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[54] **NOVEL BENZOTHIAZYL DISULFIDES, THEIR PREPARATION AND USE AS LUBRICANT ADDITIVES**

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[51] **Int. Cl.** **C10m 1/42**

[58] **Field of Search** 252/47

[56] **References Cited**

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Primary Examiner—W. Cannon

[57] **ABSTRACT**

Preparation of novel 2-benzothiazyl disulfides by reacting sulfenyl chlorides with mercaptobenzothiazoles or ammonium or alkali metal salts thereof, and the use of the novel benzothiazyl disulfides as lubricant additives. In a specific embodiment, 1,1,3,3-tetramethylbutyl 2-benzothiazyl disulfide is produced by reacting 2,4,4-trimethyl-2-pentanesulfenyl chloride with at least one of 2-mercaptobenzothiazole and the ammonium and alkali metal salts thereof. In another specific embodiment, lubricants containing 1,1,3,3-tetramethylbutyl 2-benzothiazyl disulfide exhibit improved properties.

6 Claims, No Drawings

NOVEL BENZOTHIAZYL DISULFIDES, THEIR PREPARATION AND USE AS LUBRICANT ADDITIVES

BACKGROUND OF THE INVENTION

This invention relates to the production of novel benzothiazyl disulfides. In accordance with another aspect, this invention relates to the production of benzothiazyl disulfides by reacting a sulfenyl chloride with at least one of 2-mercaptobenzothiazole or ammonium or alkali metal salts thereof. In accordance with another aspect, this invention relates to lubricants exhibiting improved properties containing at least one 2-benzothiazyl disulfide. In accordance with a further aspect, this invention relates to improved lubricants containing C_8–C_{10} benzothiazyl disulfides.

RELATED PRIOR ART

Various organic compounds have, in the past, been proposed and used as additives in lubricating oils. However, none of these compounds have been considered entirely adequate for the purpose for which they were intended because they did not sufficiently improve the antiwear and extreme pressure lubricating properties of the oils, they did not improve the resistance to oxygen and they were often corrosive, especially to copper materials.

Accordingly, an object of this invention is to provide novel compounds.

It is another object of this invention to provide a process for the production of new compositions.

A further object of this invention is to provide novel compounds useful as ashless lubricant additives.

It is another object of this invention to provide improved ashless lubricant additives which exhibit superior characteristics when compared with former lubricant additives.

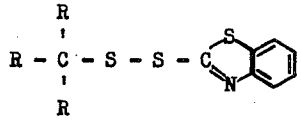
Another object of this invention is to provide improved lubricating oils and greases.

A further object of this invention is to provide lubricating oils and greases improved in high pressure or extreme pressure characteristics.

A further object of this invention is to provide lubricating oils and greases having increased stability toward oxidation and rust.

Other objects and aspects as well as the several advantages of the invention will be apparent to those skilled in the art upon reading the specification and the appended claims.

In accordance with the invention, novel compounds are produced comprising tert-alkyl 2-benzothiazyl disulfides having the formula



wherein each R is an unbranched or branched alkyl radical having 1 to about 11 carbon atoms, preferably 1 to about 9 carbon atoms, the total number of carbon atoms in all of said R groups being within the range of about 5 to about 13, preferably about 7 to about 11.

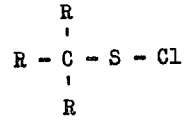
In accordance with one embodiment, 1,1,3,3-tetramethylbutyl 2-benzothiazyl disulfide, a mixture of isomeric tert-nonyl 2-benzothiazyl disulfides and isomeric tert-decyl 2-benzothiazyl disulfides, all novel compositions, are produced.

In accordance with a further embodiment, the above defined benzothiazyl disulfides are employed as ashless lubricant additives.

The compounds thus obtained are particularly useful as ashless lubricant additives. Specifically, the oils and greases to which the instant compounds are added exhibit improved resistance to oxidation and improved anti-wear and extreme pressure lubricating properties. Furthermore, the disulfide additives of this invention are liquid or low-melting solids, thus making easier their blending into oils and greases. Further, the disulfide additives of this invention can be employed in lubricants without a corrosion inhibitor and lubricant formulations containing these additives are noncorrosive to copper.

A particularly effective and presently preferred disulfide additive of this invention is 1,1,3,3-tetramethylbutyl 2-benzothiazyl disulfide.

Also in accordance with this invention, the novel tert-alkyl 2-benzothiazyl disulfides as defined by the generic formula shown above can be produced by the reaction of a sulfenyl chloride having the formula



where each R is an unbranched or branched alkyl radical having 1 to about 11 carbon atoms, preferably 1 to about 9 carbon atoms, the total number of carbon atoms in all of said R groups being within the range of about 5 to about 13, preferably about 7 to about 11, with at least one of 2-mercaptobenzothiazole or ammonium or alkali metal salt thereof.

The 2-mercaptobenzothiazole is preferably employed as an alkali metal salt, i.e., as the lithium, sodium, potassium, rubidium, or cesium salt. The sodium salt of 2-mercaptobenzothiazole is the preferred alkali metal salt. When 2-mercaptobenzothiazole is employed, it is preferable that there be used a base such as ammonium hydroxide or an alkali metal hydroxide, oxide, or carbonate at least sufficient to provide one equivalent of base per mole of 2-mercaptobenzothiazole.

The mole ratio of 2-mercaptobenzothiazole or ammonium or alkali metal salt thereof to sulfenyl chloride can vary considerably but generally will be within the range of about 0.95:1 to about 1.2:1, preferably being about 1:1.

Although the reaction temperature can vary over a considerable range, it generally will be within the range of about 0°C to about 150°C, preferably about 20°C to about 100°C. The reaction time can vary considerably, depending in part on the reaction temperature, but generally will be within the range of about 10 seconds to about 12 hours, preferably about 5 minutes to about 30 minutes.

In accordance with a preferred embodiment of the invention, the novel 1,1,3,3-tetramethylbutyl 2-benzothiazyl disulfide is prepared by the reaction of a sulfenyl chloride having the formula $CH_3C(CH_3)_2CH_2C(CH_3)_2SCl$ with at least one of (a)

2-mercaptobenzothiazole or (b) the ammonium or alkali metal salts thereof.

The sulfenyl chloride should be dissolved in a saturated aliphatic or saturated cycloaliphatic hydrocarbon having from 5 to about 16 carbon atoms per molecule and preferably 6 or 7 carbon atoms per molecule. Examples of such hydrocarbons include pentane, hexane, heptane, 2-methyloctane, dodecane, hexadecane, cyclopentane, cyclohexane, cycloheptane, methylcyclopentane, and the like, and mixtures thereof. Preferably, there is present a solvent such as water for the ammonium or alkali metal salt of the 2-mercaptobenzothiazole, regardless of whether the salt is employed as such or produced in situ.

The pressure for the reaction need be only sufficient to maintain the solvent or solvents in the liquid phase.

The sulfenyl chloride used in this reaction can be prepared conveniently be reacting the corresponding mercaptan or disulfide with chlorine or sulfuryl chloride by conventional procedures.

Examples of some sulfenyl chlorides which can be employed to produce the tert-alkyl 2-benzothiazyl disulfides of this invention include 2-methyl-2-pentanesulfenyl chloride, 3-methyl-3-hexanesulfenyl chloride, 2,4,4-trimethyl-2-pentanesulfenyl chloride, 2,3-dimethyl-3-octanesulfenyl chloride, 4-ethyl-8-methyl-4-nonanesulfenyl chloride, 2,4,6-trimethyl-4-ethylheptanesulfenyl chloride, 2,5,7,9-tetramethyl-2-decanesulfenyl chloride, 2,3,3-trimethyl-2-hexanesulfenyl chloride, 2,4,5-trimethyl-2-hexanesulfenyl chloride, 2,2,4-trimethyl-4-heptanesulfenyl chloride, and 2,2,3-trimethyl-3-heptanesulfenyl chloride, and the like, and mixtures thereof.

Examples of some tert-alkyl 2-benzothiazyl disulfides which can be produced from the sulfenyl chlorides and 2-mercaptobenzothiazole or salts thereof, and which can be employed as lubricant additives in accordance with this invention, include 1,1-dimethylbutyl 2-benzothiazyl disulfide, 1-methyl-1-ethylbutyl 2-benzothiazyl disulfide, 1,1,3,3-tetramethylbutyl 2-benzothiazyl disulfide, 1-methyl-1-isopropylhexyl 2-benzothiazyl disulfide, 1-ethyl-1-propyl-5-methylhexyl 2-benzothiazyl disulfide, 1,1,3,5-tetramethyl-3-ethylhexyl 2-benzothiazyl disulfide, 1,1,4,6,8-pentamethylnonyl 2-benzothiazyl disulfide, 1,1,2,2-tetramethylpentyl 2-benzothiazyl disulfide, 1,1,3,4-tetramethylpentyl 2-benzothiazyl disulfide, 1,3,3-trimethyl-1-propylbutyl 2-benzothiazyl disulfide, and 1-methyl-1-tert-butylpentyl 2-benzothiazyl disulfide, and the like, and mixtures thereof.

In the preparation of the lubricating compositions containing the instant 2-benzothiazyl disulfides, various mineral oils are employed. Generally, these are of petroleum origin and are complex mixtures of many hydrocarbon compounds. Preferably, the mineral oils are refined products such as are obtained by well-known refining processes, such as by hydrogenation, polymerization, dewaxing, etc. Frequently, the oils have a Saybolt viscosity at 100°F in the range from about 60 to 5,000 and a Saybolt viscosity at 210°F of about 30 to 250. The oils can be of the paraffinic, naphthenic, or aromatic types, as well as mixtures of one or more types. The additives of the invention have special advantages when employed with paraffinic types of oils such as are obtained by solvent extraction of a suitable refinery stream. Many suitable lubricating compositions are available as commercial products such as those used as motor oils, fuel oils, gear oils, automatic transmission oils, and the like.

Generally, any conventional and commercially available grease can be used in accordance with this invention. The grease employed can have been thickened in any known manner such as by the use of soaps and/or by dissolving polymers in the oil at temperatures of at least 245°F and the like.

Suitable greases include substantially any grade of flowable grease as defined by the National Lubricating Grease Institute (NLGI). For example, NLGI grade greases from 000 to 6 can be employed in this invention. Also, greases having an ASTM D 217–68 penetration at 60 strokes in the range of 85 to 475 can be employed.

The lubricating oil bases which can be employed to make grease of this invention can be mineral, vegetable, or animal in nature, preferably lubricant bases having at least a major amount of mineral origin. Such oils include refined oils having a viscosity of from about 35 to about 240 SUS at 210°F. White mineral oil as well as other specialty oils can be used and are among the preferred oils.

The amount of tert-alkyl 2-benzothiazyl disulfide, as defined above, which is incorporated into the lubricants according to the invention can range from about 0.05 in weight percent to about 10 weight percent, preferably about 0.1 weight percent to about 5 weight percent and most desirably about 0.2 weight percent to about 2 weight percent, based on the total weight of the composition, i.e., the total weight of lubricant, including any other additives which may be present, plus the tert-alkyl 2-benzothiazyl disulfide.

Thickeners for the oils can be employed in amounts up to 20 weight percent of the oil. Various soaps normally used to thicken greases can be used, and they include metal salts of high molecular weight acids, for example, acids of 10 to 30 carbon atoms, and preferably 16 to 24 carbon atoms, either synthetic or of animal or vegetable origin. Other carboxylic acids useful for making soaps of metal salts include those derived from tallows, hydrogenated fish oil, castor oil, wool grease, and rosin. Generally, the alkali metal or alkaline earth metal or aluminum or lead salts of acids such as lauric, palmitic, oleic, stearic, and the like are used. One of the preferred soaps is the lithium soap of 12-hydroxystearic acid. While soaps of a general nature can be used in the greases of this invention, it should be understood that the invention includes use with soapless greases formed essentially from polymers and oil alone, with or without small amounts of known grease additives such as fillers and the like. Thus, polymers such as polyethylene and polypropylene can be employed as thickeners, together, alone or in conjunction with other thickeners such as soap.

Other materials normally used in greases can also be employed in the greases applicable to this invention. For example, additives such as rust inhibitors, antioxidants, fillers, pigments, perfumes, and the like can be employed. Some examples of such materials include propylenediamine, phenyl-α-naphthylamine, phenothiazine, mica, asbestos, powdered lead, powdered zinc, talc, alumina, titanium dioxide, molybdenum disulfide, bentones, carbon black, nitrobenzene, and the like. Generally, the amount of these modifiers is less than about 10 percent of the total weight of the grease.

Other agents than those which have been mentioned can be present in the lubricant composition such as dyes, pour point depressants, heat thickened fatty oils, sulfurized fatty oils, sludge dispersers, foam suppressants, thickeners, viscosity index improvers, oiliness agents, resins, rubber, molten polymers, and the like.

SPECIFIC EXAMPLES

EXAMPLE I

To a stirred solution of 146 g (1.0 mole) of 2,4,4-trimethyl-2-pentanethiol and 800 ml of heptane in a 3-liter, 3-necked flask equipped with stirrer, reflux condenser, and dropping funnel was added 135 g (1.0 mole) of sulfuryl chloride over a period of about 10 minutes. There was a vigorous evolution of gas during the addition. The reaction solution was heated to reflux (about 95°C) to remove the remaining hydrogen chloride and sulfur dioxide and then cooled to about 50°C.

To the resulting mixture, comprising 2,4,4-trimethyl-2-pentanesulfenyl chloride, was added rapidly an aqueous solution prepared from 400 ml water, 44 g (1.1 moles) sodium hydroxide, and 167 g (1.0 mole) 2-mercaptobenzothiazole. The two phases thus formed were stirred together for about 20 minutes, after which the phases were separated, and the oil phase was washed twice with water (500 ml portions). The solvent was stripped from the oil phase by heating at about 1 mm Hg pressure in a steam bath to obtain 264.2 g (87.8 percent yield) of 1,1,3,3-tetramethylbutyl 2-benzothiazyl disulfide as a residual slightly viscous, reddish brown liquid which was subjected to elemental analysis. Analysis, weight percent: Calculated for $C_{15}H_{21}NS_3$: C, 57.8; H, 6.8; N, 4.5; S, 30.9. Found: C, 58.4; H, 7.7; N, 4.2; S, 31.2.

EXAMPLE II

A mixture comprising isomeric tert-nonylsulfenyl chlorides and isomeric tert-decylsulfenyl chlorides was prepared by reaction of chlorine with a mercaptan mixture comprising about 62 weight percent isomeric tert-nonyl mercaptans, about 36 weight percent isomeric tert-decyl mercaptans, and about 2 weight percent olefins. Analysis of this mercaptan mixture showed it had the following properties:

Mercaptan Sulfur, weight percent	19.14
Average Molecular Weight, Based on Mercaptan Sulfur Content	167
Specific Gravity, 60/60 F	0.8531
API Gravity	34.4
Flash Point, TOC, F	148
5 mm Hg Distillation, F	
IBP	122
5%	131
10%	134
20%	134
30%	135
40%	136
50%	136
60%	136
70%	138
80%	138
90%	140
95%	142

To prepare the sulfenyl chlorides, 278.6 g (1.67 moles, based on mercaptan sulfur content) of the above mercaptan mixture was dissolved in sufficient heptane to give 1500 ml of solution. The major portion of this solution (1350 ml, containing 1.5 moles of mercaptans) was passed through a glass mixing tee where it was contacted with a stream of chlorine (107 g, 1.5 moles) in approximately a stoichiometric ratio over a period of one and one-half hours. The resulting mixture comprising isomeric tert-nonylsulfenyl chlorides and isomeric tert-decylsulfenyl chlorides in heptane was then stirred with a solution prepared from 300 ml water, 66.0 g (1.65 moles) sodium hydroxide, and 250.5 g (1.5 moles) 2-mercaptobenzothiazole for 30 minutes on a steam bath. The organic and aqueous phases were separated, and the organic phase was washed twice with water and then filtered, after which heptane was distilled under reduced pressure on a steam bath. The residual liquid product, which weighed 449.0 g, consisted essentially of a mixture of isomeric tert-nonyl 2-benzothiazyl disulfides and isomeric tert-decyl 2-benzothiazyl disulfides, this mixture of disulfides being referred to here and in subsequent Examples as $C_{9-10}BD$. Elemental analysis of this $C_{9-10}BD$ showed it contained 59.9 weight percent carbon, 7.7 weight percent hydrogen, 4.1 weight percent nitrogen, and 27.2 weight percent sulfur.

EXAMPLE III

1,1,3,3-tetramethylbutyl 2-benzothiazyl disulfide (C_8BD) and $C_{9-10}BD$ (described in Example II) were evaluated as extreme pressure lubricant additives in the Timken O.K. load test (ASTM D 2509–68), using a commercial lithium base grease, Grade 2. For comparative purposes, the test was also conducted on the same grease with no extreme pressure lubricant additive, as well as on the same grease containing tert-butyl 2-benzothiazyl disulfide (C_4BD), a known extreme pressure lubricant additive. The results are shown in Table I. In this example, as in the examples which follow, the weight percent additive is based on the total weight of lubricant plus additive.

TABLE I

Additive	Timken O.K.Load, Lb.
None	<10
C_8BD, 1 wt. %	30
C_8BD, 2 wt. %	45
C_8BD, 3 wt. %	50
$C_{9-10}BD$, 2 wt. %	50
C_4BD, 2 wt. %	40

Table I shows that C_8BD and $C_{9-10}BD$ were effective as extreme pressure lubricant additives, and that at a comparable concentration they were superior to C_4BD.

EXAMPLE IV

The antiwear properties of 1,1,3,3-tetramethylbutyl 2-benzothiazyl disulfide (C_8BD), $C_{9-10}BD$ (described in Example II), and tert-butyl 2-benzothiazyl disulfide (C_4BD) were compared in the Falex test (ASTM D 2670–67, except wear was measured at a load of 250 pounds over a period of three hours instead of at a load of 700 pounds for 15 minutes), using an experimental ashless crankcase motor oil (SAE 10W–40) without antiwear agent and consisting of base oil, dispersant, viscosity index improver, foam suppressant, and pour depressant. The results, obtained in duplicate tests, are shown in Table II.

TABLE II

Additive Concentration	Number of Teeth Wear C_8BD	C_4BD	$C_{9-10}BD$
1 Wt. %	24 & 25	33 & 35	23 & 27

Table II shows that in the Falex test the antiwear properties of C_8BD and $C_{9-10}BD$ were substantially better than those of C_4BD.

EXAMPLE V

The antiwear properties of 1,1,3,3-tetramethylbutyl 2-benzothiazyl disulfide (C_8BD) and tert-butyl 2-benzothiazyl disulfide (C_4BD), each at a concentration of 1 weight percent, were compared in the 4-ball wear test (ASTM D 2596-69), using the ashless crankcase motor oil described in Example IV. The results are shown in Table III.

TABLE III

Load, kg	Wear, microns C_8BD	C_4BD
100	1959	1920
120	2061	2019
140	2349	2155
160	2937	2706
180	3030	2781
200	Welded	Welded

The results in Table III indicate that, within experimental error, in the 4-ball wear test the antiwear properties of C_8BD and C_4BD were substantially equivalent.

EXAMPLE VI

Formulations consisting of the ashless crankcase motor oil described in Example IV, together with either 1,1,3,3-tetramethylbutyl 2-benzothiazyl disulfide (C_8BD) or tert-butyl 2-benzothiazyl disulfide (C_4BD) as an additive, were evaluated in the rotating bomb test (ASTM D 2272-67) to determine the stability of the formulations to oxidation. The results are shown in Table IV.

TABLE IV

Additive Concentration	Minutes to 25-lb. Pressure Drop C_8BD	C_4BD
1 weight percent	30	28

The higher value shown in Table IV for C_8BD than for C_4BD indicates the formulation containing C_8BD was slightly more stable to oxidation than was the formulation containing C_4BD.

EXAMPLE VII

1,1,3,3-tetramethylbutyl 2-benzothiazyl disulfide (C_8BD) was evaluated as an antiwear additive in a fully compounded SAE 10W-40 API Service SE motor oil without antiwear agent. The evaluation was a Sequence I type valve train wear test conducted in accordance with "ASTM Special Technical Publication No. 315-A, Engine Test Sequences for Evaluating Automotive Lubricants for API Service MS," American Society for Testing and Materials, Philadelphia, Pennsylvania (September 1963), except that a 1967 Oldsmobile engine was used instead of a 1960 Oldsmobile engine. For comparative purposes, control tests were conducted using the same motor oil (1) without antiwear agent and (2) with Lubrizol 1395 (zinc dialkyl dithiophosphate), a widely used antiwear additive. The results of these tests are shown in Table V.

TABLE V

Additive	Additive Concentration Weight %	Camshaft Lobe Wear, Inches Min	Max	Avg	Valve Lifter Footcrown Wear, Inches Min	Max	Avg
None	—	0.0006	0.1994	0.0868	0.0000	0.0620	0.0189
Lubrizol 1395	0.19	0.0000	0.0012	0.0005	0.0000	0.0000	0.0000
C_8BD	0.2	0.0000	0.0014	0.0006	0.0000	0.0010	0.0006
C_8BD	0.1	0.0000	0.0517	0.0033	0.0000	0.0130	0.0001
C_8BD	0.05	0.0000	0.1717	0.0260	0.0000	0.0480	0.0056

Table V shows that use of the ashless lubricant additive C_8BD at each of the concentration levels employed provided some protection against wear. At the concentration of 0.2 weight percent, C_8BD afforded wear protection approximately comparable to that provided by Lubrizol 1395, which is not ashless, at a concentration of 0.19 weight percent.

As will be evident to those skilled in the art, there are variations and modifications of this invention which can be practiced in view of the foregoing disclosure without departing from the spirit and scope of the invention.

We claim:

1. An improved lubricating composition comprising major amounts of a mineral lubricating oil having incorporated herein a small minor amount of a tert-alkyl 2-benzothiazyl disulfide selected from the group consisting of 1, 1, 3, 3-tetramethylbutyl 2-benzothiazyl disulfide and a mixture of isomeric tert-nonyl 2-benzothiazyl disulfides and isomeric tert-decyl 2-benzothiazyl disulfides sufficient to improve at least one of the properties of the resulting lubricating composition, said properties including antiwear and extreme pressure characteristics and stability toward oxidation and rust.

2. A composition according to claim **1** wherein the quantity of tert-alkyl 2-benzothiazyl disulfide ranges from 0.05 to about 10 weight percent.

3. A composition according to claim **1** wherein said mineral lubricating oil has been thickened with an alkali metal soap to form a grease formulation.

4. A composition according to claim **1** wherein the tert-alkyl 2-benzothiazyl disulfide is 1,1,3,3-tetramethylbutyl 2-benzothiazyl disulfide.

5. A composition according to claim **1** wherein the tert-alkyl 2-benzothiazyl disulfide is a mixture of isomeric tert-nonyl 2-benzothiazyl disulfides and isomeric tert-decyl 2-benzothiazyl disulfides.

6. A composition according to claim **1** wherein the amount of tert-alkyl 2-benzothiazyl disulfide present ranges from about 0.1 to about 5 weight percent.

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