

$$\begin{array}{ccccccc} & & \text{CH} & - & \text{CH}_2 & & \text{CH}_2 \\ & & / & & \backslash & & / \\ \text{CH}_3 & - & \text{C} & & & \text{CH} & - & \text{C} \\ & & \backslash & & / & & \backslash \\ & & \text{CH}_2 & - & \text{CH}_2 & & \text{CH} \end{array}$$

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$$\begin{array}{ccccc} & & \text{CH}-\text{CH}_2 & & \text{CH}_2 \\ & & // & & / \\ \text{CH}_3-\text{C} & & & & \text{C}=\text{C} \\ & & \backslash & & \backslash \\ & & \text{CH}_2-\text{CH}_2 & & \text{CH}_2 \end{array}$$

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It will be obvious from the data shown above that, in general, the prior art preparations are not satisfactory

in situations requiring both copper strip corrosion and bearing corrosion inhibiting properties. It will be apparent that the production of a successful oxidation inhibitor of the type concerned in this invention presents peculiar problems in that it is exceedingly difficult to incorporate or to retain just the right amount of sulfur of the correct degree of chemical activity in the terpene molecule.

The differences between the sulfurized terpenes of the prior art and the sulfurized and subsequently or simultaneously desulfurized terpenes of the present invention are emphasized by inspection of comparative infra-red absorption spectra. Commercial dipentene sulfurized in the conventional manner (with no catalyst present) shows an absorption band at 10.2 microns but no absorption in the 11.28–11.4 micron range which is typical of type III olefins ($\text{CH}_2=\text{CRR}'$), cyclic olefins and cyclic diolefins including dipentene. Untreated dipentene shows strong absorption in this band. After desulfurization according to the invention, the products absorb in the 11.28–11.4 micron range, but not at 10.2 microns. This suggests that the terpenic structure is retained in the case where the sulfurization catalyst is used.

The chemical reactions occurring between sulfur and terpenic compounds are complex, which is not surprising in view of the several different types of double bonds in terpenes, the different ways in which sulfur can react, the ease of isomerization of terpenes, and the possibility of disproportionation yielding both benzene and naphthene rings. As a result of the involved nature of the reaction, the mechanism and the chemical nature of all the products have not been completely identified. However, the present inventors have found certain new and advantageous principles and procedures, which if followed will result in the production of sulfurized terpene products having the desirable property of low corrosivity toward metals such as copper, and the property also of inhibition of oil oxidation which leads to bearing corrosion in engines.

According to the present invention, it has been found that a partial desulfurization of the initial sulfur-terpene adduct is an essential step in the manufacture of high quality products. Best results are obtained when the proportion of sulfur employed in the reaction mixture is relatively high, for example, equal to or greater than one atom of sulfur per double bond in the terpene molecule, and when the subsequent desulfurization is extensive. Further, it has been found that the desulfurization should occur through the elimination of hydrogen sulfide from the sulfur-terpene adduct.

The desulfurization catalysts useful in the present invention may be selected from any of the well known materials known to the art as rubber vulcanization accelerators. Such materials are discussed in "Compounding Ingredients for Rubber" second edition, 1947, compiled by the editors of India Rubber World. Specific classes of compounds include thiazole derivatives such as mercaptobenzothiazole (Captax); aryl guanidine derivatives such as di-orthotolyl-guanidine, diphenyl guanidine (DPG), tri-phenyl guanidine, and mixtures of aryl guanidines; dithiocarbamate derivatives such as piperidinium pentamethylene dithiocarbamate (Pip-Pip), 2,4-dinitrodimethyl dithiocarbamate, and the zinc, copper, selenium and tellurium salts of dialkyl dithiocarbamates (Zimate etc.); sulfide derivatives of such compounds, such as benzothiazyl disulfide, tetramethylthiuram disulfide (Tuads), tetramethyl thiuram mono- and tetrasulfides, dibutyl xanthogen disulfide, 2-benzothiazyl-N,N-diethylthiocarbamyl sulfide (Ethylac); amino-halide condensation products such as those of aniline and formaldehyde, toluene and various aldehydes, and of aniline and acetaldehyde; thiourea derivatives such as symmetrical diphenyl thiourea; nitroso derivatives such as a polymer of p-nitroso benzene; xanthates such as zinc butyl-xanthates, and the like.

Compounds such as those listed above may be used

singly or in combination. For example, mixtures of mercaptobenzothiazole and diphenyl guanidine or of methyl thiuram disulfide and diphenyl guanidine are quite effective.

The amount of catalyst which is employed may vary from about 0.05% to about 5.0% preferably 0.3 to 1.5%, by weight of the reactants. It will be obvious from the data presented in connection with the attached drawing that the catalytic desulfurization reaction can be carried out subsequent to the sulfurization (attached drawing, curve B), or simultaneously therewith (attached drawing, curve C). This is also illustrated by Examples I to IV. Suitable temperatures for both sulfurization and desulfurization are above the melting point of sulfur and not above about 425° F., the preferred range being within the limits of about 300° to 400° F. The proportion of sulfur employed is generally in the range from about 20 to about 35% by weight, based on the total composition, from 25 to 33% being preferred.

The invention will be more fully understood by reference to the following specific examples.

EXAMPLE 1.—(METHOD A)

5.5 grams of "Captax" (mercaptobenzothiazole) and 2.75 grams of "DPG" (diphenyl guanidine) were added to 150 grams of flowers of sulfur and the mass was melted and heated to a temperature of 300° F. in a flask equipped with a stirrer and a reflux condenser. To this mixture there was gradually added 400 grams of commercial "Dipentene." The approximate composition of the commercial "Dipentene" is as follows:

	Percent by weight
Alpha pinene fraction	6
Alpha terpineol	7
Para cymene	10
Dipentene	31
Terpinolene	39
Δ 2,4(8) para-menthadiene	5
Residue	2

On a percentage basis, the amounts employed were 73% "Dipentene" and 27% sulfur, combined with about 1% "Captax" and 0.5% "DPG." The terpenic material was added over a period of about 20 minutes, during which the temperature of the mix was kept at 300° F. Thereafter, the temperature was raised to about 350° F. and held there for 5 hours. Samples of the reaction product were taken at 3 hours and at 5 hours. At the end of 5 hours, the yield was about 84% of a clear, oily sulfurized product which showed a sulfur analysis of 18.83% by weight. Using 0.5% by weight of this material in an SAE grade 20 extracted Mid-Continent lubricating oil, an excellent copper strip rating of "5" was obtained (heated in the presence of clean copper for 3 hours at 212° F.). The entire reaction ran very smoothly.

EXAMPLE 2.—(METHOD B)

2.67 grams of "Tuads" (tetramethyl thiuram disulfide), 134.0 grams of sulfur and 400 grams of the commercial "Dipentene" of Example 1, plus one drop of a defoaming solution were stirred in a one-liter, 3-neck flask equipped with a reflux condenser. The temperature was raised to 300° F. in 25 minutes and maintained in this range for 5 hours. The product showed the following characteristics:

Gravity °A. P. I.	3.3
Neutralization number	3.31
Saponification number	92.51
Sulfur, Wt. percent	23.4
Copper strip test	5

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EXAMPLE 3.—(METHOD C)

11.0 grams of "Captax" (mercaptobenzothiazole), 5.5 grams of "DPG" (diphenyl guanidine) and 770.0 grams of "Dipentene" were stirred in a 3-liter, 4-neck flask with reflux condenser and heated to 300° F. in 28 minutes. When the temperature reached 300° F. sulfur was added in small portions, maintaining the temperature between 298° F. and 307° F. 330.0 grams of sulfur were added over a period of 57 minutes. The temperature was then raised to 330° F. and held at 330°–340° F. for 5 hours. Samples taken after 1, 2, 3 and 5 hours at 330°–350° F. showed the following characteristics:

Hours at 330°–340° F.	Sulfur, Percent	Copper Strip Test
1.....	22.46	9
2.....	21.72	7
3.....	20.55	7
5.....	19.33	6

Yield at 5 hours=85%.

EXAMPLE 4.—(METHOD D)

900.0 grams of sulfur were heated in a 5-liter, 4-neck flask to 300° F. in 18 minutes. The molten sulfur was stirred and 2400 grams of "Dipentene" were added gradually at 298°–310° F. over a period of 41 minutes and the reaction continued at 306°–322° F. for one hour. At this point, with a temperature of 310° F., a solution of 6.6 grams of "Tuads" dissolved in 59.4 grams of previously sulfurized "Dipentene" was added gradually over a period of 14 minutes. The temperature had dropped to 292° F. at this point, and was gradually raised to 337° F. over the next 3 hours and to 350° F. in the fourth hour. Heating was continued for an additional 8 hours at 350° F., making a total of 12 hours after addition of the catalyst. The product contained 18.88% sulfur and gave a rating of 6 in the copper strip test.

EXAMPLE 5

A number of preparations were carried out under a variety of conditions, reactant proportions and methods, similar to those described in Examples 1 to 4. Details of these experiments and the quality of the products as measured by copper strip corrosion are given in Table I.

Table I

CATALYTIC SULFURIZATION OF DIPENTENE

Run No.	Catalyst	Soaking Temp., °F.	Soaking Time, Hrs.	Method ¹	Sulfur, Percent		Yield, Wt. Percent	Copper Strip, 3 Hrs./ 212°F.
					Added	Found		
1 (Ex. 1).....	1.5% C+D ² ...	350	5	A	27	18.8.....	84.....	5
2 (Ex. 2).....	0.5% Tuads.....	300	5	B	25	23.4.....	no analysis.....	5
3 (Ex. 3).....	1.5% C+D.....	340	5	C	30	19.3.....	85.....	6
4 (Ex. 4).....	0.2% Tuads.....	350	11.5	D	27	18.9.....	no analysis.....	6
5.....	1.0% Tuads.....	300	3	B	27	no analysis.....	do.....	10
6.....	1.0% Tuads.....	300	3	B	25	24.1.....	do.....	6
7.....	1.0% Tuads.....	300	1.75	C	27	24.6.....	84.....	5
8.....	1.0% Tuads.....	340	3.5	B	27	23.2.....	no analysis.....	5
9.....	1.0% Tuads.....	340	8	A	30	24.9.....	88.....	6
10.....	0.5% C+D.....	350	7	A	27	19.1.....	88.....	6
11.....	0.5% DPG.....	350	5	A	27	18.0.....	84.....	4
12.....	1.5% C+D.....	350	2	A	30	20.2.....	93.....	6
13.....	1.0% Captax.....	350	10	A	27	no analysis.....	85.....	10
14.....	None.....	340	6	A	20	do.....	no analysis.....	10
15.....	None.....	340	6	A	27	do.....	do.....	10
16.....	None.....	340	5	A	30	do.....	do.....	10

¹ Method A—Sulfur and catalyst heated to 300° F., dipentene added at 300° F., mixture heated as shown. Method B—All reactants mixed and heated together. Method C—Catalyst and part of dipentene heated to 300° F. Slurry of sulfur in remaining dipentene added at 300° F. and heated as shown. Method D—Sulfur heated to 300° F., dipentene added at 300° F. catalyst added as 10% solution in previously sulfurized dipentene, mixture heated as shown.

² C+D=67% "Captax" and 33% "DPG" (diphenyl guanidine).

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The data in Table I show (a) that several different methods of carrying out the reaction give satisfactory results, (b) that a variety of compounds of the rubber accelerator type are effective catalysts for the reaction yielding non-corrosive products, "Tuads" or a combination of "Captax" and "DPG" being especially useful, (c) that the reaction can be carried out in the presence of catalysts at temperatures as low as 300° F. and in as little as 1.75 hours, (d) that as much as 30% sulfur can be employed when catalysts are present, and (e) that as little as 20% sulfur yields a corrosive product when no catalyst is used, even at a relatively high temperature and long reaction time.

In general, the reaction conditions preferred are a temperature of about 300° to 350° F. and a reaction time of 1.5 to 12 hours, using 25 to 30% by weight of sulfur and 0.3 to 1.5% of catalyst. Broader ranges of 280° or 300° to 425° F., reaction time of 1 to 20 hours, sulfur range from 20 to 35%, or even as high as 40%, based on the weight of the total reactant mixture, and 0.05 to 5% of catalyst, may be employed. The reaction conditions may be varied somewhat, depending upon the proportions of sulfur and "desulfurization" catalyst employed. The monocyclic terpenes are preferred, specifically dipentene and terpinolene, but the invention is applicable to the terpenes broadly.

EXAMPLE 6

A series of sulfurized dipentene preparations were made on a pilot plant scale. These reactions, shown in Table II, show additional conditions of time and temperature which may be employed with "Captax"-"DPG" catalyst to obtain non-corrosive products. One point to be observed from the data in Table II is that non-corrosivity as indicated by the copper strip test is dependent on a decrease in original or "normal" sulfur content through evolution of hydrogen sulfide, one of the main contributions of the catalyst being apparently to promote smooth desulfurization of unstable terpene-sulfur adducts. It will also be noted from the data in Table II that when employing 27% of sulfur, a temperature of 303° F. gave a non-corrosive product in 4 hours (run 52), whereas a temperature of 275° F. did not give a non-corrosive product even in 10 hours (run 55). Further, the use of a larger amount of sulfur, 29%, gave an unsatisfactory product at 300° F. (run 53), whereas 30% sulfur gave non-corrosive products at higher temperatures (runs 59, 62, 63, 65 and 66). Thus, the required temperature and time for a particular proportion of sulfur are simply related.

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Table II

SULFURIZED "DIPENTENE" PILOT PLANT DATA
[Catalyst: 1.0% "Captax"+0.5% "DPG."]

Run No.	Hrs.	Percent S Charged	Soaking Temp., ° F.	Sulfur Found Weight, Percent	Cu Strip at 212° F. ¹
45.....	5	27.5	353	22.0	6
52.....	9	27	303	20.4	6
53.....	4	27	303	24.4	7
55.....	10	29	300	23.2	6
	10	27	275	25.2	10
	10			23.6	10
59.....	4	30	375	22.6	6
	8			21.7	6
	10			20.7	5
61.....	4	27.5	385	20.1	4
62.....	2	30	390	20.4	4
	5			25.0	6
	7			23.4	3
63.....	5	30	385	No data	5
	7			No data	3
	8			21.9	6
	10			21.5	6
64.....	10	27.5	353	20.9	6
	12			20.3	6
	14			19.9	6
	2			19.3	6
	3			24.0	10
65.....	4	30	375	23.2	10
	5			22.0	6
	6			21.5	6
	8			24.6	10
	10			23.7	10
66.....	8	30	350	23.2	10
	10			22.0	10
	12			21.4	6
	14			21.5	30

¹ Cu Strip Test—3 hrs. at 212° F., 0.5% in SAE 20 oil.

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sulfur reduced the bearing weight loss to 0.20–0.25 gm./bearing, and (3) that 1.0% of samples made with 30% sulfur reduced this value to 0.11–0.13 gm./bearing. All of these samples were acceptable in the copper strip test.

Table III

36-HOUR CRC-L-4 CHEVROLET ENGINE TESTS
[Solvent extracted Mid-Continent 95 V. I., SAE 30 grade with sulfurized "dipentene" inhibitor.]

Sulfurized "Dipentene"			Engine Deposit Demerits			Cu-Pb Bearing Wt. Loss, Gm./Bearing
Vol. Percent	Sample Table	Reference Run	Overall	Ring Zone	Varnish	
None.....			0.50	0.63	1.4	0.87
1.00.....	I	8	0.75	0.64	3.7	0.20
1.00.....	I	3	0.85	0.73	4.4	0.12
0.75.....	II	45-9	0.76	0.72	4.1	0.49
1.00.....	II	45-9	0.94	0.79	5.1	0.25
1.00.....	II	47-10	0.88	0.77	4.9	0.25
1.00.....	II	59-4	0.85	0.72	4.4	0.11
1.00.....	II	65-6	0.86	0.86	4.3	0.13

In Table IV are shown the performance characteristics of several examples of the invention in three different mineral oil base stocks, in combination with several well-known commercial detergents. It will be noted that in all cases, clean engines and low bearing weight losses resulted from using these combinations.

Table IV

36-HOUR CRC-L-4 CHEVROLET ENGINE TESTS
[Performance of sulfurized dipentene in combination with detergents.]

Base Oil	Detergent	Sulfurized Dipentene			Engine Demerits			Cu-Pb Bearing Wt. Loss, Gm-/Bearing
		Vol- ume Percent	Sample		Over- all	Ring Zone	Var- nish	
			Table	Run				
High Grade SAE 10W—20 Motor Oil Base.....	None.....	None	-----	-----	0.64	1.31	0.15	8.9
	1.5% Commercial Detergent A.....	None	-----	-----	0.59	0.72	1.31	0.80
	do.....	0.23	I	2	0.54	0.58	2.3	0.10
	do.....	0.45	II	45-9	0.60	0.58	2.8	0.05
	0.9% Commercial Detergent A.....	0.20	I	9	0.46	0.65	1.79	0.03
High Grade SAE 30—20W Motor Oil Base.....	do.....	0.20	I	8	0.50	0.71	2.00	0.20
	do.....	0.30	I	8	0.49	0.64	1.58	0.07
	do.....	0.30	I	2	0.42	0.49	1.94	0.18
	do.....	0.30	II	45-9	0.58	0.73	2.35	0.05
Regular Grade SAE-10 Motor Oil Base.....	2—5% Commercial Detergent B.....	0.23	I	2	0.36	0.51	0.9	0.10

In Table III are shown the results of 36-hour CRC-L-4 Chevrolet engine tests on a 95 viscosity index solvent-extracted Mid-Continent lubricating oil of SAE 30 grade, and the same oil containing several examples of the sulfurized commercial "Dipentene" of the present invention. It will be noted (1) that 0.75% of a sample made with 27% sulfur reduced the copper-lead bearing weight loss, in the standard test, from 0.87 to 0.49 gm./bearing, (2) that 1.0% of samples made with 27%

It will be evident from the foregoing that: (1) the effectiveness of the product is not directly related to the final sulfur content; (2) the effectiveness is directly related to the amount of sulfur originally added; (3) a substantial degree of desulfurization is necessary to yield the most desirable product; and (4) the effectiveness depends largely on the particular molecular structure which is obtained by the use of the catalysts. It is believed that the final molecular or compositional structure

obtained in the products of this invention is substantially different from any previously disclosed in the art.

It will be understood that the finished product will be used in proportions of about 0.05% to 5%, preferably in the range from 0.1% to 2% by weight of the lubricant in which it is incorporated. The quantities mentioned are suitable for corrosion and oxidation inhibition. Where load-bearing properties are more important, greater quantities may be used, up to about 10% or 12% by weight. When used in such quantities, the products add materially to the load-bearing properties of the lubricant. The higher concentrates such as oil blends containing up to 50% or more are of use mainly to facilitate handling and blending of the product in various oils and other lubricants.

The products of the present invention may be employed not only in ordinary hydrocarbon lubricating oils, but also in the "heavy duty" type of lubricating oils compounded with detergent additives such as metal soaps, metal petroleum sulfonates, and metal phenates, alcoholates, alkyl phenol sulfides and polysulfides, organo-phosphates and phosphites, thiophosphates and thiophosphites, xanthates and thioxanthates, carbamates, amines, and the like. They may be combined also with other conventional anti-oxidants, corrosion inhibitors, metal deactivators, pour point depressants, viscosity index improvers, and the like. They may be used in greases and in gear oils and other heavy lubricants as well as in crankcase lubricating oils, although their primary use is in the latter.

The compounds of the present invention may also be used as additives for other types of mineral oils such as motor fuels, diesel fuels and kerosene, engine flushing oils, industrial oils, process oils, general machinery oils, rust preventive compositions, and other mineral oil base compositions wherein it is desired to improve the oxidation resistance and other properties of the composition.

What is claimed is:

1. A mineral oil composition consisting essentially of a mineral base lubricant containing in the range of about 0.05 to 12% by weight, based on the total composition, of a sulfur containing reaction product having an infra-red absorption spectra in the 11.28 to 11.4 micron range, obtained by sulfurizing a cyclic non-aromatic unsaturated organic material selected from the class consisting of terpenes, sesqui-terpenes and diterpenes having the general formula $(C_5H_8)_n$, where n is an integer of value 2 to 4, with 20 to 35% by weight of sulfur based on the combined reactants and desulfurizing the resultant sulfurized material by heating it in the presence of 0.05 to 5% of a desulfurization catalyst of rubber vulcanization accelerator type selected from the group consisting of thi-
azole derivatives, aryl guanidine derivatives and dithio-

carbamates, said sulfurizing and desulfurizing steps being carried out at a reaction temperature between 300° and 425° F. for a total period of 1 to 20 hours until evolution of H_2S has substantially ceased and the product is substantially non-corrosive to copper.

2. A composition as in claim 1 wherein said mineral oil is a lubricating oil.

3. Composition according to claim 1 prepared by a process wherein sulfurization precedes desulfurization.

4. Composition according to claim 1 prepared by a process wherein the sulfurization and desulfurization are conducted simultaneously.

5. Composition according to claim 1, wherein the organic material is predominantly a $C_{10}H_{16}$ monocyclic terpene.

6. Composition according to claim 1, wherein the reaction temperature is between 300° and 350° F.

7. A mineral lubricating oil composition consisting essentially of a lubricant base stock containing about 0.05 to 12% by weight, based on the total composition of the reaction product having an infra-red absorption spectra in the 11.28–11.4 micron range obtained by treating a $C_{10}H_{16}$ monocyclic terpene with 25 to 33% by weight of sulfur and 0.05 to 5.0% by weight of tetramethyl thiam disulfide, said treating being carried out at a temperature in the range of about 300°–425° F. for a total period of 1 to 20 hours until evolution of H_2S has substantially ceased and the product is substantially non-corrosive to copper.

8. A mineral lubricating oil composition consisting essentially of a lubricant base stock containing about 0.05 to 12% by weight, based on the total composition of the reaction product having an infra-red absorption spectra in the 11.28–11.4 micron range obtained by treating a $C_{10}H_{16}$ monocyclic terpene with 25 to 33% by weight of sulfur and 0.05 to 5.0% by weight of a mixture of benzo-thiazole and diphenyl guanidine, said treating being carried out at a temperature in the range of about 300°–425° F. for a total period of 1 to 20 hours until evolution of H_2S has substantially ceased and the product is substantially non-corrosive to copper.

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