethylamine, dimethyl ethylamine, triethylamine, tributylamine, trioctylamine, triallylamine, triisopentylamine, tricyclohexylamine, dimethyl

- 5 octylamine, n-hexadecyldimethylamine, (e.g. Armeen DM16D), n-octadecyl-dimethylamine (e.g. Armeen DM18D), methyl dihydrogenated tallowamine (e.g. Armeen M2HT), and methyl dicocoamine (e.g. Armeen M2C).

- Non-limiting examples of arylamines are aniline 2-
10 chloroaniline; 2-chloroaniline; 4-chloroaniline; 2-methyl-4-chloroaniline; 2,4-dichloroaniline; 3,4-dichloroaniline; 2,5-dichloro-4-nitroaniline; m-tri-fluoromethylaniline; isopropylaniline; p-methoxyaniline; N-methoxymethyl-2,6-diethylaniline; a-naphthylamine; N-sec-butyl-4-t-butyl-2,6-
15 dinitroaniline; 3-amino-2,5-dichlorobenzoic acid; N,N-dipropyl,a,a,a-trifluoro-2,6-dinitro-p-toluidine; 4-bromo-3-chloroaniline; 4(4'-chlorophenoxy) aniline; N³, N³-diethyl-2,4-dinitro-6-trifluoromethyl-m-phenylenediamine; p-dimethylaminoaniline; diphenylamine; p-bromoaniline; m-
20 aminiphenyl-t-butylcarbamate; o-phenylenediamine; m-phenylenediamine; 4-dimethylamino-3,5-dimethylphenol; 4-(methylsulfonyl)-2,6-dinitro-N,N-dipropylaniline; 3,5-dinitro-N,N-dipropylsulfanilamide; N-sec-butyl-4-t-butyl-2,6-dinitroaniline; m-toluidine; p-toluidine; m-t-
25 butylaniline; o-anisidine; p-anisidine; dimethylaniline; o-nitroaniline; p-nitroaniline; and 4,4'-oxydianiline.

- Non-limiting examples of heterocyclic amines are 3-amino-1,2,4-triazole; 2-chloro-4-ethylamino-6-isopropylamino-s-triazine; pyridine; piperidine;
30 piperazine; morpholine; 4,4'-dipyridyl; 8-hydroxyquinoline; 4-amino-6-t-butyl-3-(methylthio)-1,2,4-triazine-5(4H)-one; 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline; indole; hexahydro-1H-azepine; 4-amino-5-chloro-2-phenyl-3(2H)-pyridazinone; pyrrole; imidazolidine; isoquinoline; 2,4-
35 lutidine; 2-methyl-5-ethylpyridine; 2-dimethyl

aminopyridine; α -picoline; B-picoline; γ -picoline; quinoline; and 4,4'-dipyridine.

Non limiting examples of other salt forming amino compounds contemplated are 2-chloroethyl dimethylamine, diethanilaminel guanidine; dodecylguanidine; 3-(4-chlorophenyl)-1,1-dimethylurea, 3-(3,4-dichlorophenyl)-1,1-dimethylurea, Fenuron; Tandex; B-alanine; methyl glycine; glycinamide; aminoacetonitrile; aminoethanthiol; aminoacetic acid; diethyl ethanolamine; diethylenetriamine; isopropanolamine; diisopropanolaminel triisopropanolamine; ethylenediamine; hexamethylenetetramine; hydrazine; phenothiazine; sulfanilic acid; tetraethylenepentamine; thiourea; urea; triethanolamine; triethylenetetramine; diethanol soyaamine (e.g. Ethomeen S-12) and didecaoxyethylene soyaamine (e.g. Ethomeen S-20).

Examples of highly suitable amines are:

- a) cyclic amines: dicyclohexylamine, 1,4-diaminocyclohexane, piperidine, hexamethyleneimine, etc.;
- b) heterocyclic amines: morpholine, aminopropyl morpholine (APM), aminoethyl piperazine (AEP);
- c) etheramines: C₆ to C₁₃ alkyloxypropylamines (Exxon and Sherex), polyoxyalkylene amines (Texaco Jeffamine);
- d) diamines: Exxon etherdiamines (DA-14, DA-17), Texaco polyoxyalkylene diamine, Akzo Duomeens (Duomeen C&O);
- e) straight chain amines: ethylamine, propylamine, butylamine, pentylamine, hexylamine, dioctylamine, dicocoamine, etc.;
- f) branched chain amines: 2-ethylhexylamine, isopropylamine, isobutylamine, diisobutylamine, bis(2-ethylhexyl)amine, tert-alkyl amine(C18-C22), dicocoalkyl-methylamine.

An excess of one reagent or another can be used. Molar quantities, less than molar quantities, or more than molar quantities of either amines or dithio-adducts can be used.

Conditions for the above reactions may vary widely depending upon specific reeactants, the presence or absence of a solvent and the like. Any suitable set of reaction conditions known to the art may be used. Generally
5 stoichiometric or equimolar ratios of reactnats are used. However, more than molar or less than molar amounts may be used. In any event, reaction conditions are not viewed as critical. Generally speaking, the reaction temperature may vary from ambient to about 250°C or reflux, the pressure
10 may be autogenous or vary from ambient to about 100 psi with reaction times varying from about one hour to about 48 hours or more.

Clearly the use of additive concentrations of these dithio adducts coupled with various amines provide
15 exceptional antiwear, load-carrying activity and corrosion inhibiting properties, etc. when incorporated into fuel and lubricant compositions.

The additives embodied herein are utilized in lubricating oil or grease compositions in an amount which
20 imparts significant antioxidant, load-carrying and corrosions inhibiting characteristics to oil or grease as well as reducing the friction of engines operating with the oil in its crankcase. Concentrations of 0.001 to 10 wt. % based on the total weight of the composition can be used.
25 Preferably, the concentration is from 0.1 to 3 wt. %. It is expected that these materials would also be suitable for use in liquid hydrocarbyl or alcoholic or mixed hydrocarbyl/alcoholic fuel compositions. They are generally utilized in amounts varying from 50 to 500 pounds per 1000
30 barrels of fuel.

The additives have the ability to improve the antiwear characteristics and friction reducing characteristics of various oleagenous materials such as hydrocarbyl
lubricating media which may comprise liquid oils in the
35 form of either a mineral oil or a synthetic oil, or in the

form of a grease in which the aforementioned oils are employed as a vehicle.

In general, mineral oils, both paraffinic, naphthenic and mixtures thereof, employed as the lubricant, or grease vehicle, may be of any suitable lubricating viscosity range, as for example, from 6 mm²/s at 38°C (about 45 SSU at 100°F) to 1200 mm²/s at 38°C (about 6000 SSU at 100°F) and preferably, from 7.5 (about 50) to 62 mm²/s (about 250 SSU) at 99°C (210°F). These oils which may have viscosity indexes ranging to about 95 are preferred. The average molecular weights of these oils may range from 250 to 800. Where the lubricant is to be employed in the form of a grease, the lubricating oil is generally employed in an amount sufficient to balance the total grease composition, after accounting for the desired quantity of the thickening agent, and other additive components to be included in the grease formulation.

A wide variety of materials may be employed as thickening or gelling agents. These may include any of the conventional metal salts or soaps, which are dispersed in the lubricating vehicle in grease-forming quantities in an amount to impart to the resulting grease composition the desired consistency. Other thickening agents that may be employed in the grease formulation may comprise the non-soap thickeners, such as surface-modified clays and silicas, aryl ureas, calcium complexes and similar materials. In general, grease thickeners may be employed which do not melt and dissolve when used at the required temperature within a particular environment; however, in all other respects, any materials which is normally employed for thickening or gelling hydrocarbon fluids for foaming grease can be used in preparing grease in accordance with the present invention.

In instances where synthetic oils, or synthetic oils employed as the lubricant or vehicle for the grease, are desired in preference to mineral oils, or in combination

therewith, various compounds of this type may be successfully utilized. Typical synthetic oils include, but are not limited to, polyisobutylene, polybutenes, hydrogenated polydecenes, polypropylene glycol, polyethylene glycol, trimethylolpropane esters, neopentyl and pentaerythritol esters, di(2-ethylhexyl) sebacate, di(2-ethylhexyl) adipate, dibutyl phthalate, fluorocarbons, silicate esters, silanes, esters of phosphorus-containing acids, liquid ureas, ferrocene derivatives, hydrogenated synthetic oils, chain-type polyphenyls, siloxanes and silicones (polysiloxanes), alkyl-substituted diphenyl ethers typified by a butyl-substituted bis(p-phenoxy phenyl) ether, phenoxy phenylethers.

It is to be understood, however, that the compositions contemplated herein can also contain other materials. For example, corrosion inhibitors, extreme pressure agents and the like can be used as exemplified respectively by metallic phenates sulfonates, polymeric succinimides, non-metallic or metallic phosphorodithioates and the like. These materials do not detract from the value of the compositions of this invention, rather the materials serve to impart their customary properties to the particular compositions in which they are incorporated.

The following examples are merely illustrative and are not meant to be limitations on the scope of this invention.

EXAMPLE 1

Approximately 95 gm of 2,5-bis(t-nonyl-dithio)thiadiazole (commercially obtained from Amoco Chemical Company under the trademark Amoco 158 or from Mobil Chemical Company under the trademark Mobilad C-610) and 5 gm of isodecyloxypropylamine (commercially obtained from Sherex Chemical Company under the trademark Adogen 180) were blended together in a mixer at 80°C for two hours. After a quick filtration, approximately 99.5 gm of

yellow-brown liquid was recovered as desired blending product.

EXAMPLE 2

5 Approximately 90 gm of 2,5-bis(t-nonyl-dithio) thiadiazole and 10 gm of isodecyloxypropylamine were blended together in a mixer at 80°C for two hours. After a quick filtration, approximately 99.2 gm of yellow-brown liquid was recovered as desired blending product.

EXAMPLE 3

10 The reaction procedure of Example 2 was followed with one exception: C₁₈₋₂₂ tert-alkyl primary amine (commercially obtained from Rohm Haas Chemical Company under the trademark Primene JM-T) was used instead of isodecyloxypropylamine.

EXAMPLE 4

15 The reaction procedure of Example 1 was followed with one exception: oleyl 1,3-diaminopropane (commercially obtained from AKZO Chemical Company under the trademark Duomeen 0) was used instead of isodecyloxypropylamine.

20 Evaluation

The products of Examples 2, 3 and 4 were blended into industrial oils and evaluated for antiwear performance using the Four-Ball test (Table 1).

Table 1
Four-Ball Wear Test

5	<u>Item</u>	<u>Wear Scar Diameter in mm,</u> <u>30 Minute Test - 200°F</u>	
		<u>60 Kg</u> <u>1500 rpm</u>	<u>40 Kg</u> <u>1800 rpm</u>
	Base oil (80% solvent paraffinic bright, 20% solvent paraffinic neutral mineral oils)	2.12	0.733
10	1% Mobilad C-610	0.784	0.600
	1% Example 2	0.739	0.589
	1% Example 3	0.772	0.636
	1% Example 4	0.794	0.609

As can be seen from the above wear test results, the product exhibits considerable antiwear activity.

The products of the examples were also blended into fully formulated engine oils: Example 1 was evaluated for load carrying capacity using the Four Ball EP Test (Table 2); Examples 1 and 2 were evaluated in the FZG Gear tester (Table 3).

Table 2
Four-Ball EP Test and ASTM Copper Strip Corrosion
(EP:1760 rpm/10sec./25°C; D130-6:250F/3h, D130-8:210F/3h/1%H₂O)

25	<u>Item</u>	<u>Plus 1%</u>	
		<u>Base Oil*</u>	<u>Example 1</u>
	Last Non-seizure Load (Kg)	100	126
	Weld Load (Kg)	200	250
	Load Wear Index (LWI)	41.4	53.8
	Copper Strip (D130-6)	2B	1A
30	Copper Strip (D130-8)	2A	1A

*Base oil is a fully formulated synthetic engine oil containing a performance additive package including detergent, dispersant, antioxidant, corrosion inhibitor, and a small amount of zinc dithiophosphate.

Table 3

	<u>Item</u>	<u>FZG (pass stage)</u>
5	Base Oil (fully formulated synthetic oil with additive package containing antioxidant, rust inhibitor, detergent, and dispersant)	7
	Base Oil plus 1% Example 1	10
	Base oil plus 1% Example 2	12

10 In the Four Ball Wear Test three stationary balls are placed in a lubricant cup and a lubricant containing the compound to be tested is added thereto, and a fourth ball is placed in a chuck mounted on a device which can be used to spin the ball at known speeds and loads. The examples were tested using half inch stainless steel balls of 52100

15 steel for thirty minutes under 60/40 kg load at 1500 and 1800 rpm and 93°C (200°F). If additional information concerning this test is desired consult test method ASTM D2266 and/or U.S. Pat. No. 4,761,482.

20 The Copper Strip Corrosivity Test (ASTM D-130) measures a product's propensity to corrode copper due to, for example, contained sulfur groups. Further details may be found in ASTM Standards on Petroleum Products and Lubricants, published annually by the American Society for testing Materials.

25 The Four-Ball EP Test (ASTM D-2783) measures the extreme pressure characteristics or load-carrying properties of a lubricant by determining Load Wear Index (LWI) and weld point. A test ball is rotated under load at a tetrahedral position on top of three stationary balls

30 immersed in lubricant. Measurements of scars on the three stationary balls are used to calculate LWI's, and the weld is the load at which the four balls weld together in 10 seconds. The last non-seizure load is the last load at which the measured scar diameter is not more that 5% above

35 the compensation line at the load. The compensation line

is a logarithmic plot where the coordinates are scar diameter in millimeters and applied load in kilograms obtained under dynamic conditions. The higher the LWI value the better. See U.S. 4,965,002 and ASTM D-2783.

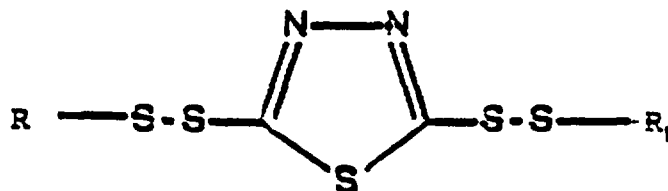
5 The FZG Gear Test (DIN-51.354). In this test, dip-lubricated gears are weighed and operated at a fixed speed and fixed initial oil temperature (90°C) in the gear oil under test. The load on the teeth is increased in increments. After each load stage, the weight changes are
10 determined and recorded. The results are reported in Table 3. The higher the Fail Stage value the better the material. The lower the wear value the better the weight change and/or visual condition. Further details can be found in CEC method L-07-A-71.

15 As shown above, the products of this invention show very good antiwear, extreme pressure activities as evidenced by improving wear characteristics and scoring load capacity from state 7 to stage 10-12 in FZG tester, and LWI in Four Ball EP test. In addition, the product of
20 this invention also shows excellent corrosivity control.

 The use of additive blends of bis(alkyl-dithio)thiadiazole and amines in premium quality industrial and engine lubricants will significantly enhance the stability, improve load-carrying, reduce the wear, and
25 extend the service life. These additive blends may also have the potential to benefit gasoline and diesel fuels by improving the antioxidation, antiwear, and anticorrosion characteristics of these fuels. These novel compositions described in this patent information are useful at low
30 concentrations and do not contain any potentially undesirable metals or phosphorus. These dual functional antiwear/EP-antioxidants can be readily commercially made.

CLAIMS:

1. An improved lubricant (or fuel) composition comprising a major proportion of an oil of lubricating viscosity or a grease prepared therefrom, or a liquid hydrocarbyl fuel and a minor proportion of a non-phosphorus, multifunctional antioxidant, load-carrying, antiwear/extreme pressure and corrosion inhibiting additive product of reaction and consisting of combinations of dimercaptothiadiaazole-mercaptan coupled dithio compounds with hydrocarbyl amines and wherein the reaction is carried out at temperatures varying from ambient to about 250°C under pressures varying from ambient to about 100 psi or is autogenous with the reaction time varying from about one hour to about 48 hours sufficient to obtain the desired additive product of reaction and where the reaction is carried out in molar ratios of reactants varying from equimolar to more than molar to less than molar.
2. The composition of claim 1 wherein said additive product of reaction is generally prepared by reacting a thiadiaazole-derived dithio compound of the structural formula



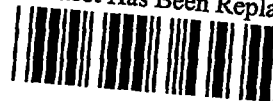
where R and R₁ are the same or different and are hydrogen or C₁ to about C₃₀ hydrocarbyl selected from alkyl, aryl, alkaryl, aralkyl and may optionally contain additional O, S, N or mixture thereof with a hydrocarbyl amine and wherein the reaction is carried out at temperatures varying from ambient to about 250°C and under pressures varying



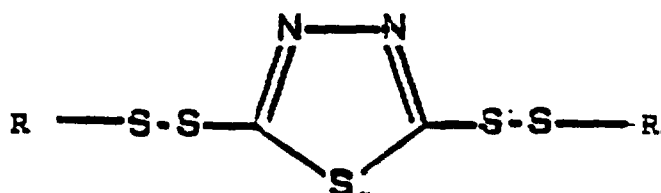
from ambient to about 100 psi or is autogenous with the reaction times varying from about one hour to about 48 hours time sufficient to obtain the desired additive product of reaction and where the reaction is carried out in molar ratios of reactants varying from equimolar to more than molar to less than molar.

3. The composition of claim 1 wherein said dithio compound is 2,5-bis(t-nonyl-dithio)thiadiazole and said amine is isodecyloxypropylamine.
4. The composition of claim 1 wherein said oil of lubricating viscosity is selected from (1) mineral oils, (2) synthetic oils, (3) or mixtures of mineral and synthetic oils or is (4) a grease prepared from any one of (1), (2) or (3).
5. The composition of claim 4 wherein the lubricant contains from 0.001 to 10 wt% based on the total weight of the composition of the additive product of reaction.
6. The composition of claim 4 wherein the lubricant is a mineral oil.
7. The composition of claim 4 wherein the lubricant is a synthetic oil.
8. The composition of claim 1 wherein the fuel is selected from liquid hydrocarbyl or hydrocarboxy or alcoholic or mixtures of hydrocarbyl and alcoholic fuels.
9. The composition of claim 8 wherein the fuel contains from 23 to 227 kg of said additive per 159000 l of fuel.





10. The composition of claim 8 wherein the fuel is a distillate fuel.
11. A lubricant fuel additive product of reaction consisting of combinations of dimercaptothiadiazo-
mercaptan coupled dithio compounds with hydrocarbyl
amines which combinations impart non-phosphorous
multifunctional, load-carrying and corrosion
inhibiting qualities to an oil of lubricating
viscosity or a grease prepared therefrom.
12. The additive product of claim 11 prepared by reacting
a thiadiazole-derived dithio compound of the
structural formula:



- where R and R₁ are the same or different and are hydrogen or C₁ to about C₃₀ hydrocarbyl selected from alkyl, aryl, alkaryl, aralkyl and may optionally contain additional O, S, N or mixtures thereof with a hydrocarbyl amine and wherein the reaction is carried out at temperatures varying from ambient to about 250°C under pressures varying from ambient to about 10 psi or is autogenous and the reaction time varying from about one hour to about 48 hours sufficient to obtain the desired additive product or reaction and where the reaction is carried out in molar ratios of reactants varying from equimolar to more than molar to less than molar.
13. The additive of claim 11 wherein the reactants are 2,5-bis(t-nonyl-dithio)thiadiazole and isodecyloxypropylamine.

