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## LUBRICATING COMPOSITIONS

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This invention relates to lubricants, particularly those useful for lubrication under severe operating conditions, such as under extreme high speed and at high temperatures.

It is well known that the high pressure occurring in certain types of gears and bearings may cause rupture of lubricant films with consequent damage to the machinery. It is known that various base lubricants can be improved in their protective properties for rubbing surfaces by the addition of certain substances, so-called extreme pressure agents, so that excessive wear, scuffing and seizure which normally follow a break in the film lubricant are minimized or prevented.

It is known that certain compounds of metal-reactive elements, such as certain compounds of chlorine, sulfur and phosphorus, as well as certain other compounds, such as some compounds of lead, impart extreme pressure properties to various lubricants. Notable among the substances heretofore used are the lead soaps, phosphoric acid esters, free or bound sulfur and certain chlorinated organic compounds. A principal objection to many of these extreme pressure agents is their generally high reactivity with the metallic surface, causing etching, corrosion and discoloration of the metal surface. Another objection to chemically reactive extreme pressure agents is that they alter the original chemical nature of the contacting surface, which under certain conditions is undesirable. Additionally, because of the activity of agents of this type, they usually are depleted rapidly resulting in only a temporary solution to the problem of extreme pressure lubrication.

It has now been discovered that improved extreme pressure lubricants are provided by a suitable lubricating oil containing oil-soluble high molecular weight mercapto-modified polymeric compounds having essentially a long linear hydrocarbon backbone chain and attached thereto in a uniform or random fashion two kinds of essential groups, one an oil-solubilizing hydrocarbyl radical, preferably an alkyl radical having an average of between 8 and 20 carbon atoms (preferably 10–16) bonded directly to the hydrocarbon backbone chain or indirectly thereto through a polar group and the other, which is attached through sulfur to the hydrocarbon backbone chain, represented by the radical  $-S-(CH_2)_n-X$ , wherein X is a polar radical such as  $-COOR$ ,  $-OR$  or  $-NR_2$ , where R is hydrogen or a hydrocarbyl radical, preferably an alkyl radical of from 1 to 10 carbon atoms and n is an integer of from 1 to 4. The number of  $-S(CH_2)_n-X$  units or groups in the final polymeric compound can vary from 10 to 1000 or more, preferably from 300 to 800, inclusive.

Oil-soluble mercapto-modified [poly(thioether)] polymers of the above type can be prepared by reacting a mercapto compound, such as mercapto acid, ester, ether, alcohol, amine, or mixtures thereof, with an oil-soluble unsaturated essentially linear hydrocarbon polymer having a plurality of oil-solubilizing alkyl radicals of from 8 to 20 carbon atoms attached directly or indirectly to a linear hydrocarbon backbone chain prepared by reacting a lower polyene hydrocarbon with a polymerizable monomer having an oil-soluble alkyl group.

The mercapto compounds include the mercapto aliphatic carboxylic acids such as mercapto acetic acid, mercapto propionic acid, mercapto butyric, or mercapto-alkanols such as 2-mercaptoethanol, 2- and 3-mercapto-

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propanol, 2-, 3- and 4-mercaptobutanol, or others of said mercaptoalcohols such as methyl or ethyl 2-mercaptoethanol or mercaptoamines such as ether or mercapto esters, e.g., ethyl mercapto acetate or ethyl mercapto butyrate, ethanthiolamine, butanthiolamine and mixtures thereof.

The unsaturated polymers which are reacted with the above mercapto compounds are long chain oil-soluble polymers prepared by polymerizing a lower (4 to 8 carbon atoms per molecule) polyene hydrocarbon with a monoolefinically polymerizable monomer having a higher hydrocarbon moiety (10- carbon atoms) such as long chain alkyl esters of alpha,beta-unsaturated acids, such as acrylic and methacrylic acids, esters of lower unsaturated alcohols, such as vinyl and allyl alcohols and long chain fatty acids, long-chain N-alkyl unsaturated fatty acid amides, such as N-alkyl acrylamides.

Suitable polyene hydrocarbons for forming the copolymers are, for example, 1,3- and 1,4-pentadiene, isoprene, 1,3-hexadiene, 1,3,5-heptatriene, 1,3-cyclopentadiene, methylcyclopentadiene, 1,3- and 1,4-cyclohexadiene, methylcyclohexadiene, and mixtures thereof.

Representative oil-solubilizing monomer compounds which are used to form the copolymers with the polyene hydrocarbons include alpha-unsaturated long chain hydrocarbons, unsaturated esters, unsaturated amides, etc., such as decene-1, dodecene-1, tridecene-1, tetradecene-1, hexadecene-1, heptadecene-1, octadecene-1, tritriacontene-1, tetratriacontene-1, heptacontene-1, 4-methyl-decene-1, 4,4-dimethyl-decene-1, 5,5-dimethylhexene-1, 5,5,7,7-tetramethyl-decene-1, 4,4,6,6-tetramethylheptene-1, etc., vinyl decanoate, vinyl laurate, vinyl tridecanoate, vinyl myristate, vinyl pentadecanoate, vinyl palmitate, vinyl margarate, vinyl stearate, vinyl nonadecanoate, vinyl arachidate, vinyl behenate, vinyl 4,5,6-trimethyldodecanoate, vinyl 6,8,9-triethyl tridecanoate, vinyl 12-hydroxystearate, vinyl 9,10-dihydroxystearate, vinyl chlorostearate, vinyl cyanostearate, vinyl acetylsteareate, vinyl dodecyl ether, vinyl tridecyl ether, vinyl tetraacosyl ether, vinyl hexacosyl ether, allyl stearate, allyl dodecyl ether, N-lauryl methacrylamide, N-stearyl methacrylamide, and N,N-distearyl methacrylamide.

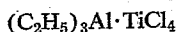
The mol ratio of the polyene hydrocarbons to the oil-solubilizing monomer compounds can be varied within relatively wide limits, e.g., from 1/10 to 10/1, preferably from 1/5 to 5/1, respectively. The polymer (prior to treatment with mercapto compound) should have a substantial amount of unsaturation and have a molecular weight of at least 500 and may be up to or over 2½ million, but preferably from about 2,000 to about 800,000 and still more preferred molecular weight range is from 100,000 to 600,000.

Depending on the monomers used the polymers can be prepared thermally or in the presence of a suitable catalyst. Thus, with monomers such as butadienes or isoprene and long chain alpha-olefins such as alpha-dodecene or alpha-octadecene, the so-called Ziegler catalysts are preferred, such as combinations of aluminum trialkyls and a variable valence metal compound, e.g., titanium tetrachloride. In the formation of other types of oil-soluble polymers, such as copolymers of the polyene (e.g., butadiene or isoprene) with lauryl methacrylate or with vinyl stearate or with N-lauryl methacrylamide, oxygen-yielding catalysts are preferred such as, for example, various organic peroxides, including aliphatic, aromatic, heterocyclic and acyl peroxides, such as diethyl peroxide, tertiary butyl hydroperoxide, dibenzoyl peroxide, dimethylthienyl peroxide, dicyclohexyl peroxide, dilauroyl peroxide and urea peroxide. These are mentioned by way of nonlimiting examples of suitable organic peroxides. Other catalysts include sodium bisulfite, diethyl sulfoxide, ammonium persulfate, alkali metal perborates, azo compounds, such as alpha, alpha-azodiisobutyronitrile, etc.

The following Examples I-X are given as representative preparations of the intermediate copolymers for reaction with mercapto compounds to form the desired poly(thioether).

#### EXAMPLE I

About 0.66 mole of 1-octadecene, 1.33 moles of 1-dodecene and 0.5 mole of isoprene in cyclohexane were reacted in the presence of a Ziegler catalyst



at room temperature for about 24 hours. The catalyst was destroyed by addition of methanol and polymer thereafter purified by benzene washing and precipitating from alcohol and vacuum drying. The polymer had an average molecular weight of 300,000 and an average of 750 double bonds per polymer molecule as shown by bromine number.

#### EXAMPLE II

About 0.5 mole of isoprene, 0.17 mole of 1-octadecene and 0.34 mole of 1-dodecene in benzene were reacted in the presence of the Ziegler catalyst and under the conditions of Example I. The polymer formed had a molecular weight between 350,000-400,000 and a bromine number of 120.

#### EXAMPLE III

About 2 moles of butadiene and 1 mole of lauryl methacrylate and 1% di-tert-butyl peroxide were reacted at 75-100° C. for about 24 hours. The polymer was purified by alcohol washing, filtered and dried. The resulting copolymer had a molecular weight of 3000-5000 and substantial unsaturation as shown by a bromine number of 80 to 100.

The sulfur content of the resulting polymer is in the range of 1% to 30% and usually is about 6 to 12% by weight.

The following Examples A-J illustrate the preparation of poly(thioether) additives for use in oil compositions in accordance with the present invention.

#### EXAMPLE A

The copolymer of Example I was mixed with about 20% excess of mercaptoacetic acid and the mixture was reacted in the presence of tert-butyl hydroperoxide for 2-4 hours at about 40° C. The reaction mixture was diluted with diethyl ether, water washed, filtered and dried. The final average polymer molecule contained over 600 units of  $-S-CH_2COOH$  groups distributed in the molecule.

#### EXAMPLE B

The procedure of Example A was followed using the polymer of Example II and 2-mercaptoethanol as the mercapto compound. The final average polymer molecule contained over 500 units of  $-S-CH_2CH_2OH$  groups distributed in the molecule.

#### EXAMPLE C

The procedure of Example A was followed using the polymer of Example I and methyl 2-mercaptoacetate as the mercapto compound. The final product contained over 500 units of  $-SCH_2COOCH_3$  groups distributed in the molecule.

Following essentially the above procedures other thia-containing polymers containing a plurality of sulfur-containing groups in the molecule were prepared in accordance with the following tabulation.

Example	Polymer	Functional Group Introduced	Catalyst	Temperature, °C.	Percent S in Polymer
D-----	Ex. IV-----	$-S-CH_2COOH$ -----	benzoyl peroxide-----	40-45	6-7
E-----	Ex. V-----	$-S-CH_2CH_2NH_2$ -----	do-----	40-45	6-7
F-----	Ex. VI-----	$-S-CH_2CH_2COOH$ -----	tert-butylperoxide-----	50-60	5-5.5
G-----	Ex. VII-----	$-S-CH_2COOC_2H_5$ -----	do-----	50-60	2
H-----	Ex. VIII-----	$-SCH_2CH_2N(C_2H_5)_2$ -----	do-----	50-60	2
I-----	Ex. IX-----	$-S-CH_2COOH$ -----	benzoyl peroxide-----	50-60	3-4
J-----	Ex. X-----	$-S-CH_2COOH$ -----	do-----	50-60	1

Following essentially the procedures of Examples I-III, other polymers were prepared in accordance with the following tabulation:

The mercapto-modified [poly(thioether)] polymers in general are oil-soluble and can be used in amounts of from about 0.5% to about 20%, preferably from about

Example	Catalyst	Temperature, °C.	Polyene/oil-soluble monoolefins ratio	Mol wt. <sup>1</sup>	Bromine No.
IV-----	Ziegler Cat-----	Room temp-----	butadiene (2)/octadecene-1 (1)-----	400,000	90
V-----	do-----	60-70-----	cyclopentadiene (1)/isoprene (2)/octadecene-1 (1)-----	250,000	80
VI-----	Benzoyl peroxide-----	80-----	isoprene (3)/lauryl methacrylate (1)-----	5,000	50
VII-----	do-----	110-----	butadiene (2)/cyclopentadiene (1) vinyl stearate (1)-----	5,000	40
VIII-----	Di-tert-butyl peroxide-----	80-----	pentadiene (3)/N-lauryl-methacrylamide (1)-----	3,000	45
IX-----	do-----	120-----	isoprene (3)/lauryl methacrylate (1) stearyl-methacrylate (1)-----	8,000	33
X-----	do-----	100-----	isoprene (3)/allyl stearate (1)-----	2,000	45

<sup>1</sup> Ml. wt. determined by light scattering technique described in Chem. Rev., vol. 40, p. 139 (1948).

The final oil-soluble polymeric additive was prepared by reacting the unsaturated copolymers, such as those of Examples I-X, with one or more of the mercapto compounds by suitable means, such as described in Jour. Am. Chem. Soc., 79, 362 (1957) or Jr. Org. Chem., 22, 197 (1957), preferably between room temperature and about 100° C. and in the presence of a free radical catalyst such as an azo or a peroxide catalyst or ultraviolet light and in a non-reactive solvent such as benzene, toluene, xylene or the like. Suitable initiators include peroxides such as tert-butyl peroxide and azo compounds such as alpha, alpha-azodiisobutyronitrile or emulsion redox systems such as a mixture of sodium bisulfite and persulfate, ammonium persulfate, alkali metal (Na) perborates, etc.

1% to about 5% by weight. However, under certain storage and use conditions, it is desirable to incorporate into oil compositions containing these polymers a small amount (0.1-10%) of an oil-soluble branched-chain aliphatic monohydric alcohol. These alcohols can effectively stabilize such compositions without destroying the extreme pressure properties of such oil compositions.

The oil-soluble alkanols particularly useful for this purpose are the so-called "OXO" alcohols derived from branched-chain olefins, such as polymers of lower alkenes of 3 to 5 carbon atoms, and copolymers of mixtures of such alkenes, by catalyzed reaction with carbon monoxide and hydrogen in accordance with the conditions of the "OXO" process, as is well known in the art. The composition of a typical C<sub>8</sub>-OXO-alcohol mixture derived

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from a mixture of C<sub>7</sub>-olefins, produced by polymerization of a typical refinery cracked gas fraction of C<sub>3</sub>-C<sub>4</sub> hydrocarbons is given below:

Alcohol	Percent, wt.
3,5-dimethyl hexanol	29
4,5-dimethyl hexanol	25
3,4-dimethyl hexanol	17
5-methyl heptanol; 3-methyl heptanol	16
5-ethyl hexanol	2.3
5,5-dimethyl hexanol	1.4
Alpha-alkyl alkanols	4.3
Others	5.0

Other examples of suitable alkanols include 6-methyl-1-heptanol, 2-n-propyl-1-pentanol, 3-n-propyl-1-hexanol, 2,2-dimethyl-1-octanol, 10,10-dimethyl-1-undecanol, 3-isopropyl-1-heptanol and mixtures thereof.

The lubricating oil base is suitably selected from various synthetic oils or natural hydrocarbon oils having a viscosity range of from 50 SUS at 100° F. to 250 SUS at 210° F. (SAE viscosity number ranging from SAE 5 to SAE 90). The natural hydrocarbon oils are obtainable from paraffinic, naphthenic, asphaltic or mixed base crudes, and/or mixtures thereof. Useful synthetic oils include polymerized olefins, alkylated aromatics, isomerized waxes, copolymers of alkylene glycols and alkylene oxide (Ucon fluid, U.S. 2,425,755, 2,425,845 and 2,774,733) organic polyesters such as esters of an aliphatic dibasic acid and a monohydric alcohol, such as di-2-ethyl hexyl sebacate or di-2-ethyl hexyl adipate esters of polyhydric alcohols and monocarboxylic acids, such as pentaerythritol tetracaprate, and the like. Useful Ucon fluids are Ucon 50HB170, Ucon 50HB660 or Ucon LB550X, which are copolymers of ethylene and 1,2-propylene oxides; the diols as well as their mono- and dialkyl ethers are useful. The hydrocarbon oils may be blended with fixed oils such as castor oil, lard oil and the like and/or synthetic oils as mentioned or silicone polymers and the like. Typical oils of this type are petroleum motor oils (A) and (B), characterized below, (A) being paraffinic in character and (B) naphthenic in character:

Petroleum Oil	(A) (SAE 10W)	(B) (SAE 30)
Pour point, ° F.	-10	-5
Flash, ° F.	390	415
Viscosity, SUS at 210° F.	44	50
Viscosity Index	90	65

Other suitable oils are specification gas turbine lube oils having the following properties:

Grade	1010	1065
Flash, COC, ° F.	300	465
Pour, ° F.	-10	0
Viscosity, SUS at 100° F.	59.4	530
Neutral Number	0.02	0.01
Ash	None	None

The following compositions are illustrative of the invention, the percentages being by weight:

#### Composition A

Example A additive	2%.
1010 Mineral oil	Balance.

#### Composition B

Example B additive	2%.
1010 Mineral oil	Balance.

#### Composition C

Example C additive	2%.
1010 Mineral oil	Balance.

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#### Composition D

Example A additive	2%.
C <sub>13</sub> H <sub>27</sub> OH ("OXO" alcohol)	6%.
1010 Mineral oil	Balance.

#### Composition E

Example D additive	1%.
1010 Mineral oil	Balance.

#### Composition F

Example B additive	2%.
C <sub>13</sub> H <sub>27</sub> OH ("OXO" alcohol)	4%.
1010 Mineral oil	Balance.

#### Composition G

Example E additive	3%.
SAE 90 Mineral oil	Balance.

#### Composition H

Example F additive	2%.
C <sub>13</sub> H <sub>27</sub> OH ("OXO" alcohol)	6%.
SAE 90 Mineral oil	Balance.

#### Composition I

Example A additive	5%.
Ucon 50HB660 (polyethylene-propylene glycol having a SUS viscosity at 100° F. of 660)	Balance.

#### Composition J

Example A additive	5%.
Di-2-ethylhexyl sebacate	Balance.

Compositions of this invention were evaluated for their extreme pressure properties on a Spur-Gear machine. The machine consists essentially of two geometrically similar pairs of gears connected by two parallel shafts. The gear pairs are placed in separate gear boxes, which also contain the supporting ball bearings. One of the shafts consists of two sections connected by a coupling. Loading is accomplished by locking one side of the coupling and applying torque to the other. The conditions of the test were:

Speed—3200

Oil temperature—100° F.

Oil flow-rate—10 cc./sec.

Load in increments 5 min, at each setting

Compositions A, B, D and F carried score loads of from 3,000 to 12,000 lbs./in., Compositions I and J are equally effective and Compositions C, E, G and H carried score loads of over 1,500 lbs./in., on the other hand, 1010 mineral oil containing separately 2% of the polymers of Ex I to X carried score loads of about 700 lbs./in. and neat 1010 mineral oil carried a score load of 600.

The sulfur-containing polymers of this invention are useful also for providing superior load-carrying properties in lubricating oils which contain minor amounts of other agents which are nonreactive with the polymer, such as silicone anti-foaming agents, alkylphenol anti-oxidants, polyacrylate ester viscosity-index improvers, and the like.

Polymeric thioether containing compounds of this invention can be used to improve other types of compositions such as fuel oils with respect to screen clogging, greases to improve their load carrying properties, hydraulic fluids of the oil, water-in-oil emulsion or synthetic type with respect to wear inhibition and the like.

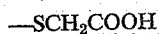
We claim as our invention:

1. A lubricating oil composition comprising a major amount of mineral lubricating oil and from about 0.5% to about 20%, of an oil-soluble high molecular weight polymer containing —C<sub>8</sub>—C<sub>20</sub> alkyl groups and —S—(CH<sub>2</sub>)<sub>n</sub>X groups attached to different carbon atoms of a linear hydrocarbon chain wherein n is an integer of 1 to 4 and X is a polar group selected from the group consisting of —COOR, —OR and —NR<sub>2</sub>, and R is selected from the group consisting of hydrogen and C<sub>1-10</sub> alkyl radicals said polymer having a sulfur content

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of from 1% to 30%; and a molecular weight from 2,000 to 800,000.

2. A lubricating oil composition comprising a major amount of mineral lubricating oil and from about 0.5% to about 20%, of an oil-soluble linear hydrocarbon polymer containing  $-C_8-C_{20}$  alkyl groups and



groups attached to different carbon atoms of the linear hydrocarbon chain, said polymer having a sulfur content of from 1% to 30% and a molecular weight of from 2,000 to 800,000.

3. A lubricating oil composition comprising a major amount of mineral lubricating oil and from about 0.5% to about 20%, of an oil-soluble linear hydrocarbon polymer containing  $-C_8-C_{20}$  alkyl groups and



groups attached to different carbon atoms of the linear hydrocarbon chain, said polymer having a sulfur content of from 1% to 30% and a molecular weight of from 2,000 to 800,000.

4. A lubricating oil composition comprising a major amount of mineral lubricating oil and from about 0.5% to about 20%, of an oil-soluble linear hydrocarbon polymer containing  $-C_8-C_{20}$  alkyl groups and



groups attached to different carbon atoms of the linear hydrocarbon chain, said polymer having a sulfur content of from 1% to 30% and a molecular weight of from 2,000 to 800,000.

5. A lubricating oil composition comprising a major amount of mineral lubricating oil and from about 0.5% to about 20%, of an oil-soluble linear hydrocarbon polymer containing  $-C_8-C_{20}$  alkyl groups and



groups attached to different carbon atoms of the linear hydrocarbon chain, said polymer having a sulfur content of from 1% to 30% and a molecular weight of from 2,000 to 800,000.

6. The composition of claim 3 wherein the  $-C_8-C_{20}$  alkyl groups are attached to the linear hydrocarbon chain through carboxyl groups.

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7. The composition of claim 4 wherein the  $-C_8-C_{20}$  alkyl groups are attached to different carbon atoms in the linear hydrocarbon chain through carboxyl groups.

8. The composition of claim 3 wherein the  $-C_8-C_{20}$  alkyl groups are attached to the linear hydrocarbon chain through amide groups.

9. A lubricating oil composition comprising a major amount of mineral lubricating oil and from about 1% to about 5% of an oil-soluble linear hydrocarbon polymer containing  $-C_8-C_{20}$  alkyl groups and  $-SCH_2CH_2OH$  groups attached to different carbon atoms of the linear hydrocarbon chain, said polymer having a sulfur content of from 6% to 12% and a molecular weight of from 100,000 to 600,000.

10. The composition of claim 1 containing from 0.1% to 10% of an oil-soluble branched-chain alkanol containing 8 to 13 carbon atoms.

11. The composition of claim 3 containing from 0.1% to 10% of an oil-soluble branched-chain alkanol containing 8 to 13 carbon atoms.

12. The composition of claim 4 containing from 0.1% to 10% of an oil-soluble branched-chain alkanol containing 8 to 13 carbon atoms.

13. The composition of claim 5 containing from 0.1% to 10% of an oil-soluble branched-chain alkanol containing 8 to 13 carbon atoms.

14. The composition of claim 6 containing from 0.1% to 10% of an oil-soluble branched-chain alkanol containing 8 to 13 carbon atoms.

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