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(54) Title: IMPROVED SULFURIZED OLEFIN EXTREME PRESSURE/ANTIWEAR ADDITIVES

(57) Abstract

A halogen-free lubricant additive composition is disclosed which comprises the reaction product of elemental sulfur, an olefin, and an aqueous solution of an alkali metal or alkaline earth metal salt of hydrosulfide. The reaction product has been found to contain little or no dithiolethiones and is useful as an extreme pressure/antiwear additive for motor fuels, as well as lubricants such as mineral- and synthetic-based oils and greases.

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IMPROVED SULFURIZED OLEFIN EXTREME PRESSURE/ANTIWEAR ADDITIVES

Field of the Invention

The present invention relates to halogen-free sulfurized olefin compounds and to their use as extreme pressure/antiwear additives. More particularly, the invention relates to compounds made by reacting sulfur, olefins, and an aqueous solution containing a metal hydrosulfide, for example sodium hydrosulfide, and the use of such compounds as additives in motor fuels as well as lubricants such as oils and greases.

Background of the Invention

Processes for improving the properties of lubricating oils by contacting the lube stock with sulfur at elevated temperatures are taught in U.S. Patents 2,356,843; 2,349,861; 2,338,829; and 2,312,750.

U.S. Patent 2,386,222 to Lincoln et al. teaches a method for the preparation of sulfurized polyisobutylene. This patent teaches at page 2, column 1, line 59 et seq. that a sulfurized polyisobutylene may be prepared from a mixture of at least one member selected from the group consisting of sulfur, sulfur chloride, and phosphorus pentasulfide, together with a specified quantity of triisobutylene.

U.S. Patent 2,658,900 to Stevens et al. discloses a process for the sulfurization of diisobutylene in which a stream of diisobutylene is charged beneath the surface of a liquid reaction mass comprising molten sulfur under controlled temperature conditions. The evolved hydrogen sulfide is removed from the reaction mass substantially as rapidly as it is formed.

U.S. Patent 3,345,380 to Hodgson discloses a method for sulfurizing olefinic hydrocarbons to favor the production of 1,2-dithiole-3-thiones.

U.S. Patent 3,350,408 to Hodgson teaches a method for sulfurizing olefins in which a C_5-hydrocarbon is contacted with elemental sulfur in the vapor phase at controlled elevated reaction temperatures. The reaction is preferably carried out in a continuous tubular flow reactor.

U.S. Patent 3,673,090 to Waldbillig et al. teaches a process for the sulfurization of triisobutylene which includes the steps of mixing triisobutylene and sulfur under specified concentrations and reaction conditions and flowing inert gas through the mixture for at least a portion of the reaction time.

U.S. Patent 3,796,661 to Suratwala et al. teaches sulfurized triisobutylene together with a method for its preparation. The preparation technique comprises mixing triisobutylene and sulfur under selected concentrations and temperatures and flowing an inert gas through the triisobutylene/sulfur mixture until the free sulfur is substantially consumed. The resulting product mixture is then blown with an inert gas and filtered. The process steps are recited at column 2, line 40 through column 3, line 2.

U.S. Patent 4,147,640 to Jayne et al. discloses a lubricant additive prepared by reacting an olefin containing from 6 to 18 carbon atoms having 1 to 3 olefinic double bonds with elemental sulfur and hydrogen sulfide to evolve a reaction intermediate. The reaction intermediate is then reacted with additional olefin which may be the same or different from that reacted in the first step. This patent notes that dicyclopentadiene and alloocimene are particularly preferred olefins. The process steps are listed at column

1, line 62, through column 2, line 12. The Jayne et al. process requires the addition of hydrogen sulfide. In contrast, the present process requires no H_2S addition, and further reacts elemental sulfur with olefins in the presence of a metal salt of hydrosulfide.

U.S. Patent 4,194,980 to Braid teaches sulfurized olefins useful as lubricant additives. The particular sulfurized olefins are prepared by reacting olefins with a cyclic polydisulfide under controlled reaction conditions.

U.S. Patent 4,204,969 to Papay et al. teaches a lubricating oil additive which is prepared by reacting sulfur monochloride with a mono-olefin, for example, isobutylene, in the presence of a lower alkanol, for example, methanol, to form an adduct. The resulting adduct is then reacted with sulfur and sodium sulfide in an aqueous alkanol. The Papay et al. patent recites the essential steps of the process at column 1, lines 34-43. The Papay et al. process specifies sulfur monochloride as feedstock and is therefore clearly distinguished from the process of the present invention which preferably employs elemental sulfur. The sulfur monochloride used in the Papay et al. process is itself toxic, and is a lachrymator. Further, the sulfur monochloride produces toxic and corrosive hydrogen chloride upon contact with even atmospheric moisture. Still further, the product of the Papay et al. process may contain small amounts of highly undesirable halogen emanating from the use of sulfur monochloride.

U.S. Patent 4,225,488 to Horodysky et al. discloses a process for preparing organic sulfides by reacting olefins with a sulfur halide to form a sulfohalogenated intermediate which is subsequently sulfurized and dehalogenated by reaction with an aqueous solution of an alkali metal sulfide. Copper strip corrosion activity is improved by resulfurizing the sulfurized olefin by contacting it with additional aqueous metal sulfide in the presence of a lower molecular weight alcohol, such as isopropanol. Specifically, the Horodysky '488 reference requires the use of sulfur halide as a starting material; the present process employs no sulfur halide feedstock.

U.S. Patents 4,344,854 and 4,119,550 to Davis et al. and U.S. Patents 4,119,549 and 4,191,659 to Davis teach processes for sulfurizing olefins which require the addition of H_2S. The '854 patent discloses the preparation of dithiolethione-free sulfurized olefin compositions by the reaction of sulfur, isobutylene, and hydrogen sulfide. Due to the toxicity and corrosivity of H_2S, it would be desirable to provide a process which produces sulfurized olefin lubricant additives but does not require the use of H_2S. The process of the present invention reacts olefins, sulfur and an aqueous metal hydrosulfide sulfide without the addition of H_2S.

U.S. Patent 4,472,306 to Powers, III, et al. teaches a method for making a sulfurized triisobutylene which comprises reacting sulfur with triisobutylene in the presence of an N-halogen substituted organic promotor selected from the group consisting of N-halo succinimide, N-halo aniline, and 1,3-N,N'-dihalo-5,5-dialkylhydantoin. Suitable halogens include bromine and chlorine. The '306 patent contains no suggestion that an alkali metal or alkaline earth metal salt of hydrosulfide could be substituted for the compounds disclosed therein.

U.S. Patent 4,563,302 to Griffin et al. discloses a process for making a sulfurized olefin in which a sulfur halide selected from S_2Cl_2 and SCl_2 is reacted with an aliphatic mono-olefin containing 3 to 6 carbon atoms to form an adduct which is then reacted with sodium sulfide, sodium hydrosulfide, sulfur and an alkyl mercaptan in an aqueous alcohol reaction medium. The '302 patent lists preferred olefins at column 1, lines 60-62, and includes isobutene at line 60. The use of an alcohol promoter is discussed at column 2, lines 8-20. In particular, this patent notes that the lower alcohols containing from about 1 to about 4 carbon atoms are preferred. The Griffin et al. process requires sulfur halide. Further, the Griffin et al. process reacts the adduct formed from the reaction of the sulfur halide and a monoolefin with a mercaptan. None of these steps is included in the present inventive process.

U.S. Patent 4,839,069 to Born et al. teaches olefin polysulfides which are prepared by reacting a sulfur monochloride with a mono-olefin, for example, isobutylene, to form an addition product. The addition product is then reacted in an alcohol solution with an alkali metal or ammonium polysulfide which is obtained by reacting a mercaptan with an alkali metal hydroxide or ammonia in the presence of elemental sulfur. The essential steps of the Born et al. process are disclosed at column 3, line 46 through column 4, line 4. In contrast to the Born et al. process, the present process reacts sulfur with an olefin in the presence of a metal salt of hydrosulfide. No sulfur halides are used in present inventive process. The Born et al. patent specifies sulfur halides; no suggestion is made that elemental sulfur is a suitable equivalent. Sulfur monochloride (S_2Cl_2) is known to be both highly corrosive and hygroscopic, releasing irritating vapors containing corrosive hydrogen chloride upon contact with atmospheric humidity. Further, the reactivity of sulfur monochloride far exceeds that of elemental sulfur monochloride in the presence of olefinic feedstocks. See M. Windholz, The

Merck Index 1288 (1983), and D.R. Harvey et al., The Aldrich Handbook of Fine Chemicals 1370 (1988).

U.S. Patent 4,906,391 to Andress discloses a sulfurized olefin lubricant additive comprising the reaction product of sulfur and phosphorus pentasulfide.

Summary of the Invention

The present invention is directed to a halogen-free extreme-pressure antiwear additive obtained by reacting sulfur, an aqueous solution of an alkali metal salt of hydrosulfide or an alkaline earth metal salt of hydrosulfide or mixtures of an alkali metal salt and an alkaline earth metal salt of hydrosulfide, and one or more olefins. It has been found that this reaction yields a high quality, extreme-pressure antiwear additive while yielding little or no dithiolethiones. Additional benefits attendant to the use of the sulfurized olefin additive of the present invention may include enhanced thermal stability and antifatigue properties, markedly reduced friction and corrosivity as well as improved cleanliness.

The invention further includes a motor fuel or lubricant containing an additive obtained by reacting sulfur, an aqueous solution of an alkali metal salt or an alkaline earth metal salt of hydrosulfide, and one or more olefins in concentrations sufficient to improve the stability and lubricity of the mixture.

The invention provides a method for making an extreme-pressure antiwear additive which comprises contacting one or more olefins with sulfur in the presence of an aqueous solution of an alkali metal salt or an alkaline earth metal salt of hydrosulfide or mixtures of an alkali metal salt and an alkaline earth metal salt of hydrosulfide.

The invention also provides a method for minimizing the production of halogen-containing byproduct waste streams from a process for producing extreme pressure-antiwear additives which comprises reacting sulfur, an aqueous solution of an alkali metal salt of hydrosulfide or an alkaline earth metal salt of hydrosulfide, and one or more olefins in the absence of added halogen. By producing an extreme pressure-antiwear additive in the absence of added halogens, the method of the invention alleviates the environmental hazards associated with the handling and disposal of halogen-containing waste streams which are typically produced by previously known methods for manufacturing extreme pressure-antiwear additives.

Description of the Preferred Embodiments

The olefin-sulfur-hydrosulfide salt reaction of the present invention is suitably carried out at temperatures of from about 75° to about 300°C, preferably from about 120° to about 220°C. The mole ratio of sulfur to hydrosulfide may range from about 20:1 to about 0.25:1. The mole ratio of sulfur plus hydrosulfide to olefin may range from about 5:1 to about 0.5:1. The pressure is not critical and may vary from less than about 100 psig to 2000 psig or more, but autogeneous pressures are typical. Reaction times vary between about 2 and 24 hours, preferably less than 8 hours.

Any suitable olefin may be used. For example, olefins containing from 2 to about 32 carbons are useful feedstocks. C_3-C_6 olefins are preferred with C_4 olefins being more preferred and isobutylene being the most preferred feedstock. Oligomeric olefins can also be used and include propylene dimer, propylene trimer, propylene tetramer, propylene pentamer, diisobutylene, triisobutylene, mixtures of the listed oligomeric olefins, as well as mixtures of the listed oligomeric olefins with monoolefins and the like, merely to name a few. The olefin or mixture of olefins may optionally be reacted with a preformed mixture of sulfurized, aqueous hydrosulfide prepared by the direct sulfurization of aqueous sodium hydrosulfide. The reaction may suitably be carried out with a sequential addition of reactants.

An aqueous solution of any suitable alkali metal or alkaline earth metal salt of hydrosulfide may be employed. Aqueous solutions of sodium hydrosulfide are preferred, and concentrated solutions of sodium hydrosulfide are preferred over dilute solutions.

The reaction products of the present invention are useful as extreme pressure/antiwear additives. Effective additive concentrations in motor fuel, lubricating oils and greases range from less than about 0.05% by weight to about 10% by weight or more, with concentrations in the range of from about 0.1% to 4% by weight of the total composition being preferred for lubricating oils and greases. Effective dosages for motor fuels, on the other hand, range from about 0.0001% by weight to about 0.1% by weight.

The additive of the present invention is effective with a broad range of motor fuel compositions including hydrocarbons, oxygenates, or mixed hydrocarbons and oxygenates. The remainder of the motor fuel, lubricating oil, or grease composition may comprise, in addition to the base stock, other additives, examples of which include other extreme pressure or antiwear agents, viscosity control agents, dispersants, corrosion inhibitors, antirust compounds, seal swell additives, anti-squawk additives, friction reducers, detergents, and antioxidants. Examples of these supplemental additives include amines, phosphates, dithiophosphates, metallic or ashless sulfonates and/or phenols, polymeric succinimides, esters, amides, or mixtures thereof, triazoles, dimercaptothiadiazole-derived components, carboxylic acids, organic borates, metallic borates, olefin copolymers, and methacrylates, merely to name a few. As used herein, the term "base stock" refers to a motor fuel, lubricating oil, or grease composition without performance enhancing additives.

The most preferred embodiment of the composition of the present invention is a lubricant composition comprising a major portion (more than 50% by weight) of an oil of lubricating viscosity, or greases prepared therefrom and a minor amount of the reaction product described above as an additive in concentrations sufficient to improve the extreme pressure and antiwear properties of the lubricant composition.

The lubricant composition of the invention may comprise any oleaginous materials that require lubricative properties under extreme pressure conditions to minimize excessive wear under operating conditions. Especially suitable for use with the additives of this invention are liquid hydrocarbon oils of lubricating viscosity. Lubricant oils, improved in accordance with the present invention, may be of any suitable lubricating viscosity. In general, the lubricant composition may comprise any mineral oil, any synthetic oil of lubricating viscosity or mixtures of synthetic and mineral oils in which the mixture is of lubricating viscosity. The additives of this invention are especially useful in greases and in automotive fluids such as brake fluids, power brake fluids, transmission fluids, power steering fluids, various hydraulic fluids, and gear oils.

The base stock may comprise a mineral oil, a synthetic oil, or a mineral oil in admixture with a synthetic oil. Synthetic oils may also be used as the vehicle or base of grease compositions. Typical synthetic lubricants include polyisobutylene, polybutenes, hydrogenated polydecenes, polypropylene glycol, polyethylene glycol, trimethylolpropane esters, neopentyl and pentaerythritol esters of carboxylic acids, di(2-ethylhexyl) sebacate, di(2-ethylhexyl) adipate, dibutyl phthalate fluorocarbons, silicate esters, silanes, esters of phosphorus-containing acids, liquid ureas, ferrocene derivatives, hydrogenated mineral oils, chain-type polyphenols, siloxanes and silicones (polysiloxanes), alkyl-substituted diphenyl ethers typified by a butyl-substituted bis(p-phenoxy phenyl) ether, phenoxy phenylethers, dialkylbenzenes, dialkylnaphthalenes and others.

As noted above, the additives of the present invention can be incorporated as additives in grease compositions. When high temperature stability is not a requirement of the finished grease, mineral oils having a viscosity of at least 40 SSU at 150°F. (65.5°C.) are useful. If high temperature stability is required, mineral oils having viscosities within the range of about 60 SSU to about 6,000 SSU at 100°F. (37.7°C.) may be used.

The grease compositions containing the additive of the present invention are combined with a grease-forming quantity of thickening agent. For this purpose, a wide variety of materials can be dispersed in the lubricating oil in grease-forming quantities in such degree so as to impart the desired consistency to the resulting grease composition. Examples of suitable thickening agents for use in the grease formulation are metal soaps as well as non-soap thickeners, such as surface-modified clays and silicas, aryl ureas, calcium complexes, metallic hydroxy stearate-derived soaps, and similar materials. In general, grease thickeners are employed which do not melt or dissolve when used at the required temperature within a particular environment; however, in all other respects, any material which is normally employed for thickening or gelling oleaginous fluids or forming greases may be used in the grease formulations of the present invention.

Example 1

The following Example illustrates the reaction of isobutylene, sulfur, and aqueous sodium hydrosulfide.

A 1-gallon pressure reactor is charged with 305.4 grams (9.52 moles) of sulfur and sodium hydrosulfide solution (14.25% sulfur by weight, density = 1.207 g/cc, 590 ml, 3.18 moles), sealed, and flushed three times by pressuring with nitrogen (500 psi) and venting. The reactor contents are then stirred and heated to 400°F. (204°C.) until a maximum pressure is obtained and then cooled to 266°F. (130°C.). Isobutylene (600 ml, 6.35 moles) is added and the reactor is heated to 320°F. (160°C.). The reactor is then cooled and vented after the pressure declines to a constant value. The recovered material is separated from the aqueous phase. The liquid organic phase is washed with water, dried over anhydrous magnesium sulfate, and filtered through diatomaceous earth.

The resulting product is blended at a 2% concentration by weight into a mineral oil based lubricant consisting of solvent refined paraffinic base stocks to provide a lubricant composition having enhanced extreme pressure/antiwear characteristics as well as reduced color, odor, and corrosivity toward copper when compared to sulfurized olefin mixtures produced by direct reaction of an olefin with sulfur.

Example 2

A 1 gallon high-pressure reactor is charged with sulfur (785 g, 24.5 moles) and 45% aqueous sodium hydrosulfide (533.5 g). The sealed reactor is pressurized to 500 psi with nitrogen and vented three times. The reactor is heated to 400°F. (204°C.) overnight, then cooled to 266°F. (130°C.) Isobutylene (1200 cc, 12.7 moles) is added via a high pressure pump to the stirred mixture. The temperature is raised to 320°F. (160°C.). The reactor pressure rises and falls from a maximum of about 550 psi to about 150 psi over about 9 hrs. Heating is stopped and the reactor is allowed to cool. The residual pressure is vented and the liquid reactor contents removed. The organic product is decanted from the aqueous by-product and filtered through 55.6 g of diatomaceous earth. Additional organic product may be recovered by extracting the aqueous by-product with several portions of hexane, combining the extracts, and evaporating the hexane. The crude organic product (1231 g) is combined with 5% aqueous NaOH (122 g) in a 2 L round-bottom flask equipped with a mechanical stirrer. This mixture is stirred and heated to 90°C. for 1 hr., allowed to cool, and transferred to a separatory funnel. The aqueous phase is removed and the organic product is washed twice with water (approximately 120 g per wash). The organic product is transferred to a 2 L round-bottom flask, sparged with nitrogen, and heated to 100°C. for 1.5 hrs. The organic product is allowed to cool to room temperature under the nitrogen sparge and is then filtered through diatomaceous earth (22.9 g) to give an orange liquid (1174 g) which analyzes for 49.6% sulfur.

Example 3

A 1 gallon high-pressure reactor is charged with sulfur (740 g, 23.1 moles) and 45% aqueous sodium hydrosulfide (303.0 g). The sealed reactor is pressurized

(500 psi) with nitrogen and vented three times. The reactor is heated to 356°F. (180°C.) and isobutylene (1200 cc, 12.7 moles) is immediately added via a high pressure pump to the stirred mixture. The reactor pressure rises and falls from a maximum of about 490 psi to about 190 psi over about 1.5 hrs. The reactor is cooled to 200°F. (93.3°C.), vented, and sparged with nitrogen for 2 hrs. Then, 5% aqueous NaOH (212 g) is added and the mixture is stirred at 200°F. (93.3°C.) for 1 hr. This mixture is cooled to room temperature and the product is removed from the reactor. The aqueous reactor rinses (143 g) are combined with the crude product. The crude product is transferred to a separatory funnel. The organic product is separated from aqueous by-product and washed twice with water (approximately 116 g per wash). The organic product is transferred to a 2 L round-bottom flask, sparged with nitrogen, and heated to 105°C. for 2 hrs. The organic product is allowed to cool to room temperature under the nitrogen sparge and is then filtered through diatomaceous earth (10.3 g) to give an orange liquid (1313 g).

Example 4

A 1 gallon high-pressure reactor is charged with sulfur (237.9 g, 7.42 moles) and 45% aqueous sodium hydrosulfide (95.4 g). The sealed reactor is pressurized (500 psi) with nitrogen and vented three times. The reactor is heated to 356°F. (180°C.) and propylene oligomers (345 g of a mixture of approximately 93% C_6H_{12} and 6% C_9H_{18}) is immediately added via a high pressure pump to the stirred mixture. The reactor is cooled to 200°F. (93.3°C.) after about 2.5 hrs., vented, and sparged with nitrogen for 2 hrs. Then, 5% aqueous_NaOH (212 g) is added and the mixture is stirred at 200°F.

(93.3°C.) for 1 hr. This mixture is cooled to room temperature and the product is removed from the reactor. The aqueous reactor rinses (84 g) are combined with the crude product. The crude product is transferred to a separatory funnel. The organic product is separated from aqueous by-product and washed three times with water (approximately 130 g per wash). The organic product is dried over magnesium sulfate and filtered through diatomaceous earth to give a red liquid (396 g).

Examples 5-8

Examples 5-8 compare the extreme pressure performance of the sulfurized olefin produced in Examples 2 and 3 with the performance of a commercial sulfurized isobutylene prepared in accordance with Example 1 of U.S. Patent 3,703,504 to Horodysky. Each of the additives was dissolved in a mixture of solvent-refined paraffinic bright stock and solvent-refined paraffinic neutral stock in weight ratios of 80% bright stock and 20% neutral stock to provide a final sulfur content of 0.5% by weight. The solutions were then tested with the Four Ball Extreme-Pressure Test (ASTM D-2783). The data are shown in Table 1.

Table 1
Four Ball Extreme Pressure Test

	Test Temperature, °C	Load Wear Index	Weld Load, kg
Ex. 5 Base Oil	75	22.3	160
Ex. 6 Base Oil + the sulfurized olefin additive produced in Example 1 of U.S. 3,703,504 (Horodysky)	75 150	54.2 48.8	315 315
Ex. 7 Base Oil + sulfurized isobutylene prepared by direct reaction of sulfur and isobutylene	75	50.7	315
Ex. 8 Base Oil + the sulfurized olefin additive produced in Example 2, above	75 150 200	52.2 58.1 59.5	315 400 400

Examples 9-12

Examples 9-12 compare the antiwear properties of the sulfurized olefin additives produced in Examples 2 and 3 with the sulfurized isobutylene of Example 6, above. The comparison tests of Examples 9-12 were conducted with a mixed lubricating stock as described above with reference to Examples 5-8. The sulfurized olefin additives were admixed with the lubricating stock samples to provide solutions which were 1% and 3% sulfurized isobutylene by weight. These solutions were tested on a Cameron Plint High Frequency Friction Machine TE.77 using a steel ball on a steel plate. The test conditions were 150 N force and 2.63 mm vibrational amplitude at 50°C. for 1 hr. The wear scars on the ball were measured after the test was completed. The results are shown in Table 2.

Table 2

	Wear Scar Diameter (mm)	
Ex. 9 Base Oil	0.99	0.99
Ex. 10 Base Oil + the sulfurized olefin additive produced in Example 1 of U.S. 3,703,504 (Horodysky)	0.48	0.70
Ex. 11 Base Oil + sulfurized isobutylene prepared by direct reaction of sulfur and isobutylene	0.55	0.70
Ex. 12 Base Oil + the sulfurized olefin additive produced in Example 2, above	0.47	0.63

The above results demonstrate the improved antiwear activity of the compositions of this invention.

What is claimed is:

1. A halogen-free extreme pressure/antiwear lubricant additive prepared by the reaction of (1) elemental sulfur, (2) an olefin having from 2 to about 32 carbon atoms, and (3) an alkali metal or alkaline earth metal salt of hydrosulfide, or mixtures of alkali metal or alkaline earth metal salts of hydrosulfide.

2. The composition of claim 1 wherein said alkali metal salt of hydrosulfide comprises sodium hydrosulfide.

3. The composition of claim 2 wherein said reaction is carried out at a temperature of from about 75° to about 300°C. under autogeneous pressure for about 2 to about 24 hours.

4. The composition of claim 2 wherein said elemental sulfur and said hydrosulfide are initially present in molar ratios ranging from about 20:1 to about 0.25:1 and wherein the reaction temperature is from 120° to 220°C.

5. The composition of claim 2 wherein the elemental sulfur and the sodium hydrosulfide are initially present in a molar ratio of sulfur plus hydrosulfide to olefin of from about 5:1 to about 0.5:1.

6. The composition of claim 2 wherein said olefin has from 3 to 6 carbon atoms.

7. The composition of claim 2 wherein said olefin is isobutylene.

8. A lubricant composition comprising a major proportion of a hydrocarbon base stock and a minor amount of a halogen-free additive comprising the reaction product of (1) elemental sulfur, (2) an olefin having from 2 to about 32 carbon atoms, and (3) an alkali metal or alkaline earth metal salt of hydrosulfide, or mixtures of alkali metal or alkaline earth metal salts of hydrosulfide.

9. The composition of claim 8 wherein said alkali metal salt of hydrosulfide comprises sodium hydrosulfide.

10. The composition of claim 9 wherein said reaction is carried out at a temperature of from about 75° to about 300°C. under autogeneous pressure for about 2 to about 24 hours.

11. The composition of claim 9 wherein said elemental sulfur and said hydrosulfide are initially present in molar ratios ranging from about 20:1 to about 0.25:1 and wherein the reaction temperature is from 120 to 220°C.

12. The composition of claim 9 wherein the elemental sulfur and the sodium hydrosulfide are initially present in a molar ratio of sulfur plus hydrosulfide to olefin of from about 5:1 to about 0.5:1.

13. The composition of claim 9 wherein said olefin has from 3 to 6 carbon atoms.

14. The composition of claim 9 wherein said olefin is isobutylene.

15. The composition of claim 9 wherein said hydrocarbon base stock comprises a mineral oil.

16. The composition of claim 9 wherein said hydrocarbon base stock comprises a synthetic oil.

17. The composition of claim 9 wherein said hydrocarbon base stock comprises a grease.

18. A motor fuel composition having enhanced extreme pressure/antiwear characteristics comprising a major proportion of a motor fuel base stock and a minor amount of the reaction product of (1) elemental sulfur, (2) an olefin having from 2 to about 32 carbon atoms, and (3) an alkali metal or alkaline earth metal salt of hydrosulfide, or mixtures of alkali metal or alkaline earth metal salts of hydrosulfide.

19. The composition of claim 18 wherein said alkali metal salt of hydrosulfide comprises sodium hydrosulfide.

20. The composition of claim 19 wherein said olefin is isobutylene.

21. A method for producing a halogen-free extreme pressure/antiwear additive which comprises reacting (1) elemental sulfur, (2) an olefin having from 2 to about 32 carbon atoms, and (3) an alkali metal or alkaline earth metal salt of hydrosulfide, or mixtures of alkali metal or alkaline earth metal salts of hydrosulfide.

22. A method of minimizing the production of a halogen-containing waste stream in a process for producing extreme pressure/antiwear additives, said method comprising effecting reaction of (1) elemental sulfur, (2) an olefin having from 2 to about 32 carbon atoms, and (3) an alkali metal or alkaline earth metal salt of hydrosulfide, or mixtures of alkali metal or alkaline earth metal salts of hydrosulfide, in the absence of added halogen, whereby halogen-free waste streams are evolved.

23. Use of a halogen-free extreme pressure/antiwear lubricant additive according to any of claims 1-7 in a lubricant composition comprising a major amount of a hydrocarbon base stock and a minor amount of said lubricant additive to improve the extreme pressure/antiwear properties of the lubricant composition.

24. The use according to claim 23 wherein said hydrocarbon base stock is a mineral oil, a synthetic oil or a grease.

25. Use of a halogen-free extreme pressure/antiwear additive according to any of claims 1-7 in a motor fuel composition comprising a major amount of a motor fuel base stock and a minor amount of said additive to improve the extreme pressure/antiwear properties of the motor fuel composition.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/05589

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT (5): C10M 135/04
U.S. CL: 252/45; 044/304 568/18

II FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
U.S. CL.	252/45 568/18 044/304 568/59

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	US, A, 4,795,576, 03 JANUARY 1989 (BORN ET AL.) col.2, lines 12 to 30; claims 1 and 10.	1-17; 21-23
X	US, A, 4,344,854, 17 AUGUST 1982 (DAVIS ET AL.) see entire document.	1-17; 21-23
X	US, A, 4,225,488, 30 SEPTEMBER 1980 (HORODYSKY ET AL.) col.1, lines 59-60; col.3, lines 45-50 claim 5.	1-17; 21-23
A	US, A, 4,929,253, 29 MAY 1990 (CARDIS) col.1, lines 49-68, col.2, lines 1-15; col.2, line 61.	18-20

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 21 OCTOBER 1991	Date of Mailing of this International Search Report 08 NOV 1991
International Searching Authority ISA/US	Signature of Authorized Officer JACQUELINE V. HOWARD