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(54) ALKYL-SUCCINHYDRAZIDE ADDITIVES FOR LUBRICANTS

ALKYLBERNSTEINSÄUREHYDRAZID-ADDITIVE FÜR SCHMIERMITTEL

ADDITIFS A BASE D'ALKYLE-SUCCINHYDRAZIDE POUR LUBRIFIANTS

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(73) Proprietor: **Chemtura Corporation**
Middlebury, CT 06749 (US)

(72) Inventor: **NALESNIK, Theodore, E.**
Hopewell Junction, NY 12533 (US)

(74) Representative: **Spott, Gottfried**
Spott, Weinmiller & Böhm
Patentanwälte
Sendlinger-Tor-Platz 11
80336 München (DE)

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- **FEUER H ET AL: "THE REACTIONS OF SUCCINIC ANHYDRIDE WITH HYDRAZINE HYDRATE" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, AMERICAN CHEMICAL SOCIETY, WASHINGTON, DC, US, vol. 73, 1951, pages 4716-4719, XP001121824 ISSN: 0002-7863**

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Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] This invention is related to lubricants, especially lubricating oils, and, more particularly, to a class of ashless and non-phosphorus-containing anti-wear, anti-fatigue, and extreme pressure additives derived from alkyl-succinhydrazides, i.e., 4-alkyl-1,2-dihydropyridazine-3,6-diones.

2. Description of Related Art

[0002] In developing lubricating oils, there have been many attempts to provide additives that impart anti-fatigue, anti-wear, and extreme pressure properties thereto. Zinc dialkyldithiophosphates (ZDDP) have been used in formulated oils as anti-wear additives for more than 50 years. However, zinc dialkyldithiophosphates give rise to ash, which contributes to particulate matter in automotive exhaust emissions, and regulatory agencies are seeking to reduce emissions of zinc into the environment. In addition, phosphorus, also a component of ZDDP, is suspected of limiting the service life of the catalytic converters that are used on cars to reduce pollution. It is important to limit the particulate matter and pollution formed during engine use for toxicological and environmental reasons, but it is also important to maintain undiminished the anti-wear properties of the lubricating oil.

[0003] In view of the aforementioned shortcomings of the known zinc and phosphorus-containing additives, efforts have been made to provide lubricating oil additives that contain neither zinc nor phosphorus or, at least, contain them in substantially reduced amounts.

[0004] Illustrative of non-zinc, i.e., ashless, non-phosphorus-containing lubricating oil additives are the reaction products of 2,5-dimercapto-1,3,4-thiadiazoles and unsaturated mono-, di-, and tri-glycerides disclosed in U.S. Patent No. 5,512,190 and the dialkyl dithiocarbamate-derived organic ethers of U.S. Patent No. 5,514,189.

[0005] U.S. Patent No. 5,512,190 discloses an additive that provides anti-wear properties to a lubricating oil. The additive is the reaction product of 2,5-dimercapto-1,3,4-thiadiazole and a mixture of unsaturated mono-, di-, and triglycerides. Also disclosed is a lubricating oil additive with anti-wear properties produced by reacting a mixture of unsaturated mono-, di-, and triglycerides with diethanolamine to provide an intermediate reaction product and reacting the intermediate reaction product with 2,5-dimercapto-1,3,4 thiadiazole.

[0006] U.S. Patent No. 5,514,189 discloses that dialkyl dithiocarbamate-derived organic ethers have been found to be effective anti-wear/antioxidant additives for lubricants and fuels.

[0007] U.S. Patent No. 3,284,234 discloses a stabilized cellulosic material which comprises a cellulosic material impregnated with at least 0.1 percent by weight of the cellulosic material of a hydrazide selected from the group consisting of the following compounds and mixtures thereof:

(I) $RCONHNH_2$

(II) $RCONHNHCOR$

(III) $R'(CONHNH_2)_2$

wherein each R is independently selected from the group consisting of hydrogen and alkyl containing from 1 to 2 carbon atoms and wherein R' is selected from the group consisting of $(-CH_2-)_n$, wherein n is an integer having a value of 0 to 5 and an alkylene of 2 to 6 carbon atoms interrupted by from 1 to 2 atoms selected from the group consisting of oxygen and sulfur.

[0008] U.S. Patent Nos. 5,084,195 and 5,300,243 disclose N-acyl-thiourethane thioureas as anti-wear additives specified for lubricants or hydraulic fluids.

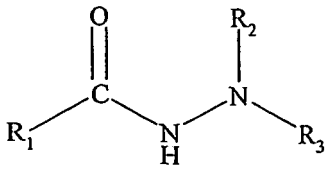
[0009] German Patent 1,260,137 discloses ethylene polymers that are said to exhibit reduced film blocking that are prepared by adding fatty acid hydrazides with more than six carbon atoms in addition to the usual internal lubricants. Lauroyl hydrazide, palmitoyl hydrazide, and stearoyl hydrazide were specifically used.

[0010] Japanese Published Application No. 03140346 discloses rigid vinyl chloride resin compositions said to have improved processability comprising 100 parts vinyl chloride resins and 3-20 parts of compounds selected from $(R_1CONH)_2(CH_2)_n$ (wherein R_1 is an OH-substituted C_1-C_{23} alkyl and n is 1-10), $(R_2CONH)_2(CH_2)_n$ (wherein R_2 is an OH-substituted C_4-C_{23} alkyl and n is 1-10), $R_3CONHNH_2$ (wherein R_3 is an OH-substituted C_4-C_{23} alkyl), $R_4NHCONHR_5$ (wherein R_4 is an OH-substituted alkyl, and $R_6NHCONH)_2R_7$ (wherein R_6 is an OH-substituted C_7-C_{23} alkyl and R_7 is a C_1-C_{10} alkylene, phenylene, or phenylene derivative). Stearic acid hydrazide and capric acid hydrazide are specifically men-

tioned.

[0011] U.S. Appl. No. 09/871,120 filed May 31, 2001, discloses a composition comprising:

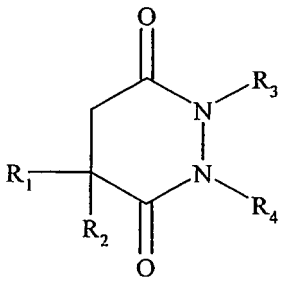
(A) a lubricant, and
(B) at least one alkyl hydrazide compound of the formula:



wherein R_1 is a hydrocarbon or functionalized hydrocarbon of from 1 to 30 carbon atoms, R_2 and R_3 are independently selected from the group consisting of hydrocarbon or functionalized hydrocarbons of from 1 to 30 carbon atoms and hydrogen.

SUMMARY OF THE INVENTION

[0012] The present invention relates to compounds of the formula



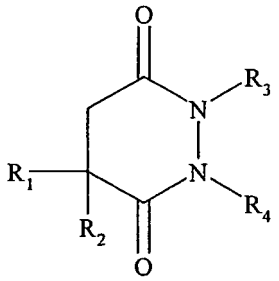
wherein

R_1 is a linear or branched alkyl, alkenyl, alkaryl, alkyl ether, or alkyl ester group, preferably of from 1 to 30 carbon atoms;
R_2 is hydrogen, a linear or branched alkyl, alkenyl, alkyl ether, or alkyl ester group, preferably of from 1 to 30 carbon atoms; and
R_3 and R_4 can be the same or different while being hydrogen or a linear or branched alkyl, aryl, alkenyl, or alkaryl group, preferably of from 1 to 30 carbon atoms.

[0013] The alkyl-succinhydrazide compounds of this invention are useful as ashless, non-phosphorus, non-sulfur-containing anti-fatigue, anti-wear, extreme pressure, anti-corrosion additives for lubricating oils.

[0014] The present invention also relates to lubricating oil compositions comprising a lubricating oil and a functional property-improving amount of at least one alkyl-succinhydrazide compound of the above formula. More particularly, the present invention is directed to a composition comprising:

(A) a lubricant, and
(B) at least one alkyl succinhydrazide compound of the formula:



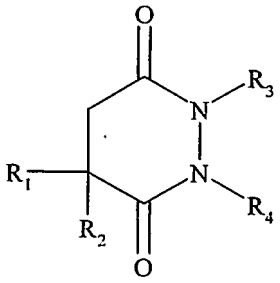
wherein:

R_1 is selected from the group consisting of linear or branched alkyl, alkenyl, alkaryl, alkyl ether, alkyl ester, and alkylene ester groups;
R_2 is selected from the group consisting of hydrogen, linear or branched alkyl, alkenyl, alkyl ether, and alkyl ester groups; and
R_3 and R_4 are independently selected from the group consisting of hydrogen, linear or branched alkyl and alkenyl groups, aryl groups, and alkaryl groups.

[0015] Preferably, the alkyl-succinhydrazide is present in the compositions of the present invention in a concentration in the range of from 0.01 to 10 wt%.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0016] The alkyl-succinhydrazide compounds of the present invention are compounds of the formula:



wherein:

R_1 is selected from the group consisting of linear or branched alkyl, alkenyl, alkaryl, alkyl ether, and alkyl ester groups;
R_2 is selected from the group consisting of hydrogen, linear or branched alkyl, alkenyl, alkyl ether, and alkyl ester groups; and
R_3 and R_4 are independently selected from the group consisting of hydrogen, linear or branched alkyl and alkenyl groups, aryl groups, and alkaryl groups.

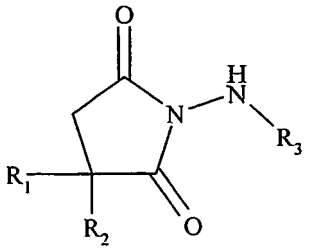
[0017] In the above structural formula, where R_1, R_2, R_3 and/or R_4 comprise an alkyl or alkenyl moiety, such moiety can be a straight or branched hydrocarbon chain, fully saturated or partially unsaturated, preferably having from 1 to 30 carbon atoms, more preferably 1 to 22, most preferably 1 to 18 carbon atoms, e.g., methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, oleyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, triacontyl, ethenyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, tridecenyl, tetradecenyl, pentadecenyl, hexadecenyl, heptadecenyl, octadecenyl, nonadecenyl, eicosenyl, heneicosenyl, docosenyl, tricosenyl, tetracosenyl, pentacosenyl, triacontenyl, and the like, and isomers and mixtures thereof. Additionally, R_1 and R_2 can be a linear or branched, saturated or partially unsaturated hydrocarbon chain, as described above, within which may be ester or oxygen

ether groups, and R_3 and/or R_4 can be alkaryl groups, such as nonylphenyl, dodecylphenyl, and the like. R_2, R_3 and R_4 may be the same. R_2, R_3 and R_4 may be hydrogen.

[0018] The use of the alkyl-succinhydrazide compounds of this invention can improve the anti-fatigue, anti-wear, and extreme pressure properties of a lubricant.

General Synthesis of Additives of this Invention

[0019] The general process for preparing the alkyl succinhydrazides of the present invention involves charging an alkyl succinic anhydride to a reaction vessel with a solvent that boils above 80° C and is capable of azeotroping off the water by-product. This solvent should also be unreactive with all the reactants and the product. Examples of solvent are hydrocarbons, such as heptane, decane, and dodecanes, and aromatic solvents, such as toluene, tetralins, and xylenes. The hydrazine hydrate is added slowly to the reaction vessel with the initial reaction temperature at room temperature or about 20° C. After the hydrazine addition is complete, the reaction media temperature may exotherm about 20 to 30° C, depending on the amount of solvent present and hydrazine used. The temperature of the reaction media is then raised to reflux to complete the reaction and remove the water by-product. The solvent is then removed under reduced pressure or under vacuum to yield the final product. This product may be polish filtered if necessary. When preparing products based on mono alkyl or unsymmetrical hydrazines, such as methyl and phenyl hydrazine, a minor amount of possible side product may also be a hydrazine succinimide of the structure:



wherein R_1, R_2, and R_3 are as described above. It is believed that this material, present in the product as a minor component, may also exhibit anti-wear properties in lubricant fluids

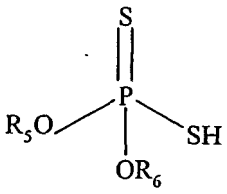
Use with Other Additives

[0020] The alkyl-succinhydrazide additives of this invention can be used as either a partial or complete replacement for the zinc dialkyldithiophosphates currently used. They can also be used in combination with other additives typically found in lubricating oils, as well as with other ashless, anti-wear additives. These alkyl-succinhydrazides may also display synergistic effects with these other typical additives to improve oil performance properties. The additives typically found in lubricating oils are, for example, dispersants, detergents, corrosion/rust inhibitors, antioxidants, anti-wear agents, anti-foamants, friction modifiers, seal swell agents, demulsifiers, VI improvers, pour point depressants, and the like. See, for example, U.S. Patent No. 5,498,809 for a description of useful lubricating oil composition additives, the disclosure of which is incorporated herein by reference in its entirety. Examples of dispersants include polyisobutylene succinimides, polyisobutylene succinate esters, Mannich Base ashless dispersants, and the like. Examples of detergents include alkyl metallic phenates, alkyl metallic sulfurized phenates, alkyl metallic sulfonates, alkyl metallic salicylates, and the like. Examples of antioxidants include alkylated diphenylamines, N-alkylated phenylenediamines, hindered phenolics, alkylated hydroquinones, hydroxylated thiodiphenyl ethers, alkylidenebisphenols, oil soluble copper and molybdenum compounds, and the like. Examples of anti-wear additives that can be used in combination with the additives of the present invention include organo borates, organo phosphites, organic sulfur-containing compounds, zinc dialkyldithiophosphates, zinc diaryldithiophosphates, phosphosulfurized hydrocarbons, and the like. The following are exemplary of such additives and are commercially available from The Lubrizol Corporation: Lubrizol 677A, Lubrizol 1095, Lubrizol 1097, Lubrizol 1360, Lubrizol 1395, Lubrizol 5139, and Lubrizol 5604, among others. Examples of friction modifiers include fatty acid esters and amides, organo sulfurized and unsulfurized molybdenum compounds, molybdenum dialkylthiocarbamates (molybdenum monomers, dimers, and trimers), molybdenum dialkyl dithiophosphates, and the like. An example of an anti-foamant is polysiloxane, and the like. An example of a rust inhibitor is a polyoxyalkylene polyol, and the like. Examples of VI improvers include olefin copolymers and dispersant olefin copolymers, and the like. An example of a pour point depressant is polymethacrylate, and the like.

[0021] Representative conventional anti-wear agents that can be used include, for example, the zinc dialkyl dithio-

phosphates and the zinc diaryl dithiophosphates.

[0022] Suitable phosphates include dihydrocarbyl dithiophosphates, wherein the hydrocarbyl groups contain an average of at least 3 carbon atoms. Particularly useful are metal salts of at least one dihydrocarbyl dithiophosphoric acid wherein the hydrocarbyl groups contain an average of at least 3 carbon atoms. The acids from which the dihydrocarbyl dithiophosphates can be derived can be illustrated by acids of the formula:



wherein R_5 and R_6 are the same or different and are alkyl, cycloalkyl, aralkyl, alkaryl or substituted substantially hydrocarbon radical derivatives of any of the above groups, and wherein the R_5 and R_6 groups in the acid each have, on average, at least 3 carbon atoms. By "substantially hydrocarbon" is meant radicals containing substituent groups (e.g., 1 to 4 substituent groups per radical moiety) such as ether, ester, nitro, or halogen that do not materially affect the hydrocarbon character of the radical.

[0023] Specific examples of suitable R_5 and R_6 radicals include isopropyl, isobutyl, n-butyl, sec-butyl, n-hexyl, heptyl, 2-ethylhexyl, diisobutyl, isooctyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, butylphenyl,o,p-depentylphenyl, octylphenyl, polyisobutene-(molecular weight 350)-substituted phenyl, tetrapropylene-substituted phenyl, beta-octylbutylnaphthyl, cyclopentyl, cyclohexyl, phenyl, chlorophenyl, o-dichlorophenyl, bromophenyl, naphthenyl, 2-methylcyclohexyl, benzyl, chlorobenzyl, chloropentyl, dichlorophenyl, nitrophenyl, dichlorodecyl and xenyl radicals. Alkyl radicals having from about 3 to about 30 carbon atoms and aryl radicals having from about 6 to about 30 carbon atoms are preferred. Particularly preferred R_5 and R_6 radicals are alkyl of from 4 to 18 carbon atoms.

[0024] The phosphorodithioic acids are readily obtainable by the reaction of phosphorus pentasulfide and an alcohol or phenol. The reaction involves mixing, at a temperature of about 20° C. to 200° C., 4 moles of the alcohol or phenol with one mole of phosphorus pentasulfide. Hydrogen sulfide is liberated as the reaction takes place. Mixtures of alcohols, phenols, or both can be employed, e.g., mixtures of C_3 to C_{30} alcohols, C_6 to C_{30} aromatic alcohols, etc.

[0025] The metals useful to make the phosphate salts include Group I metals, Group II metals, aluminum, lead, tin, molybdenum, manganese, cobalt, and nickel. Zinc is the preferred metal. Examples of metal compounds that can be reacted with the acid include lithium oxide, lithium hydroxide, lithium carbonate, lithium pentylate, sodium oxide, sodium hydroxide, sodium carbonate, sodium methylate, sodium propylate, sodium phenoxide, potassium oxide, potassium hydroxide, potassium carbonate, potassium methylate, silver oxide, silver carbonate, magnesium oxide, magnesium hydroxide, magnesium carbonate, magnesium ethylate, magnesium propylate, magnesium phenoxide, calcium oxide, calcium hydroxide, calcium carbonate, calcium methylate, calcium propylate, calcium pentylate, zinc oxide, zinc hydroxide, zinc carbonate, zinc propylate, strontium oxide, strontium hydroxide, cadmium oxide, cadmium hydroxide, cadmium carbonate, cadmium ethylate, barium oxide, barium hydroxide, barium hydrate, barium carbonate, barium ethylate, barium pentylate, aluminum oxide, aluminum propylate, lead oxide, lead hydroxide, lead carbonate, tin oxide, tin butylate, cobalt oxide, cobalt hydroxide, cobalt carbonate, cobalt pentylate, nickel oxide, nickel hydroxide, and nickel carbonate.

[0026] In some instances, the incorporation of certain ingredients, particularly carboxylic acids or metal carboxylates, such as, small amounts of the metal acetate or acetic acid, used in conjunction with the metal reactant will facilitate the reaction and result in an improved product. For example, the use of up to about 5% of zinc acetate in combination with the required amount of zinc oxide facilitates the formation of a zinc phosphorodithioate.

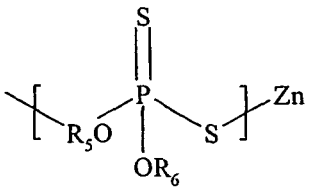
[0027] The preparation of metal phosphorodithioates is well known in the art and is described in a large number of issued patents, including U.S. Patent Nos. 3,293,181; 3,397,145; 3,396,109 and 3,442,804, the disclosures of which are hereby incorporated by reference. Also useful as anti-wear additives are amine derivatives of dithiophosphoric acid compounds, such as are described in U.S. Patent No. 3,637,499, the disclosure of which is hereby incorporated by reference in its entirety.

[0028] The zinc salts are most commonly used as anti-wear additives in lubricating oil in amounts of 0.1 to 10, preferably 0.2 to 2, wt. %, based upon the total weight of the lubricating oil composition. They may be prepared in accordance with known techniques by first forming a dithiophosphoric acid, usually by reaction of an alcohol or a phenol with P_2S_5 and then neutralizing the dithiophosphoric acid with a suitable zinc compound.

[0029] Mixtures of alcohols can be used, including mixtures of primary and secondary alcohols, secondary generally for imparting improved anti-wear properties and primary for thermal stability. Mixtures of the two are particularly useful.

In general, any basic or neutral zinc compound could be used, but the oxides, hydroxides, and carbonates are most generally employed. Commercial additives frequently contain an excess of zinc owing to use of an excess of the basic zinc compound in the neutralization reaction.

[0030] The zinc dihydrocarbyl dithiophosphates (ZDDP) are oil soluble salts of dihydrocarbyl esters of dithiophosphoric acids and can be represented by the following formula:



wherein R_5 and R_6 are as described in connection with the previous formula.

[0031] Especially preferred additives for use in the practice of the present invention include alkylated diphenylamines, hindered alkylated phenols, hindered alkylated phenolic esters, and molybdenum dithiocarbamates.

Lubricant Compositions

[0032] Compositions, when they contain these additives, are typically blended into the base oil in amounts such that the additives therein are effective to provide their normal attendant functions. Representative effective amounts of such additives are illustrated in TABLE 1.

TABLE 1

Additives	Preferred Weight %	More Preferred Weight %
V.I. Improver	1-12	1-4
Corrosion Inhibitor	0.01-3	0.01-1.5
Oxidation Inhibitor	0.01-5	0.01-1.5
Dispersant	0.01-10	0.01-5
Lube Oil Flow Improver	0.01-2	0.01-1.5
Detergent/Rust Inhibitor	0.01-6	0.01-3
Pour Point Depressant	0.01-1.5	0.01-0.5
Antifoaming Agent	0.001-0.1	0.001-0.01
Anti-wear Agent	0.001-5	0.001-1.5
Seal Swellant	0.1-8	01.-4
Friction Modifier	0.01-3	0.01-1.5
Lubricating Base Oil	Balance	Balance

[0033] When other additives are employed, it may be desirable, although not necessary, to prepare additive concentrates comprising concentrated solutions or dispersions of the subject additives of this invention, together with one or more of said other additives (said concentrate when constituting an additive mixture being referred to herein as an additive-package) whereby several additives can be added simultaneously to the base oil to form the lubricating oil composition. Dissolution of the additive concentrate into the lubricating oil can be facilitated by solvents and/or by mixing accompanied by mild heating, but this is not essential. The concentrate or additive-package will typically be formulated to contain the additives in proper amounts to provide the desired concentration in the final formulation when the additive-package is combined with a predetermined amount of base lubricant. Thus, the subject additives of the present invention can be added to small amounts of base oil or other compatible solvents along with other desirable additives to form additive-packages containing active ingredients in collective amounts of, typically, from about 2.5 to about 90 percent, preferably from about 15 to about 75 percent, and more preferably from about 25 percent to about 60 percent by weight

additives in the appropriate proportions with the remainder being base oil. The final formulations can typically employ about 1 to 20 weight percent of the additive-package with the remainder being base oil.

[0034] All of the weight percentages expressed herein (unless otherwise indicated) are based on the active ingredient (AI) content of the additive, and/or upon the total weight of any additive-package, or formulation, which will be the sum of the AI weight of each additive plus the weight of total oil or diluent.

[0035] In general, the lubricant compositions of the invention contain the additives in a concentration ranging from about 0.05 to about 30 weight percent. A concentration range for the additives ranging from about 0.1 to about 10 weight percent based on the total weight of the oil composition is preferred. A more preferred concentration range is from about 0.2 to about 5 weight percent. Oil concentrates of the additives can contain from about 1 to about 75 weight percent of the additive reaction product in a carrier or diluent oil of lubricating oil viscosity.

[0036] In general, the additives of the present invention are useful in a variety of lubricating oil base stocks. The lubricating oil base stock is any natural or synthetic lubricating oil base stock fraction having a kinematic viscosity at 100° C of about 2 to about 200 cSt, more preferably about 3 to about 150 cSt, and most preferably about 3 to about 100 cSt. The lubricating oil base stock can be derived from natural lubricating oils, synthetic lubricating oils, or mixtures thereof. Suitable lubricating oil base stocks include base stocks obtained by isomerization of synthetic wax and wax, as well as hydrocrackate base stocks produced by hydrocracking (rather than solvent extracting) the aromatic and polar components of the crude. Natural lubricating oils include animal oils, such as, lard oil, vegetable oils (e.g., canola oils, castor oils, sunflower oils), petroleum oils, mineral oils, and oils derived from coal or shale.

[0037] Synthetic oils include hydrocarbon oils and halo-substituted hydrocarbon oils, such as, polymerized and interpolymerized olefins, alkylbenzenes, polyphenyls, alkylated diphenyl ethers, alkylated diphenyl sulfides, as well as their derivatives, analogs, homologues, and the like. Synthetic lubricating oils also include alkylene oxide polymers, interpolymers, copolymers, and derivatives thereof, wherein the terminal hydroxyl groups have been modified by esterification, etherification, etc.

[0038] Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids with a variety of alcohols. Esters useful as synthetic oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols and polyol ethers.

[0039] Silicon-based oils (such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxysiloxane oils and silicate oils) comprise another useful class of synthetic lubricating oils. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids, polymeric tetrahydrofurans, poly α-olefins, and the like.

[0040] The lubricating oil may be derived from unrefined, refined, rerefined oils, or mixtures thereof. Unrefined oils are obtained directly from a natural source or synthetic source (e.g., coal, shale, or tar and bitumen) without further purification or treatment. Examples of unrefined oils include a shale oil obtained directly from a retorting operation, a petroleum oil obtained directly from distillation, or an ester oil obtained directly from an esterification process, each of which is then used without further treatment. Refined oils are similar to unrefined oils, except that refined oils have been treated in one or more purification steps to improve one or more properties. Suitable purification techniques include distillation, hydrotreating, dewaxing, solvent extraction, acid or base extraction, filtration, percolation, and the like, all of which are well-known to those skilled in the art. Rerefined oils are obtained by treating refined oils in processes similar to those used to obtain the refined oils. These rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques for removal of spent additives and oil breakdown products.

[0041] Lubricating oil base stocks derived from the hydroisomerization of wax may also be used, either alone or in combination with the aforesaid natural and/or synthetic base stocks. Such wax isomerate oil is produced by the hydroisomerization of natural or synthetic waxes or mixtures thereof over a hydroisomerization catalyst. Natural waxes are typically the slack waxes recovered by the solvent dewaxing of mineral oils; synthetic waxes are typically the wax produced by the Fischer-Tropsch process. The resulting isomerate product is typically subjected to solvent dewaxing and fractionation to recover various fractions having a specific viscosity range. Wax isomerate is also characterized by possessing very high viscosity indices, generally having a VI of at least 130, preferably at least 135 or higher and, following dewaxing, a pour point of about -20° C or lower.

[0042] The additives of the present invention are especially useful as components in many different lubricating oil compositions. The additives can be included in a variety of oils with lubricating viscosity, including natural and synthetic lubricating oils and mixtures thereof. The additives can be included in crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines. The compositions can also be used in gas engine lubricants, turbine lubricants, automatic transmission fluids, gear lubricants, compressor lubricants, metal-working lubricants, hydraulic fluids, and other lubricating oil and grease compositions. The additives can also be used in motor fuel compositions.

[0043] The advantages and the important features of the present invention will be more apparent from the following examples.

EXAMPLES

Example 1

Preparation of Branched Hexadecenyl Hydrazide

[0044] Into a 250 mL three-necked round-bottomed flask, equipped with a mechanical stirrer, Dean-Stark water trap, addition funnel, thermocouple to temperature controller, heating mantle, and a nitrogen blanket is charged 75 mL of toluene and 31.8 grams (0.1 mole) of hexadecenyl succinic anhydride. In the addition funnel is charged 5.0 grams (0.1 mole) of hydrazine monohydrate. The hydrazine is slowly added dropwise to the stirred reaction media at room temperature over a five minute period. The reaction media will exotherm about 20° C. The temperature is then raised to reflux the toluene to the Dean-Stark trap. The reaction media are refluxed until 3.7 mL of water is removed and the infrared analysis of a sampled product shows that all the anhydride has been converted to succinhydrazide. The reaction media are now cooled to room temperature and placed on a Roto-Evaporator to remove the toluene solvent. The reaction product is now filtered through a bed of Celite filter-aid to yield 33 grams of a clear yellow liquid.

Example 2

Preparation of Branched N-Methyl Octadecenyl Succinhydrazide

[0045] Into a 250 mL three-necked round-bottomed flask, equipped with a mechanical stirrer, Dean-Stark water trap, addition funnel, thermocouple to temperature controller, heating mantle, and a nitrogen blanket is charged 75 mL of toluene and 17.1 grams (0.05 mole) of octadecenyl succinic anhydride. In the addition funnel is charged 2.3 grams (0.05 mole) of methylhydrazine. The hydrazine is slowly added dropwise to the stirred reaction media at room temperature over a five minute period. The reaction media showed little exotherm. The temperature is then raised to reflux the toluene to the Dean-Stark trap. The reaction media are refluxed until water is no longer removed and the infrared analysis of a sampled product shows all the anhydride has been converted to succinhydrazide. The reaction media are now cooled to room temperature and placed on a Roto-Evaporator to remove the toluene solvent. The reaction product is now filtered through a bed of Celite filter-aid to yield 18.4 grams of a clear yellow liquid.

Examples 3-6

[0046] Linear dodecenyl succinhydrazide, branched dodecenyl succinhydrazide, N-phenyl dodecyl succinhydrazide, and branched octadecenyl succinhydrazide are all prepared using the procedures described above.

Example 7

Four-Ball Anti-wear Testing

[0047] The anti-wear properties of the alkyl-succinhydrazides of the present invention at a level of 1.0 wt% in a fully formulated SAE 5W-20 GF-3 motor oil formulation were determined in the Four-Ball Wear Test under the ASTM D 4172 test conditions. The fully formulated lubricating oils tested also contained 1 weight percent cumene hydroperoxide to help simulate the environment within a running engine. The additives were tested for effectiveness in a motor oil formulation (See description in Table 2) and compared to identical formulations with and without any zinc dialkyldithiophosphate. In Table 3, the numerical value of the test results (Average Wear Scar Diameter, mm) decreases with an increase in effectiveness.

TABLE 2
SAE 5W-20 Prototype GF-3 Motor Oil Formulation

Component	Formulation A (wt%)
Solvent Neutral 100	22.8
Solvent Neutral 150	60
Succinimide Dispersant	7.5
Overbased Calcium Phenate Detergent	2.0

(continued)

TABLE 2 SAE 5W-20 Prototype GF-3 Motor Oil Formulation	
Component	**Formulation A (wt%)**
Neutral Calcium Sulfonate Detergent	0.5
Rust Inhibitor	0.1
Antioxidant	0.5
Pour Point Depressant	0.1
OCP VI Improver	5.5
Anti-wear Additive[1]	1.0
[1] In the case of No anti-wear additive in Table 3, solvent neutral 100 is put in its place at 1.0 weight percent.	

TABLE 3 Four-Ball Wear Results		
Compound	**Formulation**	**Wear Scar Diameter, mm**
No anti-wear additive	A	0.73 (0.74)*
1.0 weight % Zinc dialkyldithiophosphate	A	0.50 (0.51)
0.5 weight % Zinc dialkyldithiophosphate	A	0.70 (0.67)
Linear dodecenyl-succinhydrazide	A	0.39 (0.39)
Branched dodecenyl-succinhydrazide	A	0.39
N-phenyl dodecenylsuccinhydrazide	A	0.66 (0.41)
N-methyl dodecenylsuccinhydrazide	A	0.38 (0.39)
Branched hexadecenyl succinhydrazide	A	0.40 (0.39)
Branched octadecenylsuccinhydrazide	A	0.40 (0.61)
*Numbers in parentheses are repeat test results.		

Example 8

Cameron-Plint TE77 High Frequency Friction Machine Anti-wear Testing

[0048] Another test used to determine the anti-wear properties of these products is the Cameron-Plint Anti-wear test based on a sliding ball on a plate. The specimen parts (6 mm diameter AISI 52100 steel ball of 800 $\pm$ 20 kg/mm^2 hardness and hardened ground NSOH BO1 gauge plate of RC 60/0.4 micron) are rinsed and then sonicated for 15 minutes with technical grade hexanes. This procedure is repeated with isopropyl alcohol. The specimens are dried with nitrogen and set into the TE77. The oil bath is filled with 10 mL of sample. The test is run at a 30 Hertz Frequency, 100 Newton Load, 2-35 mm Amplitude. The test starts with the specimens and oil at room temperature. Immediately, the temperature is ramped over 15 minutes to 50° C, where it dwells for 15 minutes. The temperature is then ramped over 15 minutes to 100° C, where it dwells for 45 minutes. A third temperature ramp over 15 minutes to 150° C is followed by a final dwell at 150° C for 15 minutes. The total length of the test is 2 hours. At the end of the test, the wear scar diameter on the 6 mm ball is measured using a Leica StereoZoom6® Stereomicroscope and a Mitutoyo 164 series Digimatic Head. In the Examples below, the fully formulated lubricating oils tested contained 1 wt. % cumene hydroperoxide to help simulate the environment within a running engine. The test additive was blended at 1.0 wt. % in a fully formulated SAE 5W-20 Prototype GF-4 Motor Oil formulation containing no ZDDP. The additives were tested for effectiveness in this motor oil formulation (See description in Table 4) and compared to identical formulations with and without any zinc dialkyldithiophosphate. In Table 4 the numerical value of the test results (Ball Wear Scar Diameter, Plate Scar

Width, and Plate Scar Depth) decreases with an increase in effectiveness.

Table 4
Cameron-Plint Wear Test

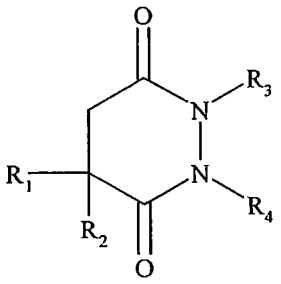
Additive at 1.0 Weight Percent	Ball Scar (mm)	Plate Scar Width (mm)	Plate Scar Depth (μm)
Branched dodecenyl-succinhydrazide	0.59 (0.54)	0.43 (0.56)	10.59 (10.07)
No anti-wear additive[1]	0.66	0.74	15.05
Zinc dialkyldithiophosphate (1.0 wt %)	0.39	0.72	1.83
Zinc dialkyldithiophosphate (0.5 wt %)	0.62	0.76	14.77
[1]In the case of No anti-wear additive in Table 4, solvent neutral 100 is put in its place at 1.0 weight percent.			

[0049] In view of the many changes and modifications that can be made without departing from principles underlying the invention, reference should be made to the appended claims for an understanding of the scope of the protection to be afforded the invention.

Claims

1. A composition comprising:

(A) a lubricant, and
(B) at least one alkyl succinhydrazide compound of the formula:



wherein:

R_1 is selected from the group consisting of linear or branched alkyl, alkenyl, alkaryl, alkyl ether, alkyl ester, and alkylene ester groups;
R_2 is selected from the group consisting of hydrogen, linear or branched alkyl, alkenyl, alkyl ether, and alkyl ester groups; and
R_3 and R_4 are independently selected from the group consisting of hydrogen, linear or branched alkyl and alkenyl groups, aryl groups, and alkaryl groups.

2. The composition of claim 1 wherein the lubricant is a lubricating oil.

3. The composition of claim 1 wherein R_1 is a straight chain hydrocarbon, a branched chain hydrocarbon, a fully saturated hydrocarbon chain, or a partially unsaturated hydrocarbon chain.

4. The composition of claim 1 wherein R_1 is a hydrocarbon chain of from 1 to 30 carbon atoms.

5. The composition of claim 1 wherein R_1 is a linear or branched hexadecylene chain.

6. The composition of claim 1 wherein the alkyl-succinhydrazide is present in a concentration in the range of from 0.01

to 10 wt%.

7. The composition of claim 1 wherein R_2, R_3, and R_4 are independently selected from the group consisting of hydrogen, aryl, alkyl, alkaryl, and alkenyl.

8. The composition of claim 11 wherein R_2, R_3, and R_4 are the same.

9. The composition of claim 13 wherein R_2, R_3, and R_4 are hydrogen.

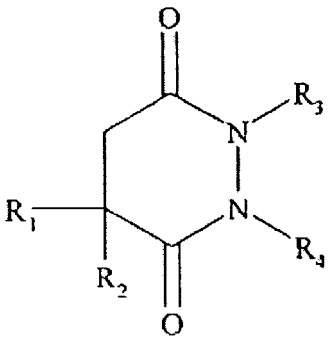
10. The composition of claim 1 further comprising at least one additive selected from the group consisting of dispersants, detergents, corrosion/rust inhibitors, zinc dialkyldithiophosphates, VI improvers, pour point depressants, antioxidants, and friction modifiers.

11. The composition of claim 1 further comprising at least one member selected from the group consisting of zinc dialkyldithiophosphates, zinc diaryldithiophosphates, and mixtures thereof.

Patentansprüche

1. Zusammensetzung, umfassend:

   (A) ein Schmiermittel, und
   (B) mindestens eine Alkylbernsteinsäurehydrazidverbindung der Formel:



   wobei

   R_1 ausgewählt ist aus der Gruppe, bestehend aus linearen oder verzweigten Alkyl-, Alkenyl-, Alkylaryl-, Alkylether-, Alkylester- und Alkylenestergruppen;
   R_2 ausgewählt ist aus der Gruppe, bestehend aus Wasserstoff, linearen oder verzweigten Alkyl-, Alkenyl-, Alkylether- und Alkylestergruppen; und
   R_3 und R_4 unabhängig ausgewählt sind aus der Gruppe, bestehend aus Wasserstoff, linearen oder verzweigten Alkyl- und Alkenylgruppen, Arylgruppen und Alkylarylgruppen.

2. Zusammensetzung nach Anspruch 1, wobei das Schmiermittel für ein Schmieröl steht.

3. Zusammensetzung nach Anspruch 1, wobei R_1 für einen geradkettigen Kohlenwasserstoff, einen verzweigtkettigen Kohlenwasserstoff, eine vollständig gesättigte Kohlenwasserstoffkette oder eine teilweise ungesättigte Kohlenwasserstoffkette steht.

4. Zusammensetzung nach Anspruch 1, wobei R_1 für eine Kohlenwasserstoffkette mit 1 bis 30 Kohlenstoffatomen steht.

5. Zusammensetzung nach Anspruch 1, wobei R_1 für eine lineare oder verzweigte Hexadecylenkette steht.

6. Zusammensetzung nach Anspruch 1, wobei das Alkylbernsteinsäurehydrazid in einer Konzentration in dem Bereich

von 0,01 bis 10 Gew.-% vorliegt.

7. Zusammensetzung nach Anspruch 1, wobei R_2, R_3 und R_4 unabhängig ausgewählt sind aus der Gruppe, bestehend aus Wasserstoff, Aryl, Alkyl, Alkylaryl und Alkenyl.

8. Zusammensetzung nach Anspruch 1, wobei R_2, R_3, und R_4 gleich sind.

9. Zusammensetzung nach Anspruch 1, wobei R_2, R_3, und R_4 für Wasserstoff stehen.

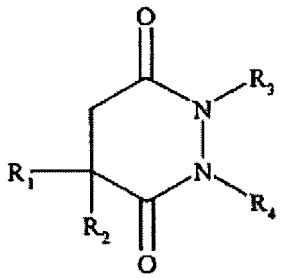
10. Zusammensetzung nach Anspruch 1, ferner umfassend mindestens ein Additiv, das ausgewählt ist aus der Gruppe, bestehend aus Dispergiermitteln, Detergenzien, Korrosions-/Rostinhibitoren, Zinkdialkyldithiophosphaten, Viskositätsindex(VI)-Verbesserern, Stockpunkterniedrigern, Antioxidantien und Reibungsmodifikatoren.

11. Zusammensetzung nach Anspruch 1, ferner umfassend mindestens ein Element, das ausgewählt ist aus der Gruppe, bestehend aus Zinkdialkyldithiophosphaten, Zinkdiaryldithiophosphaten und Gemischen davon.

Revendications

1. Composition qui comprend :

   (A) un lubrifiant et
   (B) au moins un composé d'alkylsuccinhydrazide de formule :



   dans laquelle :

   R_1 est sélectionné dans l'ensemble constitué des groupes alkyle linéaires ou ramifiés, akényle, alkylaryle, alkyléther, alkylester et ester d'alkylène,
   R_2 est sélectionné dans l'ensemble constitué de l'hydrogène et des groupes alkyle linéaires ou ramifiés, akényle, alkyléther et alkylester et
   R_3 et R_4 sont sélectionnés indépendamment dans l'ensemble constitué de l'hydrogène, des groupes alkyle linéaires ou ramifiés, akényle, aryle et alkylaryle.

2. Composition selon la revendication 1, dans laquelle le lubrifiant est une huile de lubrification.

3. Composition selon la revendication 1, dans laquelle R_1 représente un hydrocarbure à chaîne linéaire, un hydrocarbure à chaîne ramifiée, une chaîne d'hydrocarbure entièrement saturée ou une chaîne d'hydrocarbure partiellement insaturée.

4. Composition selon la revendication 1, dans laquelle R_1 représente une chaîne d'hydrocarbure qui compte de 1 à 30 atomes de carbone.

5. Composition selon la revendication 1, dans laquelle R_1 est une chaîne d'hexadécylène linéaire ou ramifiée.

6. Composition selon la revendication 1, dans laquelle l'alkylsuccinhydrazide est présent à une concentration comprise entre 0,01 et 10 % en poids.

7. Composition selon la revendication 1, dans laquelle R_2, R_3 et R_4 sont sélectionnés indépendamment dans l'ensemble constitué de l'hydrogène et des groupes aryle, alkyle, alkylaryle et akényle.

8. Composition selon la revendication 11, dans laquelle R_2, R_3 et R_4 sont identiques.

9. Composition selon la revendication 13, dans laquelle R_2, R_3 et R_4 représentent l'hydrogène.

10. Composition selon la revendication 1, qui comprend en outre un additif sélectionné dans l'ensemble constitué des agents dispersants, des détergents, des inhibiteurs de corrosion et de rouille, des dialkydithiophosphates de zinc, des agents d'amélioration VI, des agents d'abaissement du point de solidification, des agents antioxydants et des agents de modification du frottement.

11. Composition selon la revendication 1, qui comprend en outre au moins un élément sélectionné dans l'ensemble constitué des dialkyldithiophosphates de zinc, des diaryldithiophosphates de zinc et de leurs mélanges.

REFERENCES CITED IN THE DESCRIPTION

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