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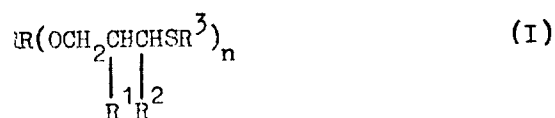
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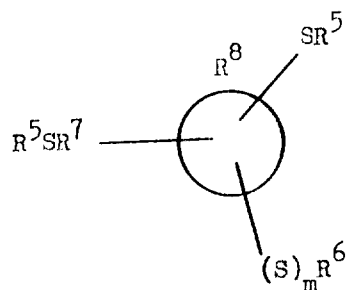
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SULFIDE ANTIOXIDANTS FOR STABILIZING
CROSSLINKED POLYOLEFINS

ABSTRACT

The present invention is a composition
 5 comprising crosslinked polyolefin resins and an
 amount of organic sulfide antioxidants
 sufficient to stabilize the resin against
 thermal or oxidative degradation, wherein the
 organic sulfide antioxidant is represented by
 10 Formula I, II or III





(III)

wherein m , n , R , R^1 , R^2 , R^3 , R^5 , R^6 , R^7 and R^8 are as set forth in the Summary of the Invention.

SULFIDE ANTIOXIDANTS FOR STABILIZING
CROSSLINKED POLYOLEFINS

FIELD OF THE INVENTION

The present invention relates to stabilized
5 crosslinked polyolefin resin compositions.

BACKGROUND OF THE INVENTION

The use of sulfide-type antioxidants as
stabilizers in polyolefin resin compositions is
known in the art.

10 For example, the use of diesters of
thiodipropionic acid, such as the dilauryl,
dimyristyl and distearyl esters of the
thiodipropionic acid, as well as
thiodipropionic acid itself, as antioxidants
15 in crosslinked polyolefins is known in the art.
For example, U.S. Pat. Nos. 3,876,613 and
4,028,332 disclose the use of such diesters of
thiodipropionic acid in producing useful molded
articles from peroxide-induced crosslinked
20 polyethylene homopolymers and copolymers. The

resultant crosslinked copolymers have high impact strength and a high resistance to stress cracking.

5 Likewise, U.S. Pat. No. 4,514,539 teaches the use of thiodipropionic esters as antioxidants in resin systems which comprise a combination of ethylene-vinyl acetate copolymers and polyethylene. The resin systems are crosslinked with peroxides. U.S. Pat. No.
10 4,526,916 discloses the use of thiodipropionate esters as antioxidants in peroxide-induced crosslinked polyethylene compositions, which are capable of being used in rotational molding processes.

15 U.S. Pat. No. 4,221,699 teaches the use of thio-bisphenols as antioxidants in polyolefin compositions which are also crosslinked with peroxides.

The crosslinking of polymer compositions
20 has the effect of changing a plastic from a

thermoplastic material to thermosetting material. This change has the effect of increasing the strength, heat and electrical resistance of the plastic, in addition to
5 increasing its resistance to solvents, chemicals creep and stress cracking.
(See, e.g., The Condensed Chemical Dictionary, 10th Ed., p. 287 (1981)). Furthermore, the crosslinking of polymer compositions extends
10 the useful upper temperature limit of the polymer as well as improves the heat-shrinking properties of the polymer discussed in The Encyclopedia of Polymer Science and Engineering 2nd Ed., Vol. 4, p. 385 (1986). The types of
15 polymers which can be crosslinked in order to cause an increase in their mechanical properties are known to those skilled in the art and are discussed in numerous references, such as e.g., The Encyclopedia of
20 Polymer Science and Engineering 2nd Ed. Vol. 4, pp. 418-449 (1986).

Crosslinked polyolefin resin compositions

are useful in a wide variety of applications.
For example, crosslinked polyolefin
compositions are useful as wire and cable
coatings, insulation, pipe and molded fittings,
5 and rotational molded articles, such as
gasoline tanks, barrels, containers, storage
tanks, etc.

As indicated above, the use of organic
sulfides as antioxidants in polyolefin resin
10 compositions is known in the art.
Particularly, the sulfide antioxidants are
conventionally used in combination with various
phenolic and arylamine auxiliary antioxidants
to stabilize polyolefin resin compositions
15 against the damaging effects of thermal and
oxidative degradation both during processing
and aging. For example, the use of organic
sulfides as stabilizers in polyolefin resin
compositions is taught in U.S. Pat. Nos.
20 3,180,850, 3,258,493, 3,293,209, 3,574,165,
3,652,680 and 3,772,246. However, conventional
antioxidants have demonstrated certain

drawbacks when used in polyolefin resins which are crosslinked.

Polyolefin resin compositions may generally be crosslinked through the use of (1) peroxide crosslinking agents or (2) high energy radiation. For polyolefin resin compositions crosslinked with peroxide, the range of useful antioxidants is limited, since the antioxidant itself must be compatible with the peroxide crosslinking agent, as discussed in U.S. Pat. No. 4,028,332. As further discussed in this patent, the thiodipropionate ester antioxidants, such as dilauryl thiodipropionate (DLTDP), are peroxide-compatible and provide a good low temperature impact strength, at least in polyolefin resins. However, these thiodipropionate ester antioxidants suffer several drawbacks. Namely, the antioxidant causes the resultant polymer compositions to discolor and to display an unpleasant odor.

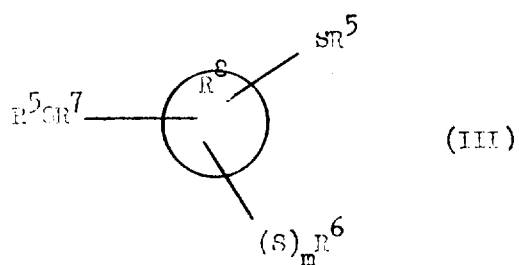
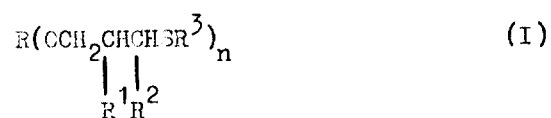
Likewise, when high energy radiation is

employed to induce crosslinking in the polyolefin resin compositions, the same criteria set forth above for the peroxide-induced crosslinked polymer compositions holds true. Similarly, conventional antioxidants used with polymer composition crosslinked with high energy radiation may cause the polymer compositions to discolor and have an unpleasant odor. The antioxidants used in these types of crosslinked polyolefin resins must be stable in the presence of the high energy radiation while providing its stabilizing effects.

Accordingly, one of the objects of the present invention is to provide crosslinked polymer compositions stabilized with organic sulfide antioxidants which are stable to the effects of heat and oxygen, and provide stabilized resin compositions which are hydrolytically stable, odor-free and color stable.

SUMMARY OF THE INVENTION

The present invention is a composition comprising crosslinked polyolefin resins and an amount of organic sulfide antioxidants sufficient to stabilize the resin against thermal or oxidative degradation, wherein the organic sulfide antioxidant is represented by Formula I, II or III



wherein:

m is 0 or 1;

n is an integer of 2 to 15;

R is a substituted or unsubstituted alkyl
5 group of 2 to 30 carbons, a substituted or
unsubstituted cycloalkyl group of 5 to 20
carbons, a substituted or unsubstituted alkyl
group of 2 to 30 carbons where any of up to 6
carbon atoms are replaced with an O or S
10 heteroatom, a substituted or unsubstituted
cycloalkyl group of 5 to 20 carbon where any of
up to 6 carbon atoms are replaced with an O or
S heteroatom, with the proviso that the
heteroatoms must be separated from each other
15 and from the portion of the compound to which
the R group is bonded by at least one carbon
atom, the substituents for R being -OH, -SR⁴ or
-OR⁴, wherein R⁴ is an alkyl group of 1 to 30
carbons or cycloalkyl group of 5 to 20 carbons.

20 R¹ and R² are independently H or an alkyl
group of 1 to 4 carbons;

R³ is an alkyl group of 1 to 24 carbons or
a cycloalkyl group of 5 to 20 carbons;

R⁵ is an alkyl group of 1 to 24 carbons;

R⁶ is H or an alkyl group of 1 to 24 carbons, with the proviso that when $m = 0$, R⁶ is H or an alkyl group of 1 to 7 carbons and
5 when $m = 1$, R⁶ is an alkyl group of 1 to 24 carbons;

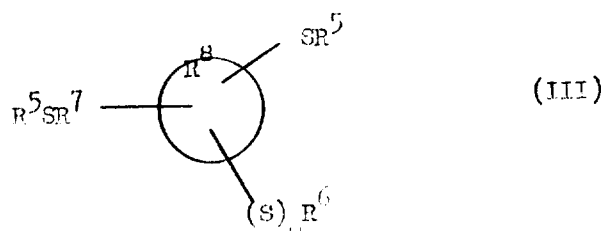
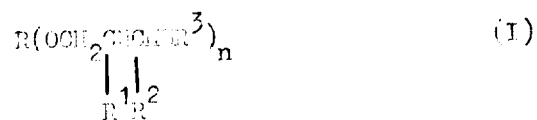
R⁷ is a direct bond or an alkylene group of 1 to 4 carbons; and

R⁸ is a monocyclic, bicyclic or tricyclic
10 cycloalkyl group of 5 to 16 carbons.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present compositions comprise a crosslinked polyolefin resin and an organic
15 sulfide antioxidant in an amount sufficient to provide antioxidant and thermal stabilizing effects. The present organic sulfide antioxidants stabilize the resins to the effects of oxygen and high temperature, while
20 not interfering with the crosslinking process. The present organic sulfide antioxidants are

represented by Formula I, II or III set forth below:



wherein:

- m is 0 or 1;
- n is an integer of 2 to 15;
- R is a substituted or unsubstituted alkyl group of 2 to 30 carbons, a substituted or

unsubstituted cycloalkyl group of 5 to 20
carbons, a substituted or unsubstituted alkyl
group of 2 to 30 carbons where any of up to 6
carbon atoms are replaced with an O or S
5 heteroatom, a substituted or unsubstituted
cycloalkyl group of 5 to 20 carbons where any
of up to 6 carbon atoms are replaced with an O
or S heteroatom, with the proviso that the
heteroatoms must be-separated from each other
10 and from the portion of the compound to which
the R group is bonded by at least one carbon
atom, the substituents for R being -OH, -SR⁴
or -OR⁴, wherein R⁴ is an alkyl group of 1 to
30 carbons or cycloalkyl group of 5 to 20
15 carbons.

R¹ and R² are independently H or an alkyl
group of 1 to 4 carbons;

R³ is an alkyl group of 1 to 24 carbons or
a cycloalkyl group of 5 to 20 carbons;

20 R⁵ is an alkyl group of 1 to 24 carbons;

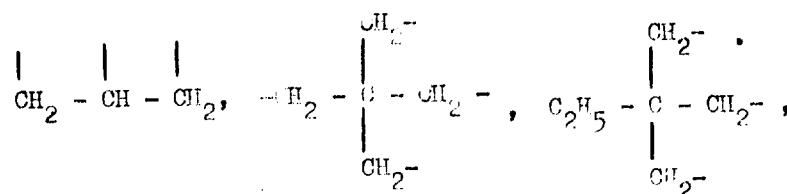
R⁶ is H or an alkyl group of 1 to 24
carbons, with the provisos that when m = 0, R⁶

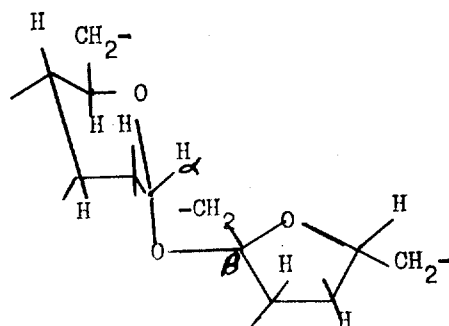
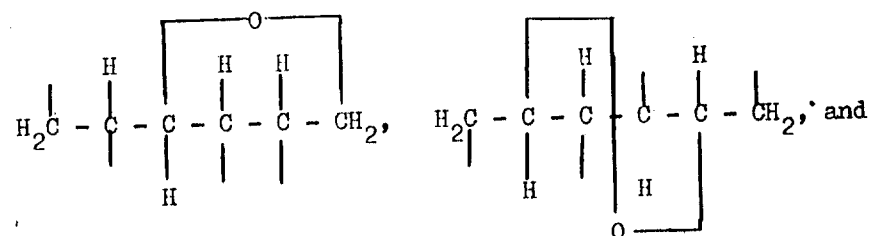
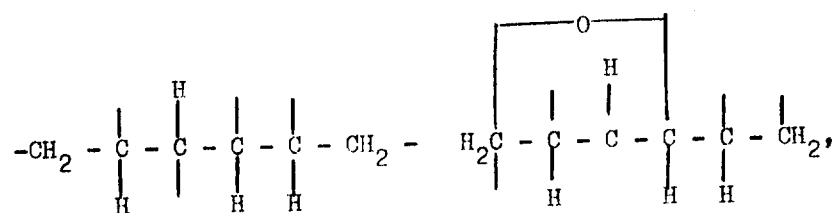
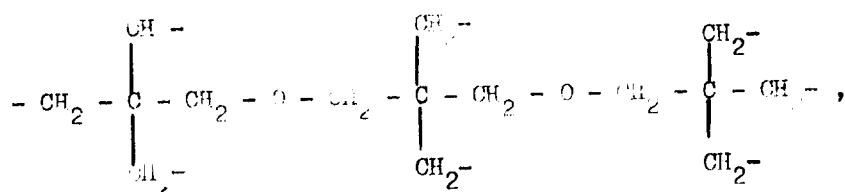
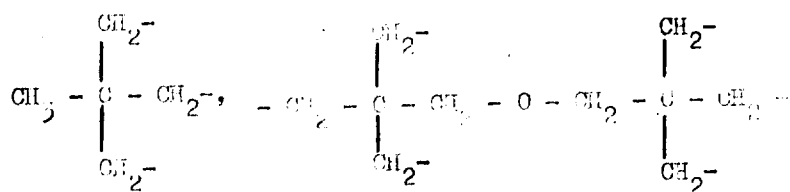
is H or an alkyl group of 1 to 7 carbons and
 when $m = 1$, R^6 is an alkyl group of 1 to 24
 carbons;

R^7 is a direct bond or an alkylene group
 5 of 1 to 4 carbons; and

R^8 is a monocyclic, bicyclic or tricyclic
 cycloalkyl group of 5 to 16 carbons.

Preferably, the organic sulfides of the
 present invention are those represented by
 10 Formulas I or II, wherein R is selected from
 the group consisting of

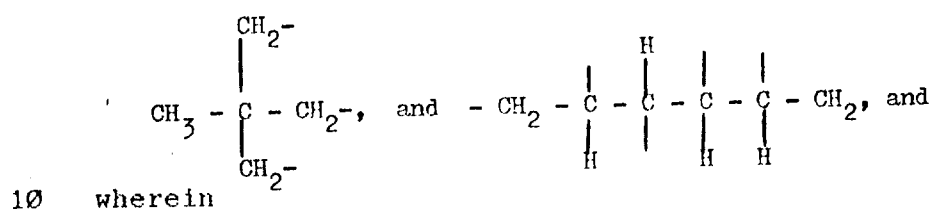
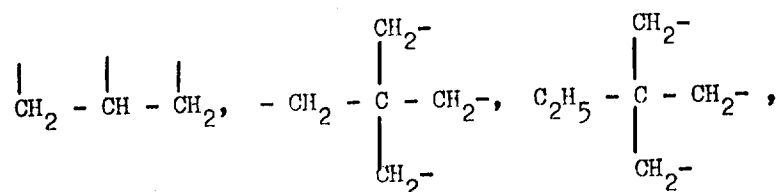




wherein α and β are the types of linkages;
 wherein

- R^1 is H or $-\text{CH}_3$;
 R^2 is H; and
 5 R^3 is an alkyl group of 10 to 18 carbons.

More preferably, the organic sulfide antioxidants useful in the present composition are represented by Formula I or II, wherein R is represented by



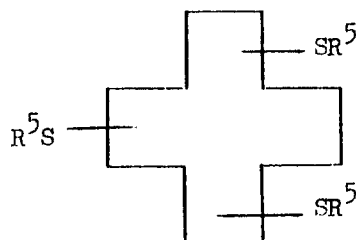
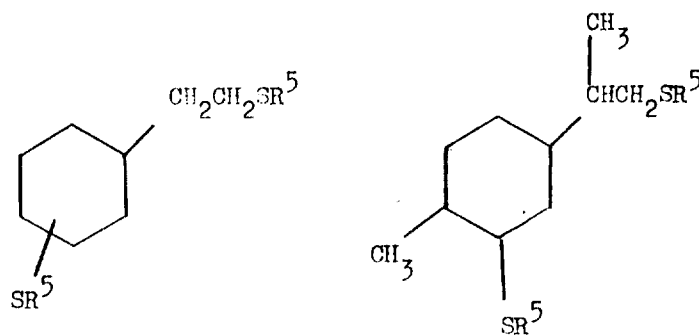
R^1 and R^2 are H, and

R^3 is an alkyl group of 12 to 18 carbons.

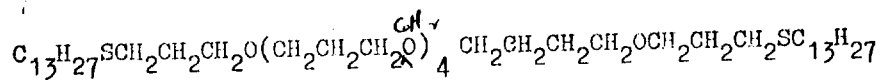
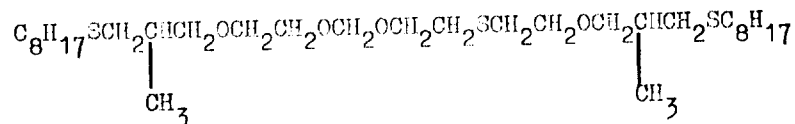
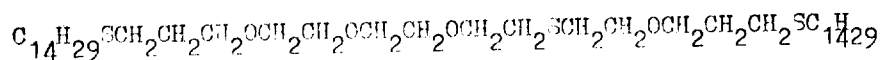
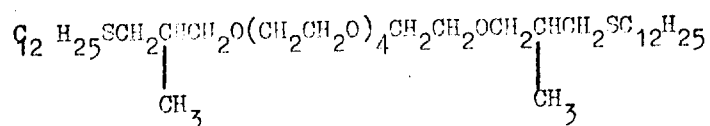
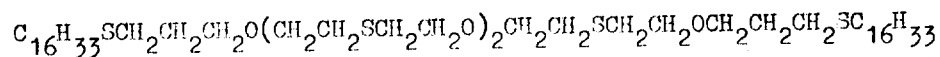
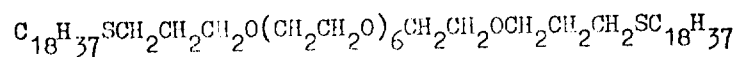
In the above-identified preferred and more preferred compounds, n is determined by the number of unattached bonds present in each

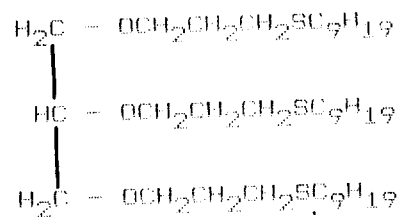
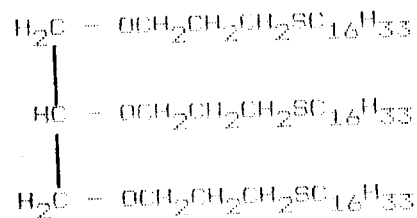
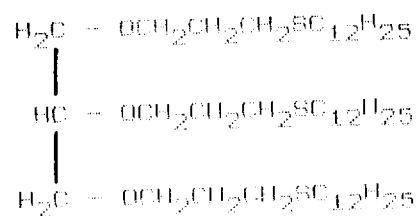
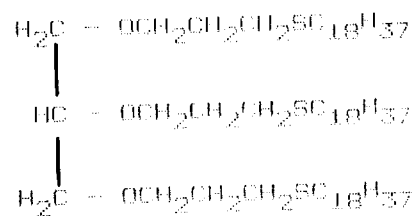
5 R group.

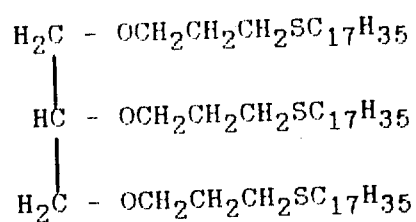
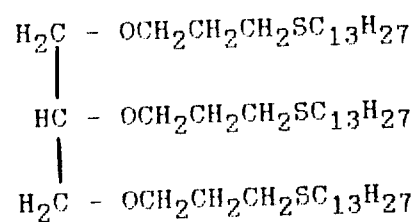
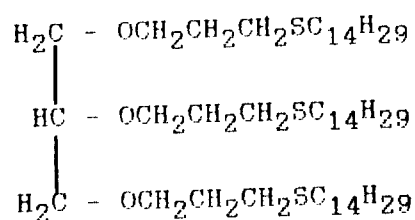
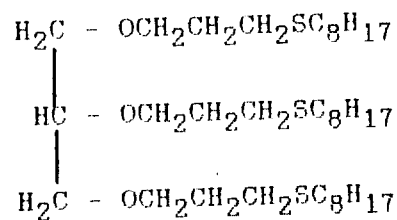
The preferred organic sulfide antioxidants represented by Formula III are represented by one of the following structure:

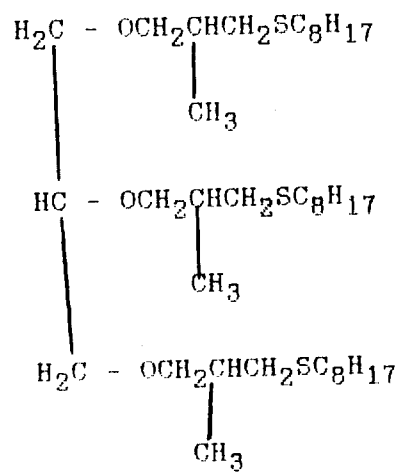
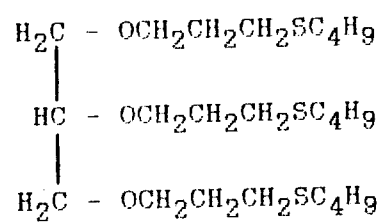
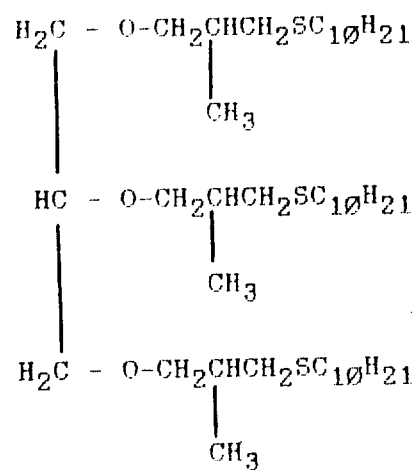


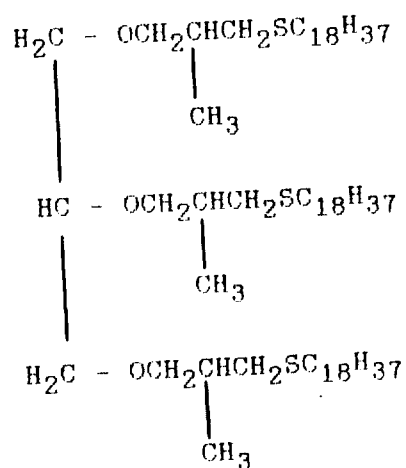
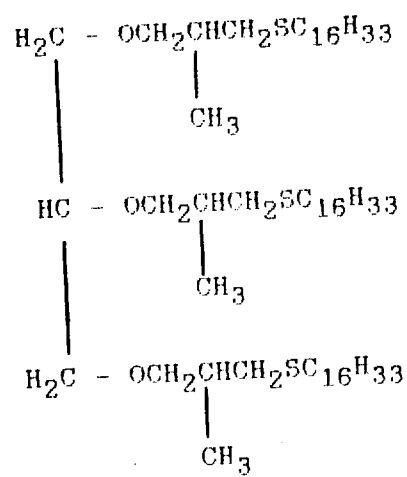
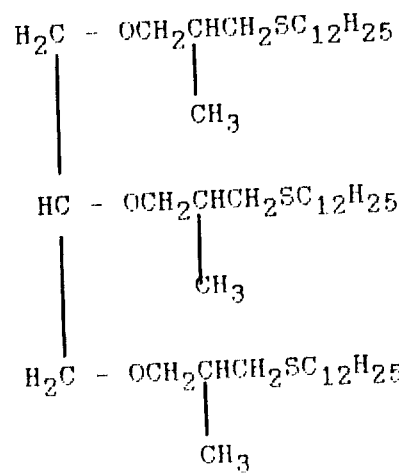
Non-limiting examples of representative organic sulfide antioxidants which are useful in the present composition are set forth below:

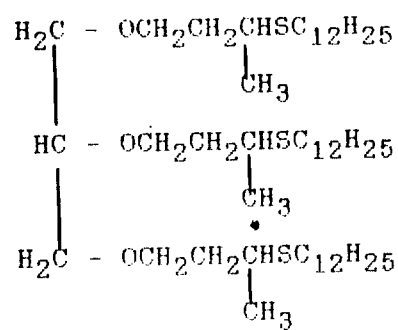
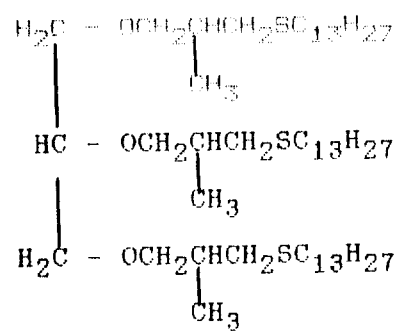
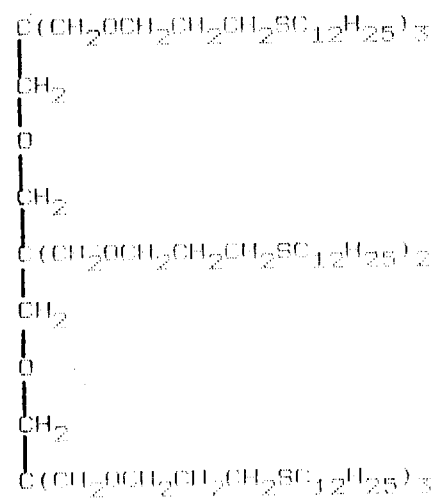


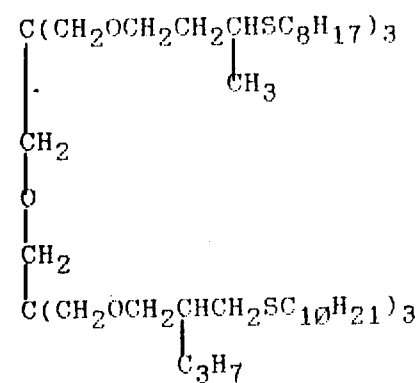
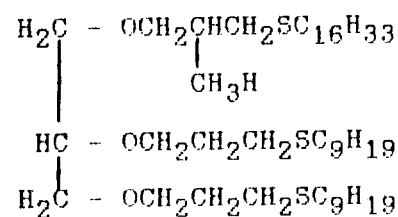
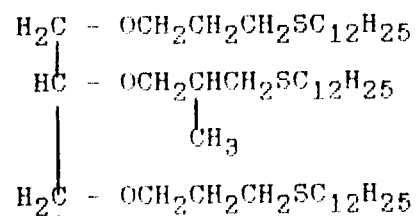
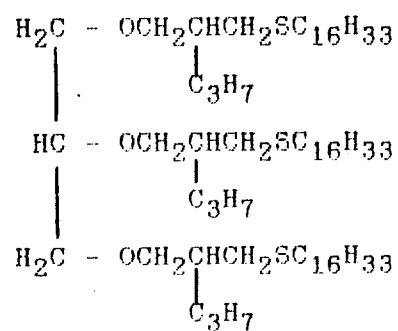


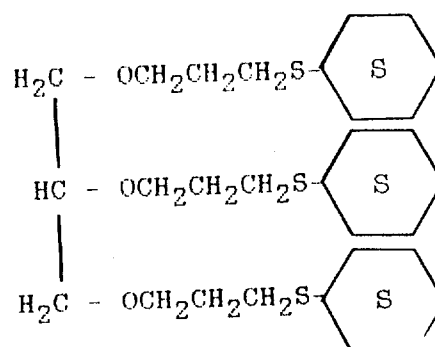
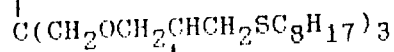
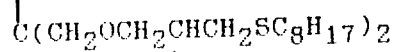
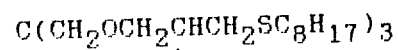


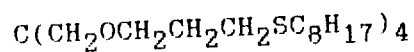
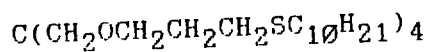
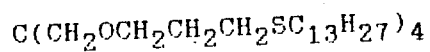
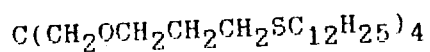
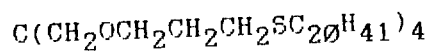
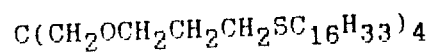
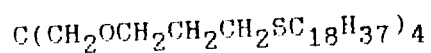
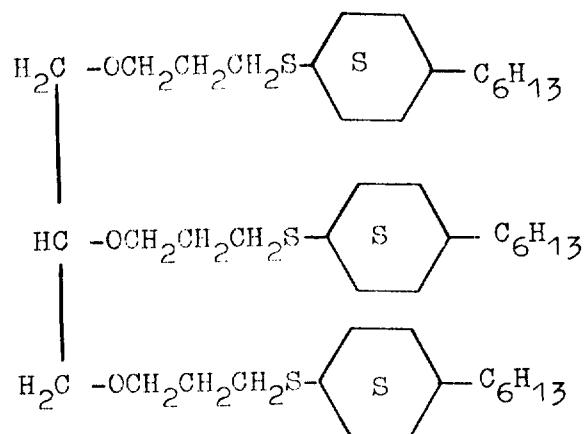


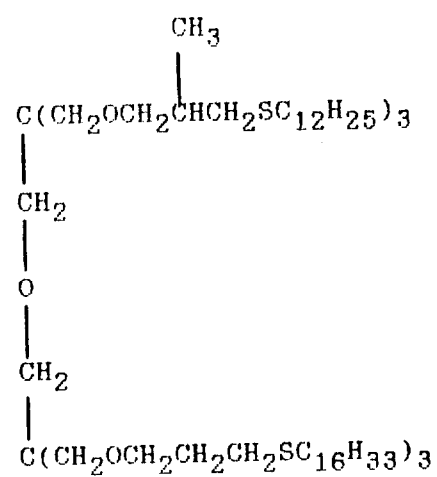
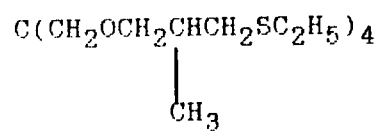
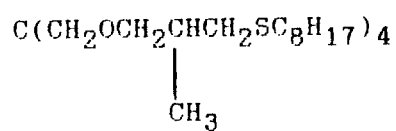
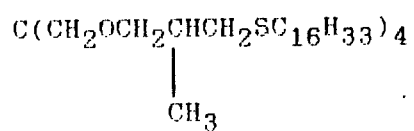
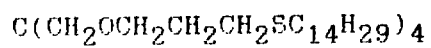


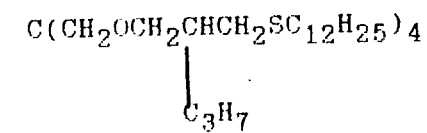
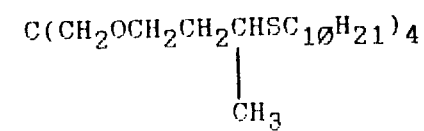
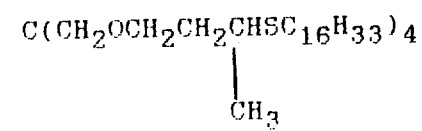
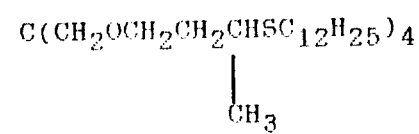
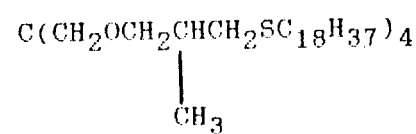
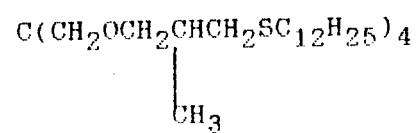
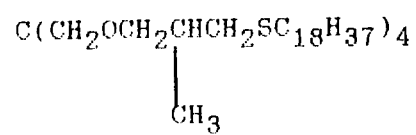


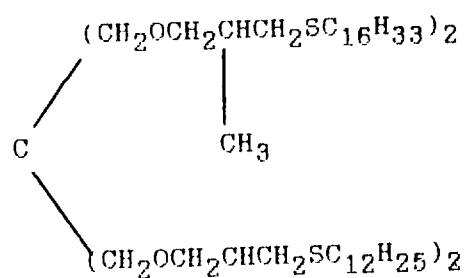
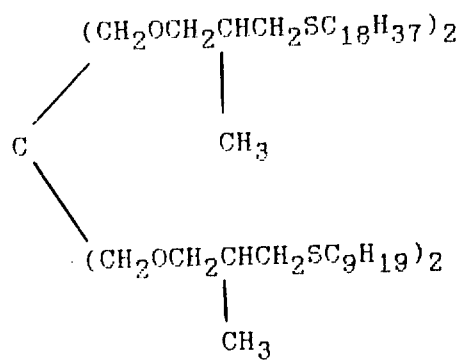
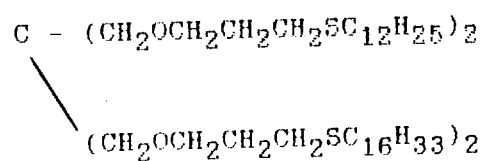
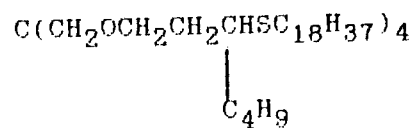


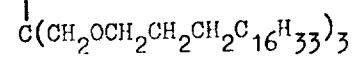
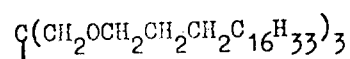
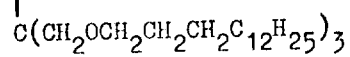
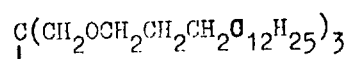
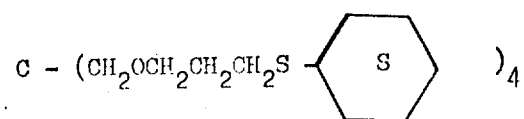
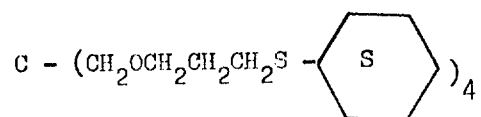


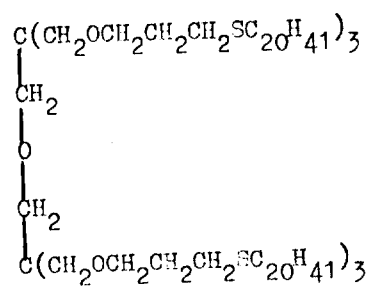
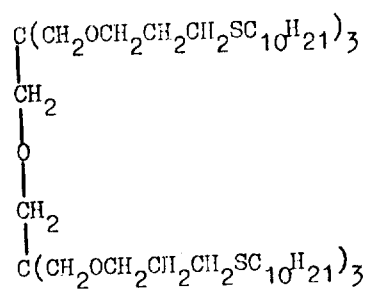
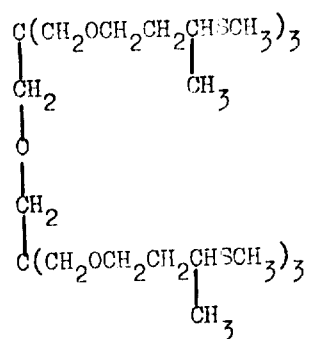
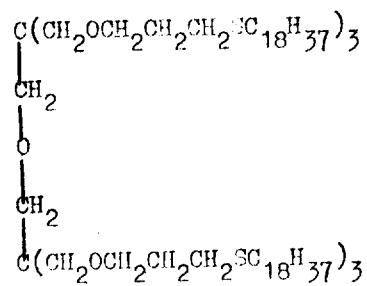


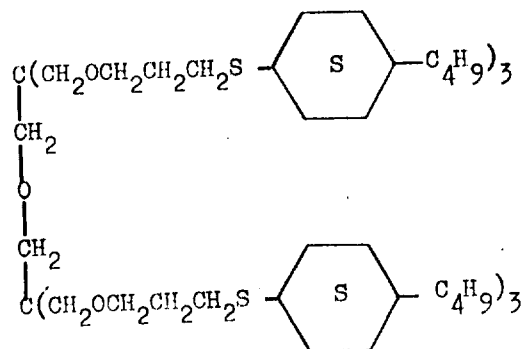
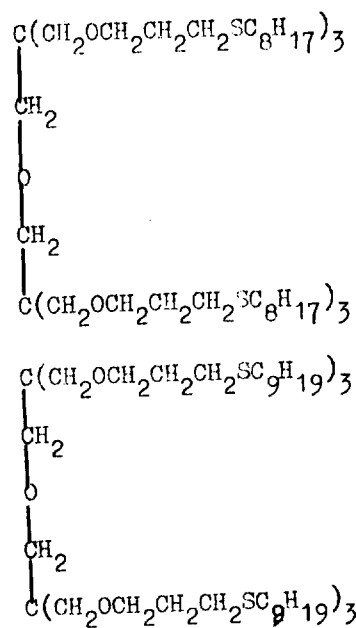
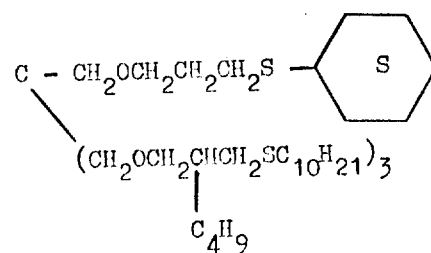
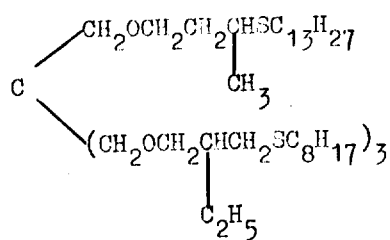


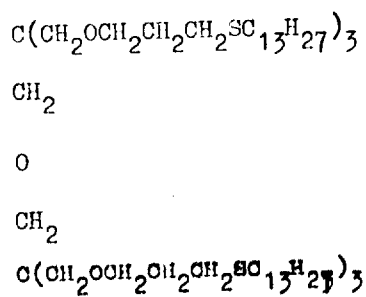
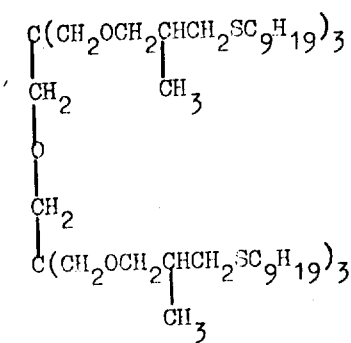
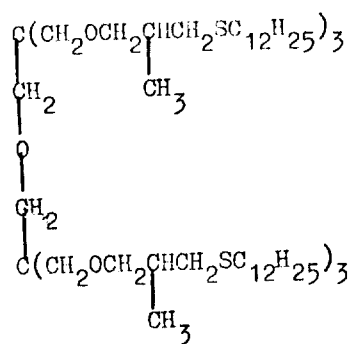
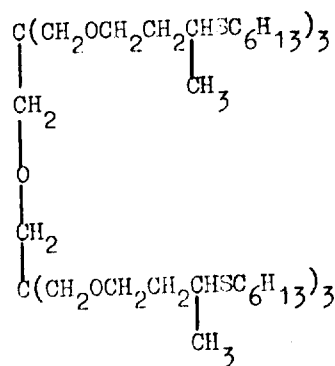


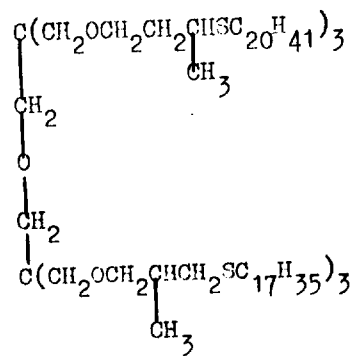
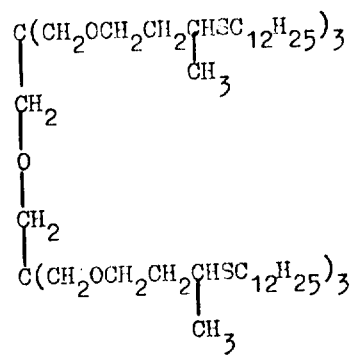
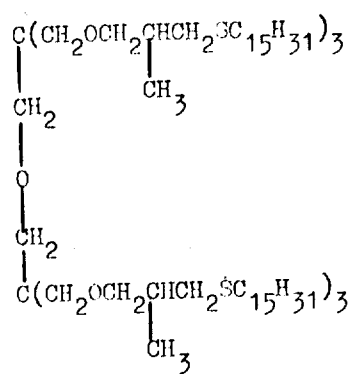
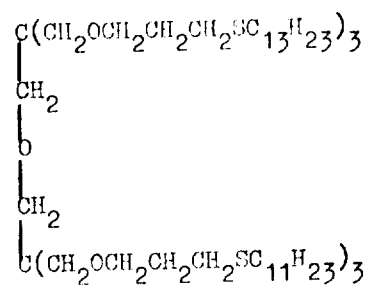


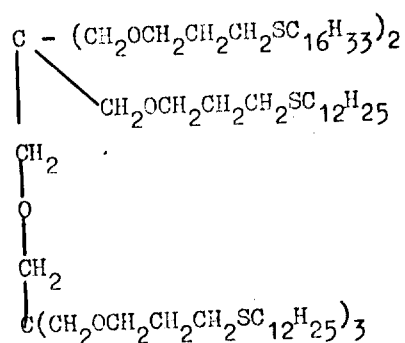
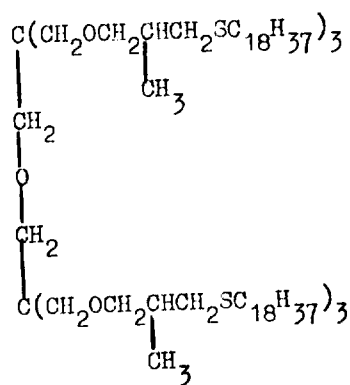
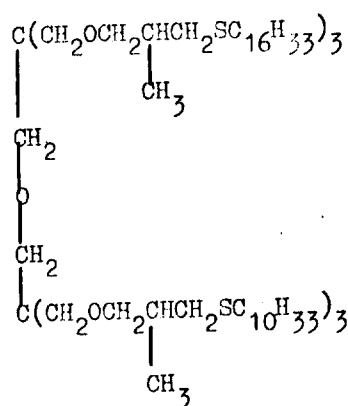
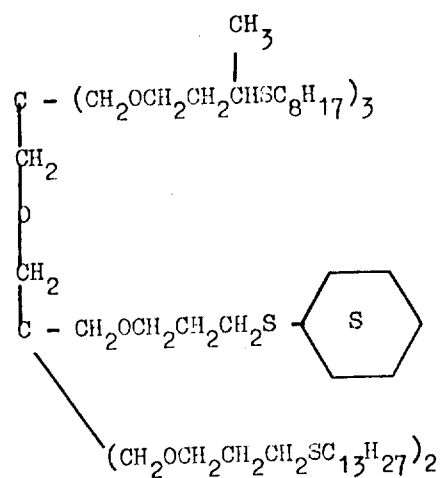




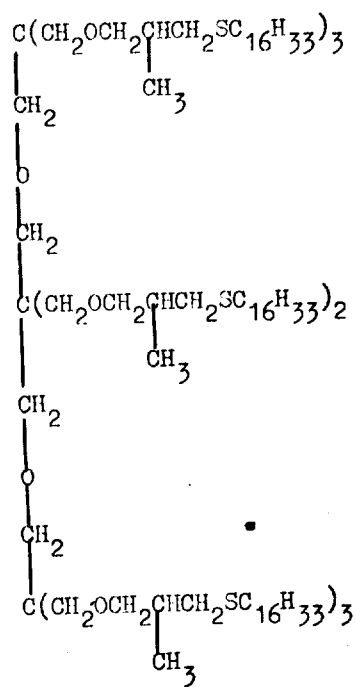
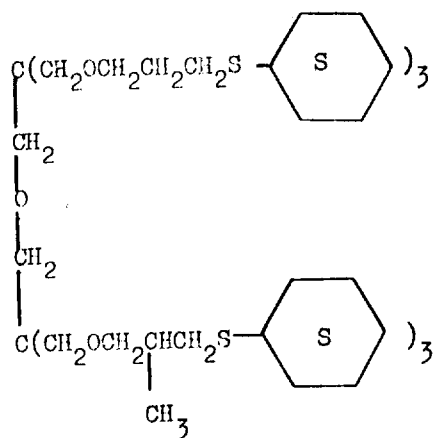
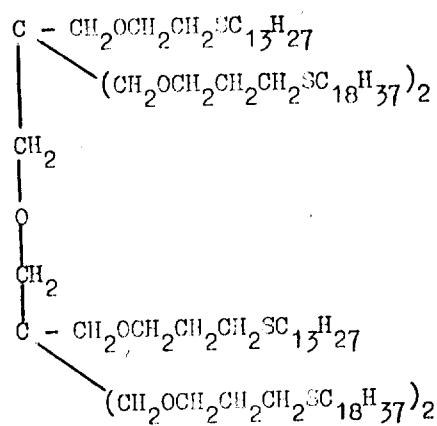


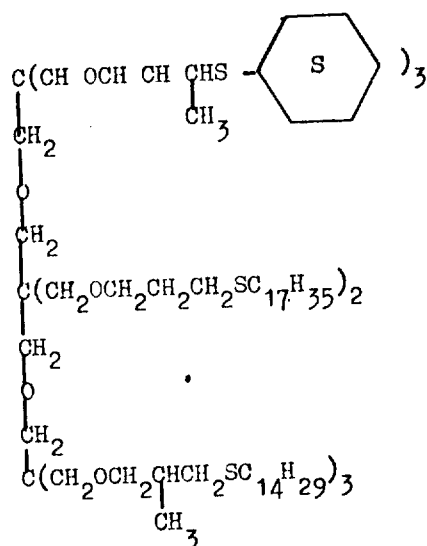
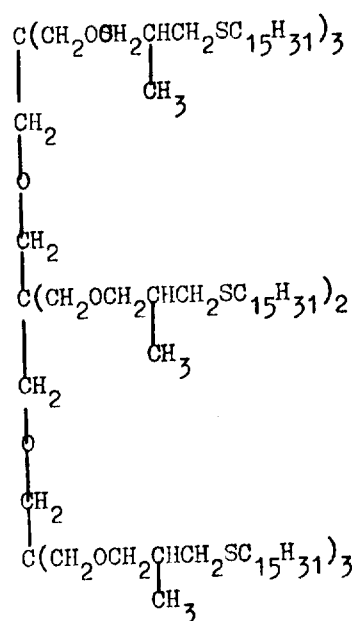
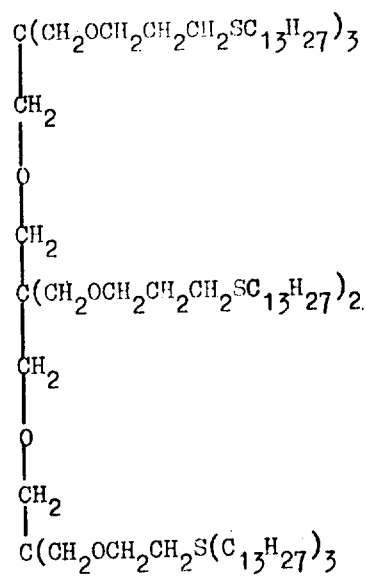


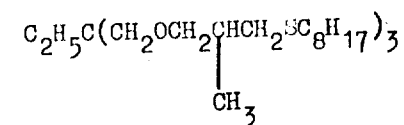
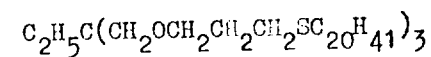
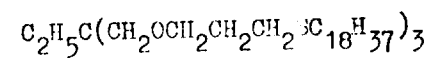
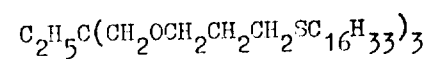
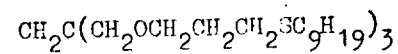
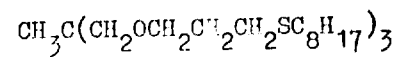
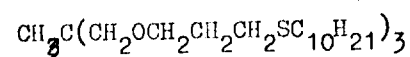
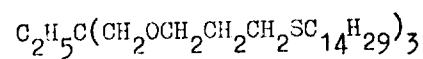
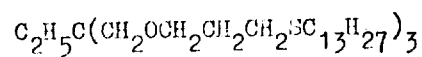
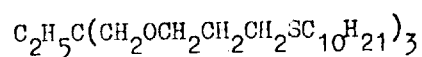
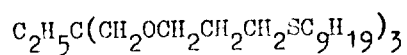
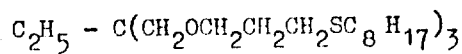


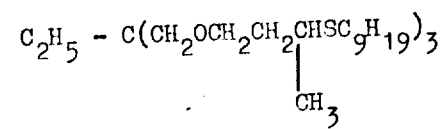
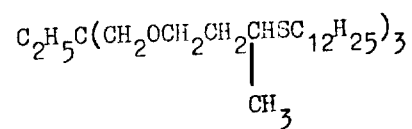
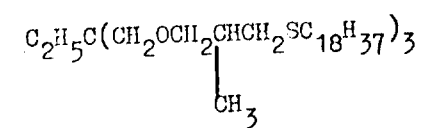
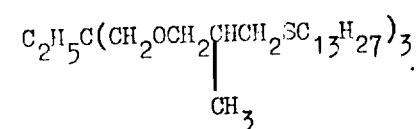
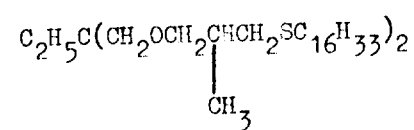
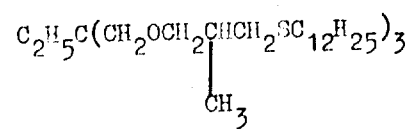
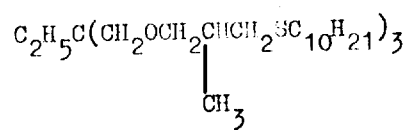


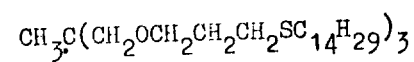
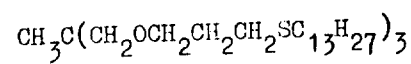
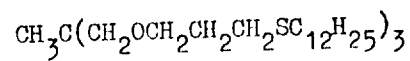
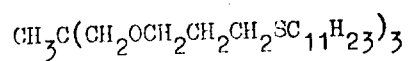
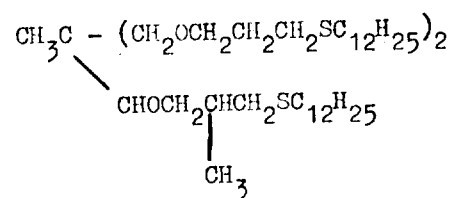
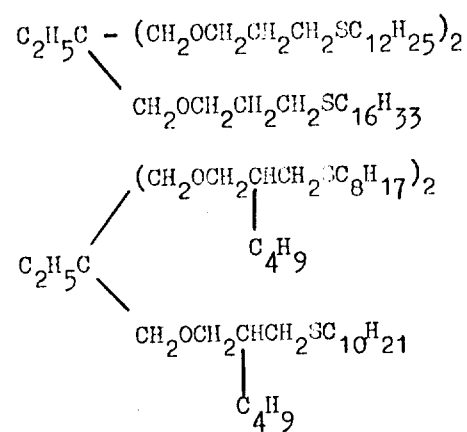
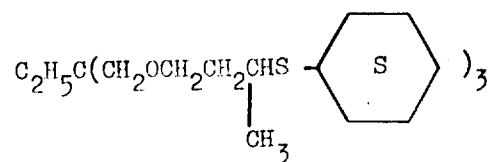
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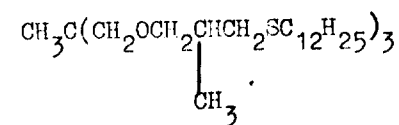
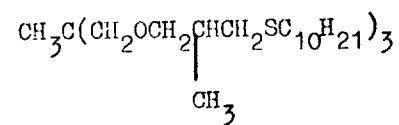
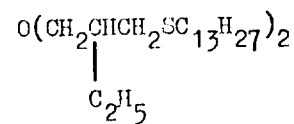
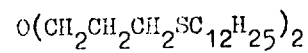
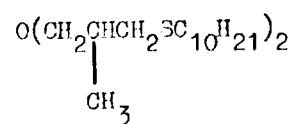
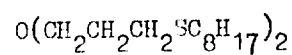
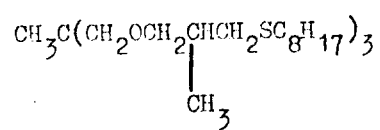
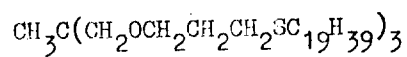
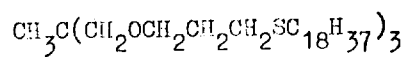
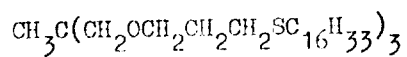


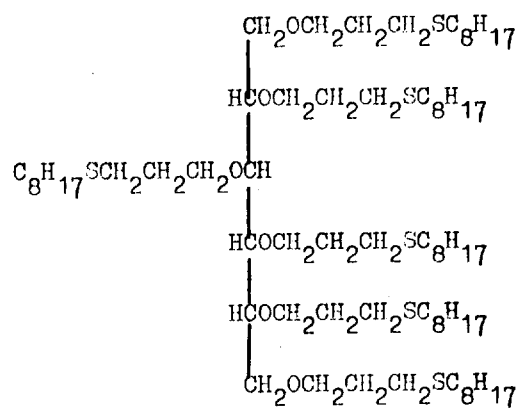
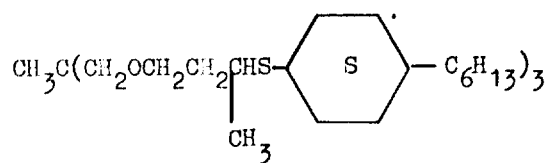
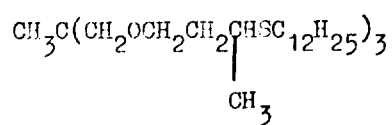
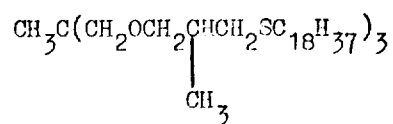
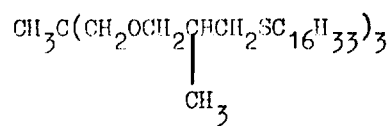


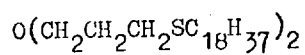
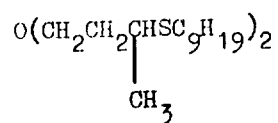
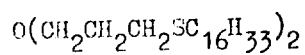
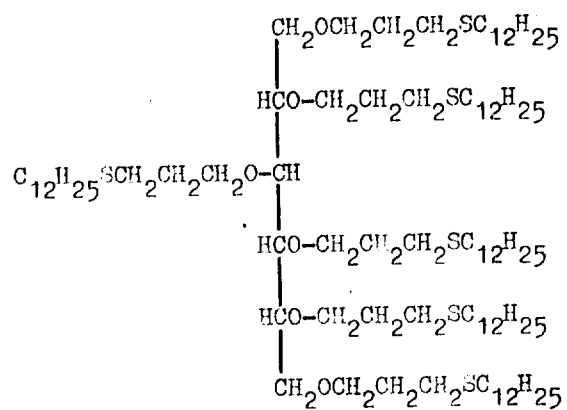
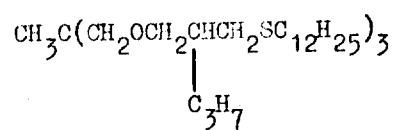
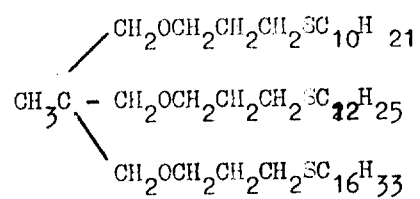


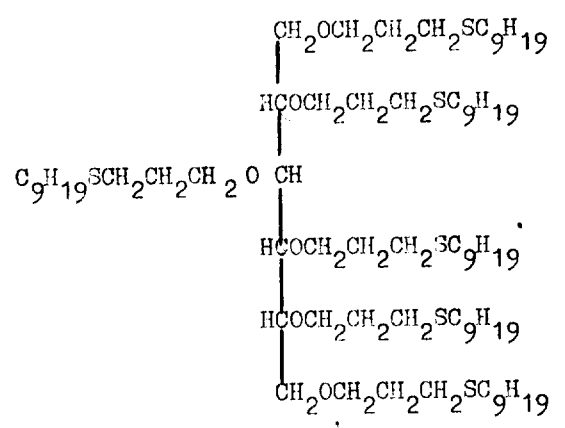
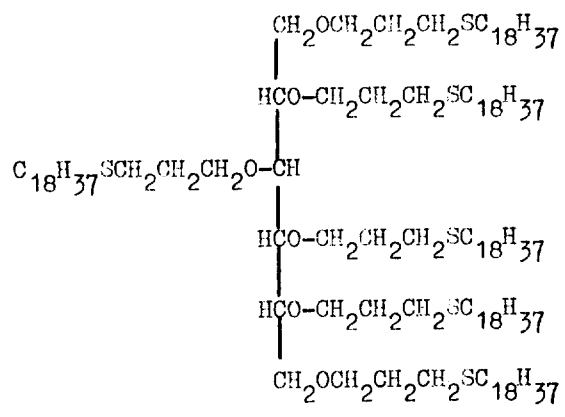
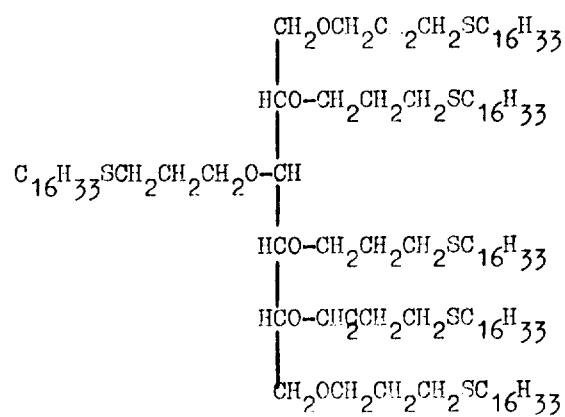


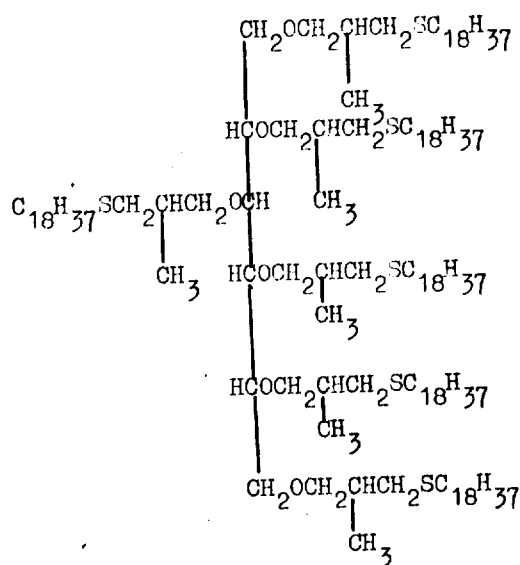
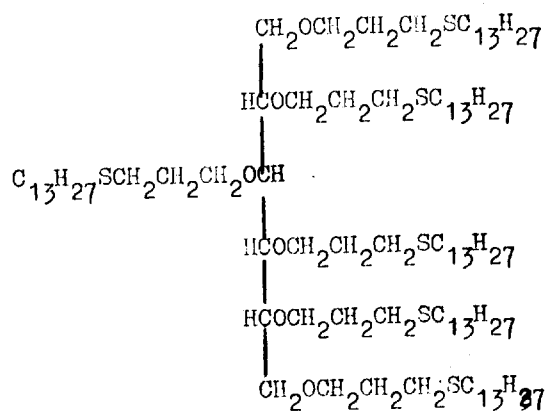
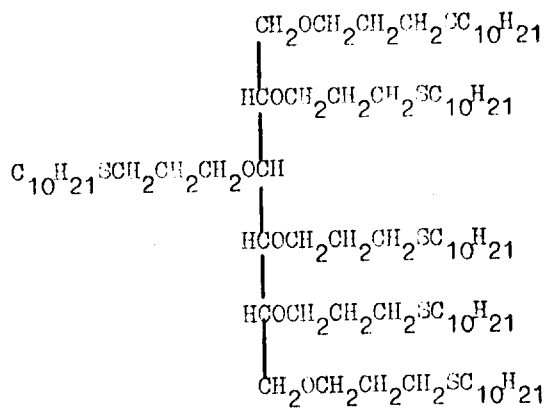


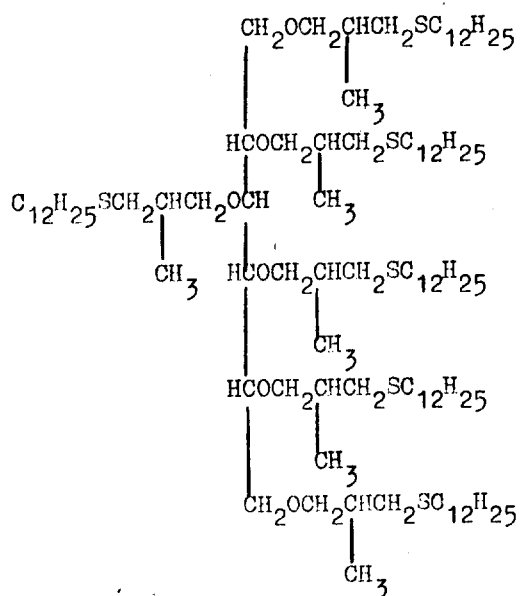
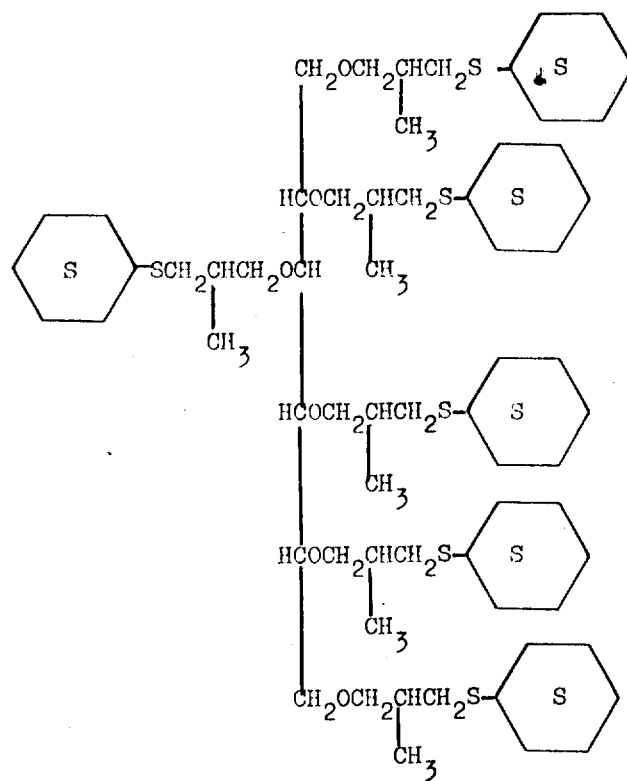


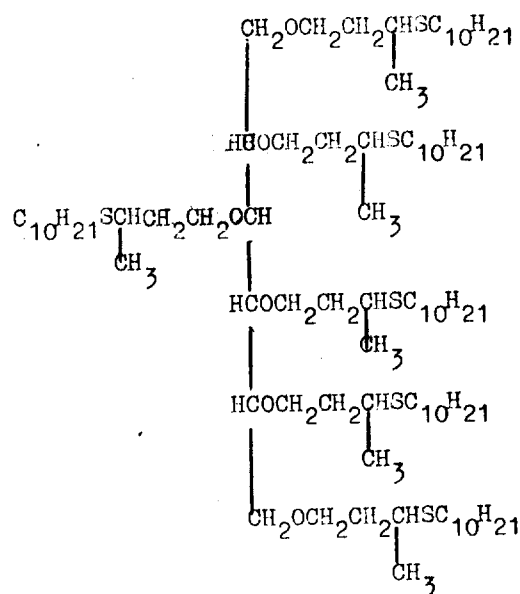
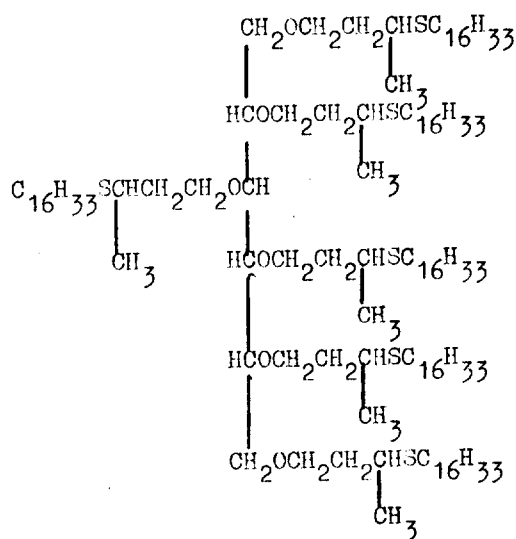
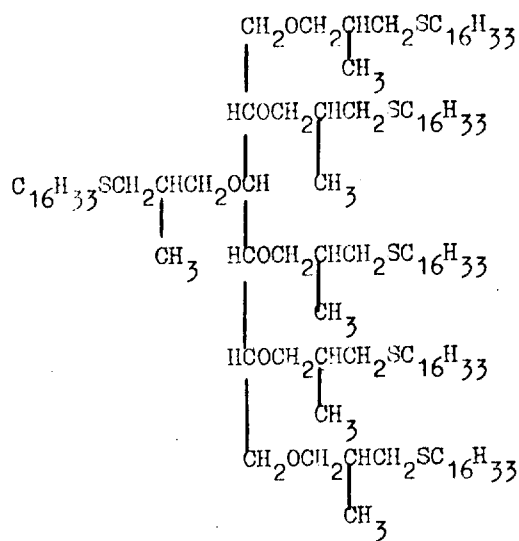


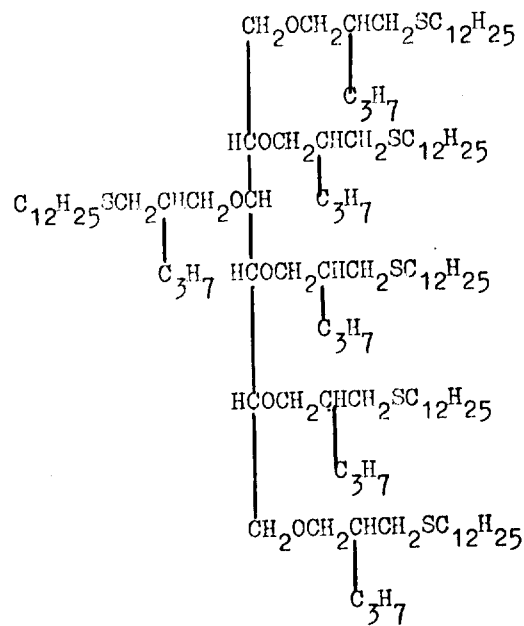
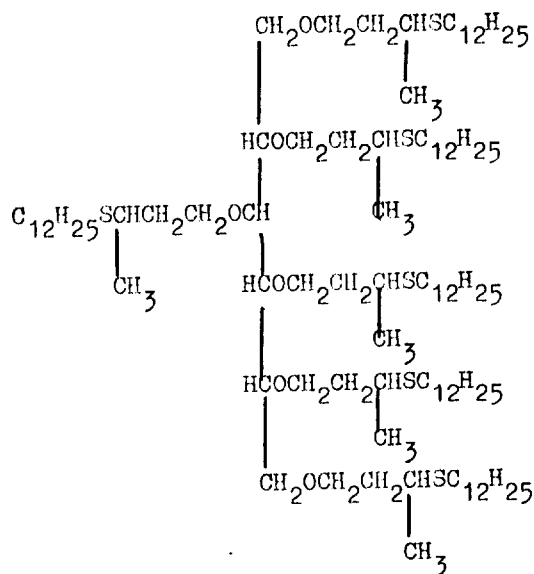






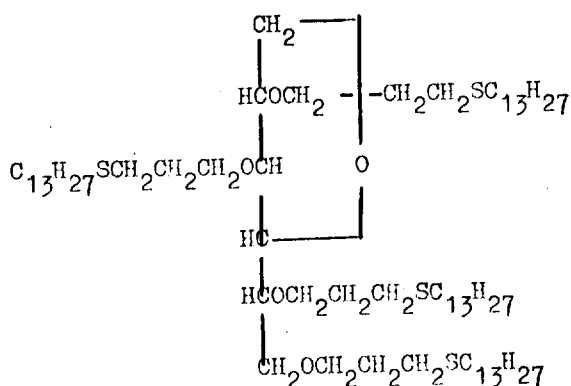
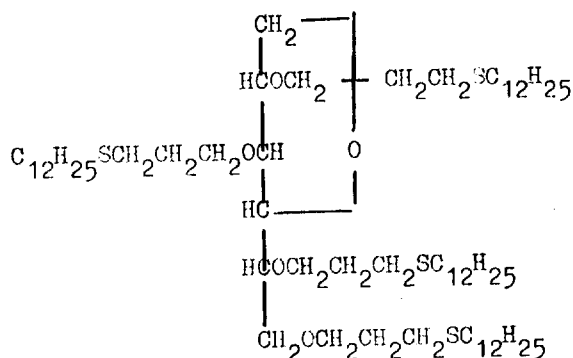


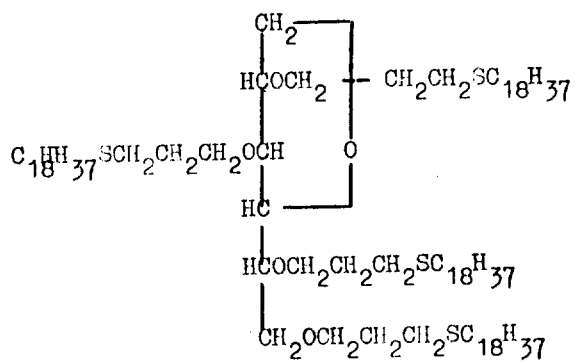
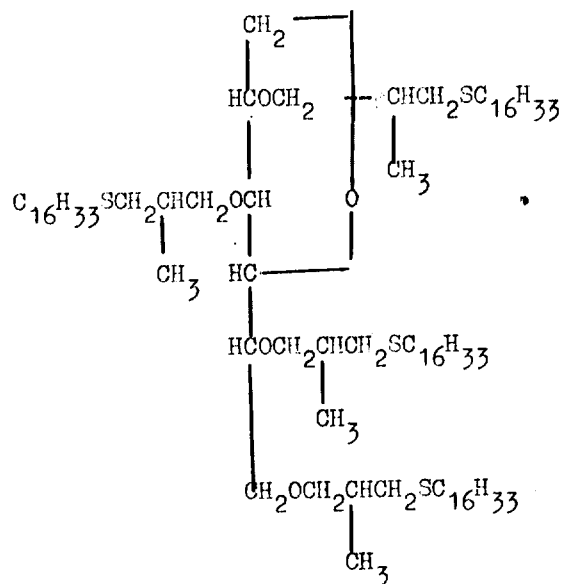
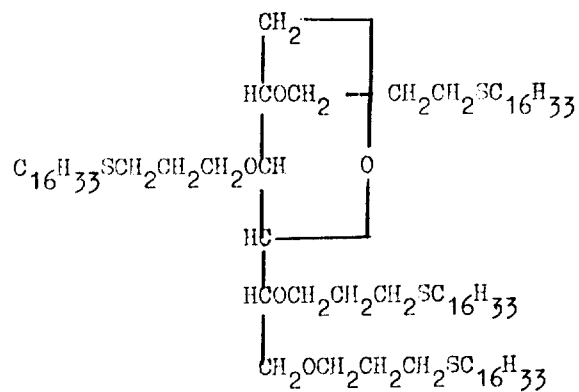


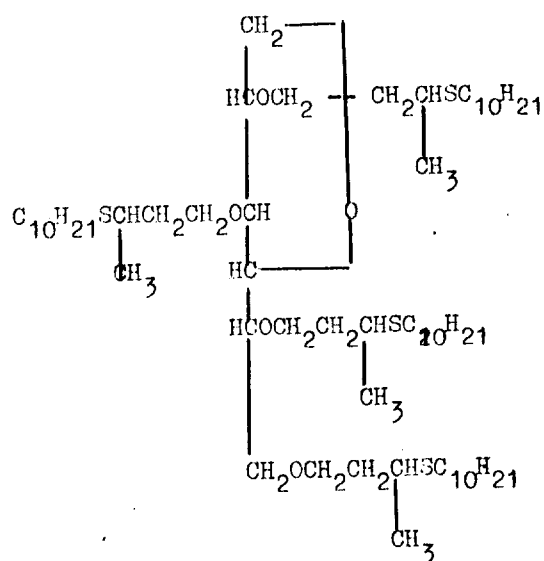
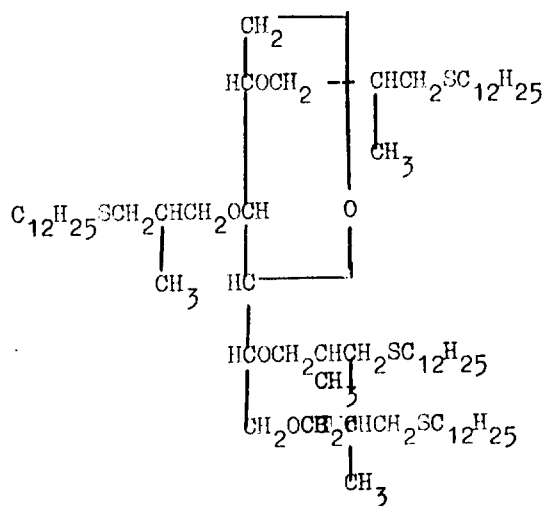
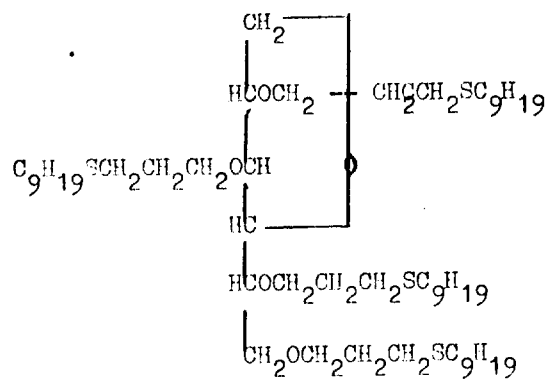


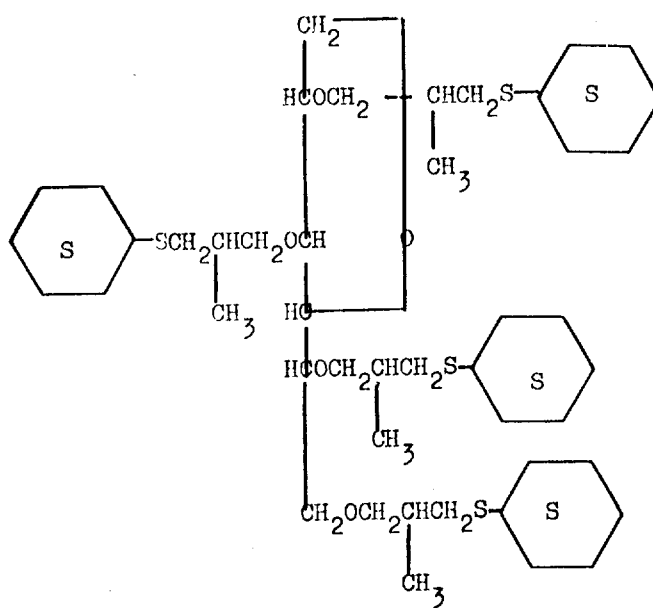
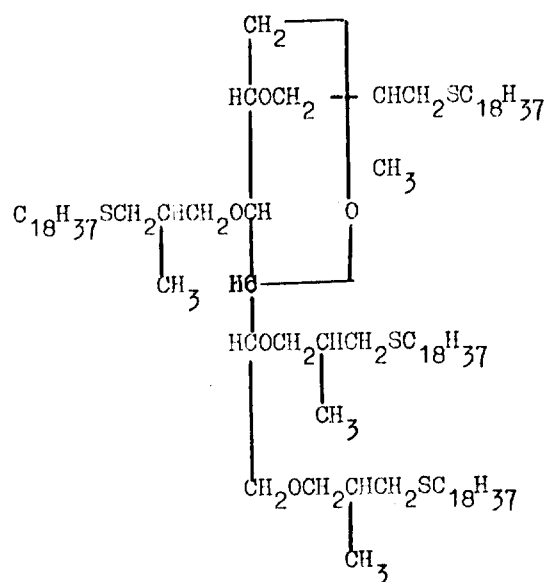
In the following non-limiting examples of representative structures for the organic sulfide antioxidants of the present invention, the sorbitan backbone shown is a

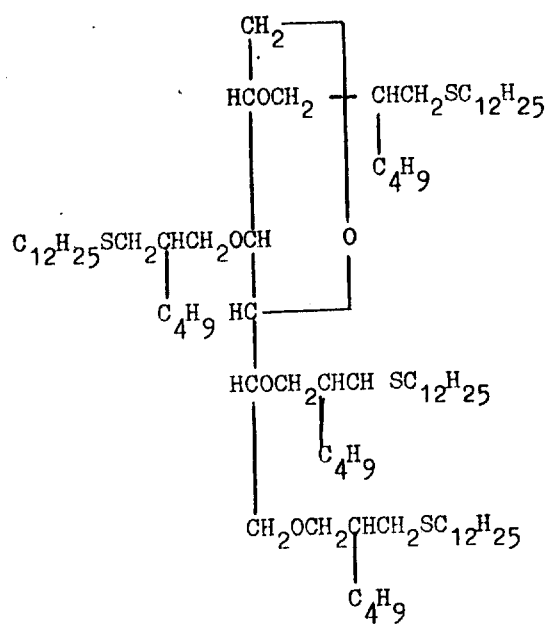
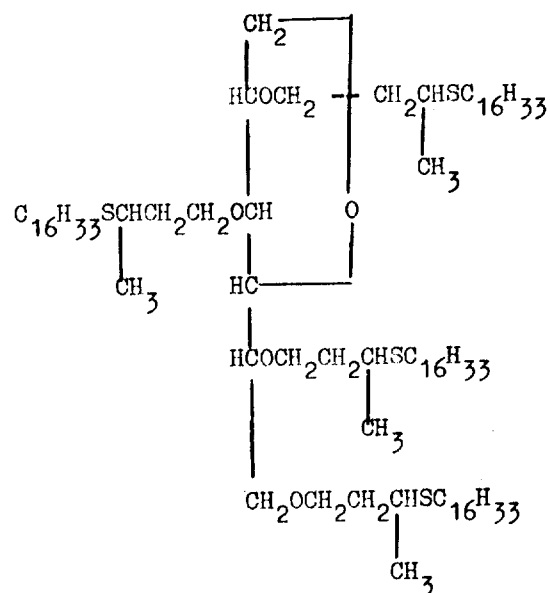
1,4-sorbitan, which comprises approximately 85% of the sorbitan conventionally used. Sorbitan also contains approximately 13% of 3,6-sorbitan and about 2% of 2,5-anhydro-L-~~iditol~~ (both isomers of 1,4-sorbitan). According to it will be understood by one skilled in the art that the organic sulfide antioxidants set forth below, which are derived from 1,4-sorbitan, also include those derived from 3,6-sorbitan and 2,5-anhydro-L-iditol.









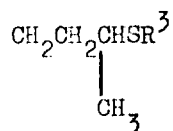


In the following non-limiting examples of representative organic sulfide antioxidants useful in the present invention which are derived from sucrose,

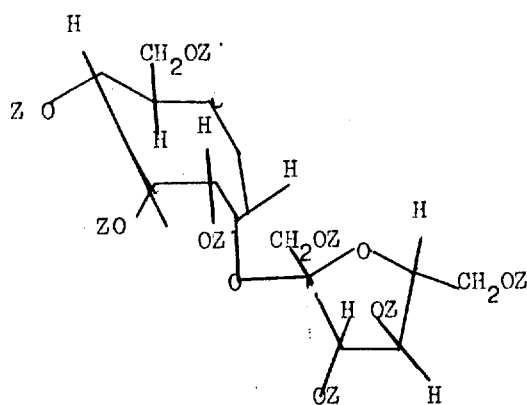
Z is $\text{CH}_2\text{CH}_2\text{CH}_2\text{SR}^3$; Z^1 is

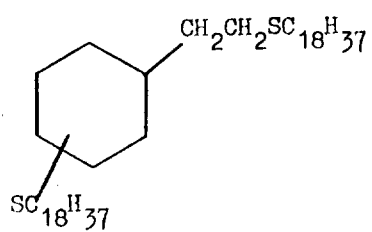
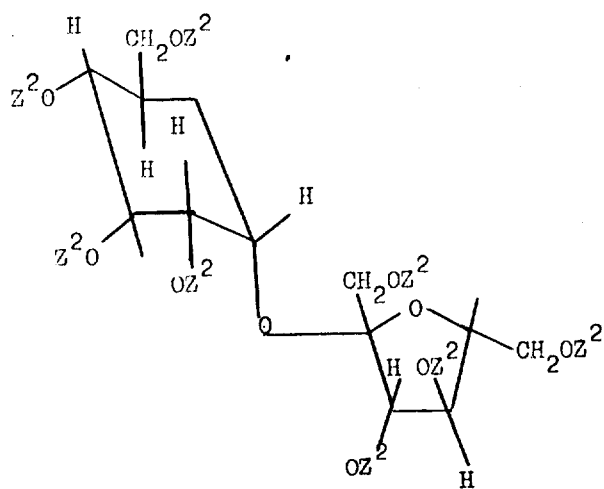
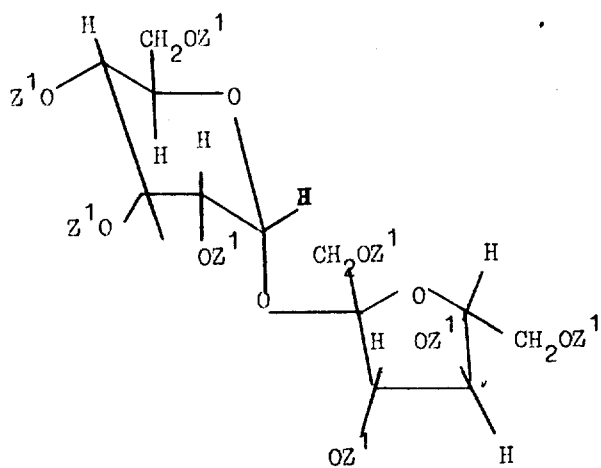


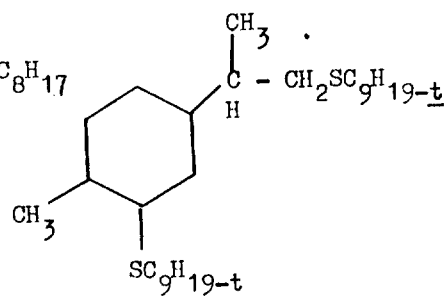
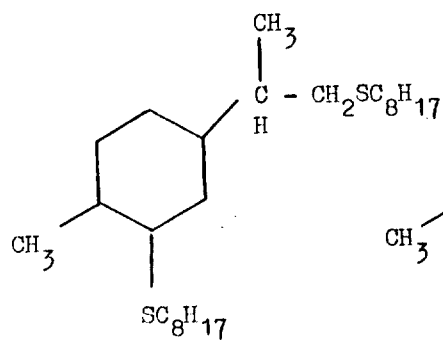
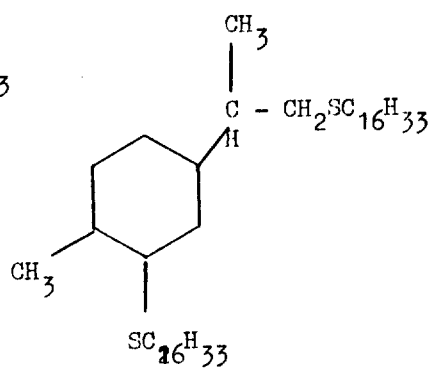
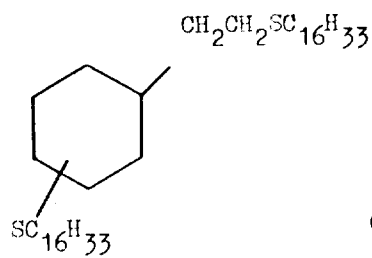
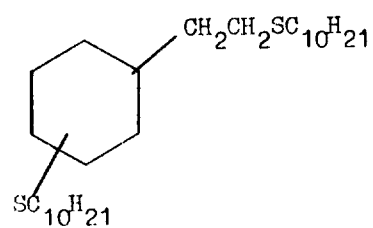
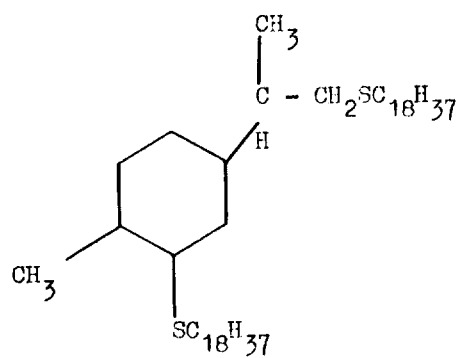
Z^2 is

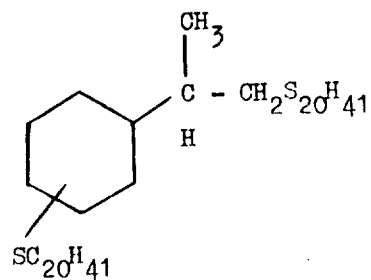
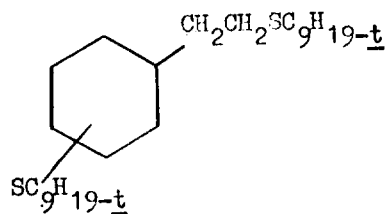
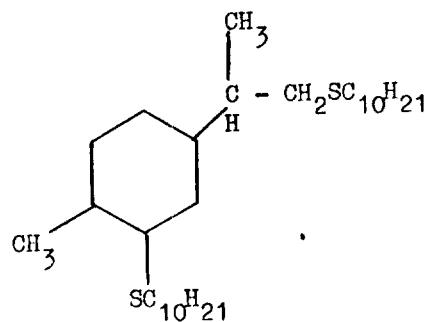
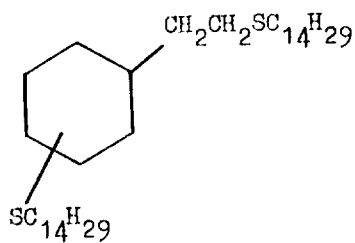
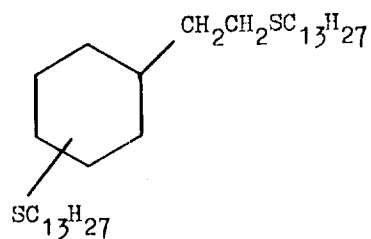
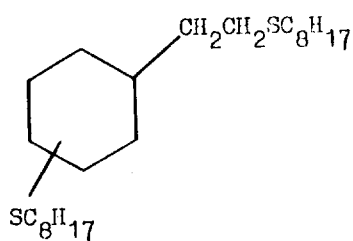
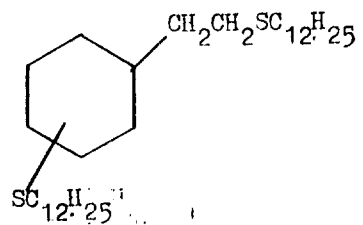
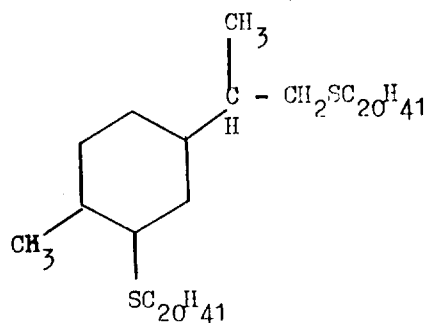


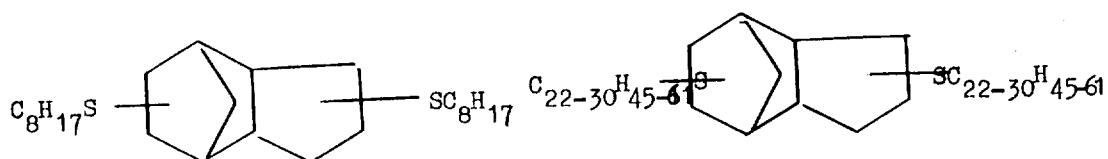
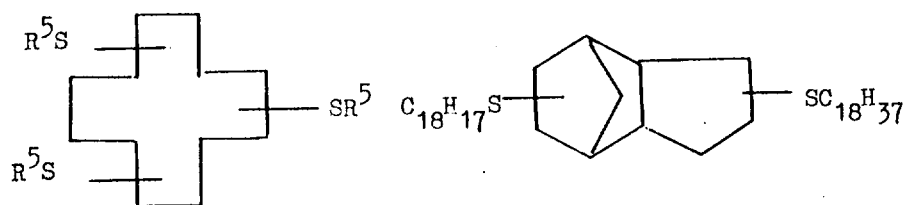
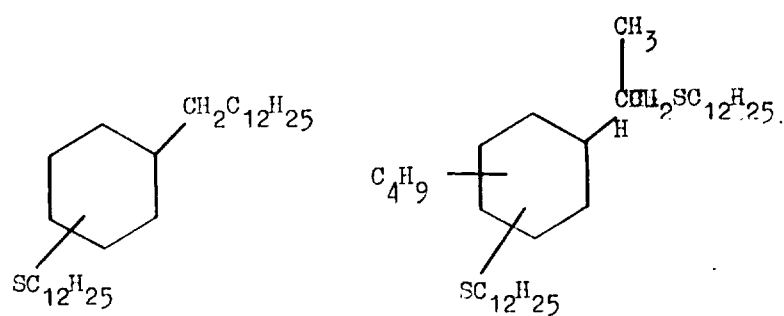
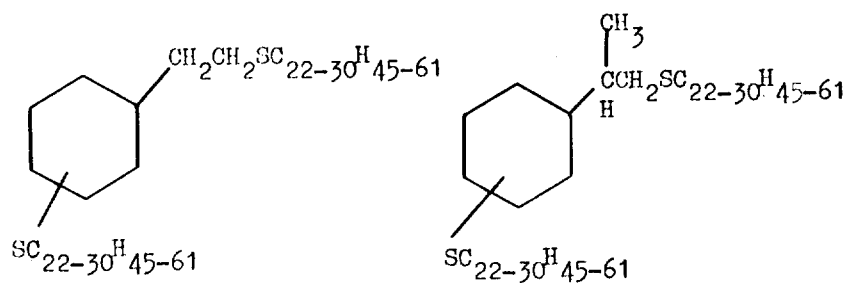
and R^3 is as defined above.

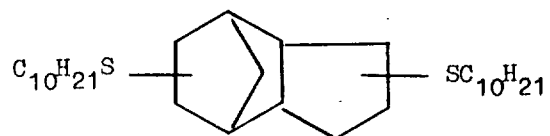
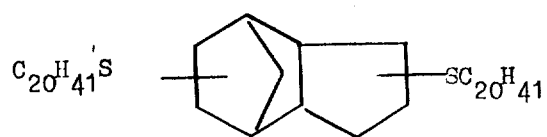
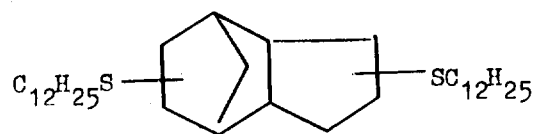
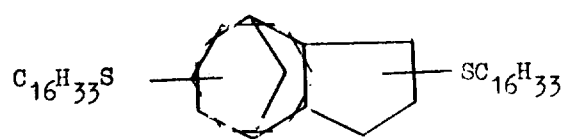
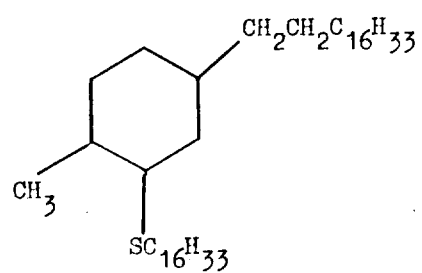
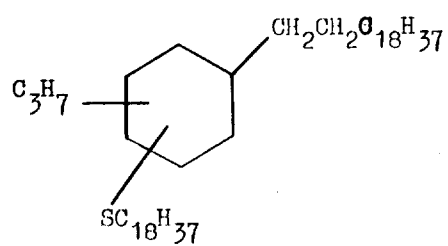
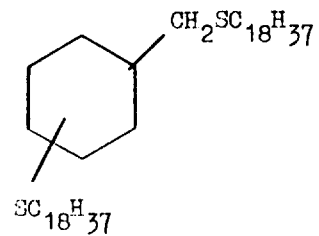
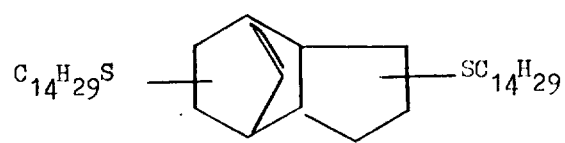


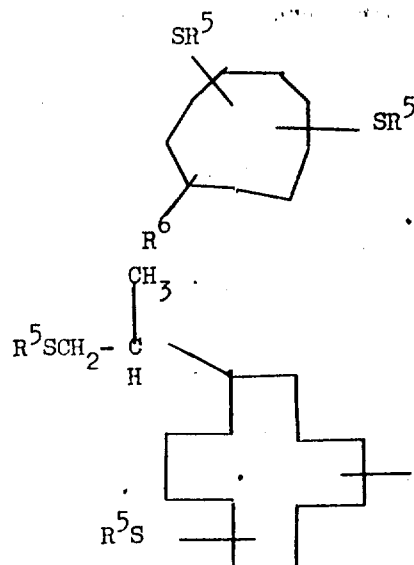
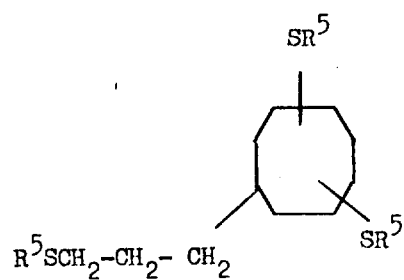
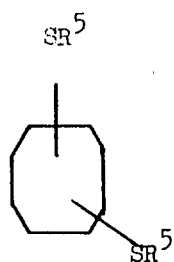
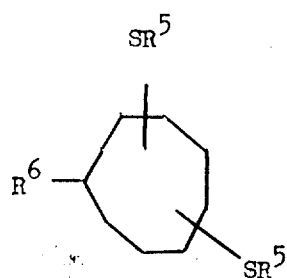
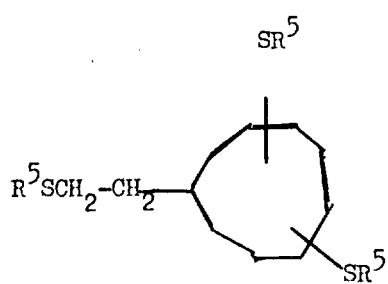
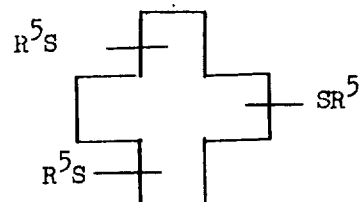
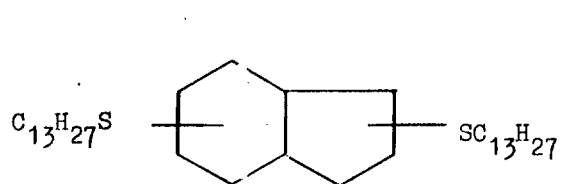


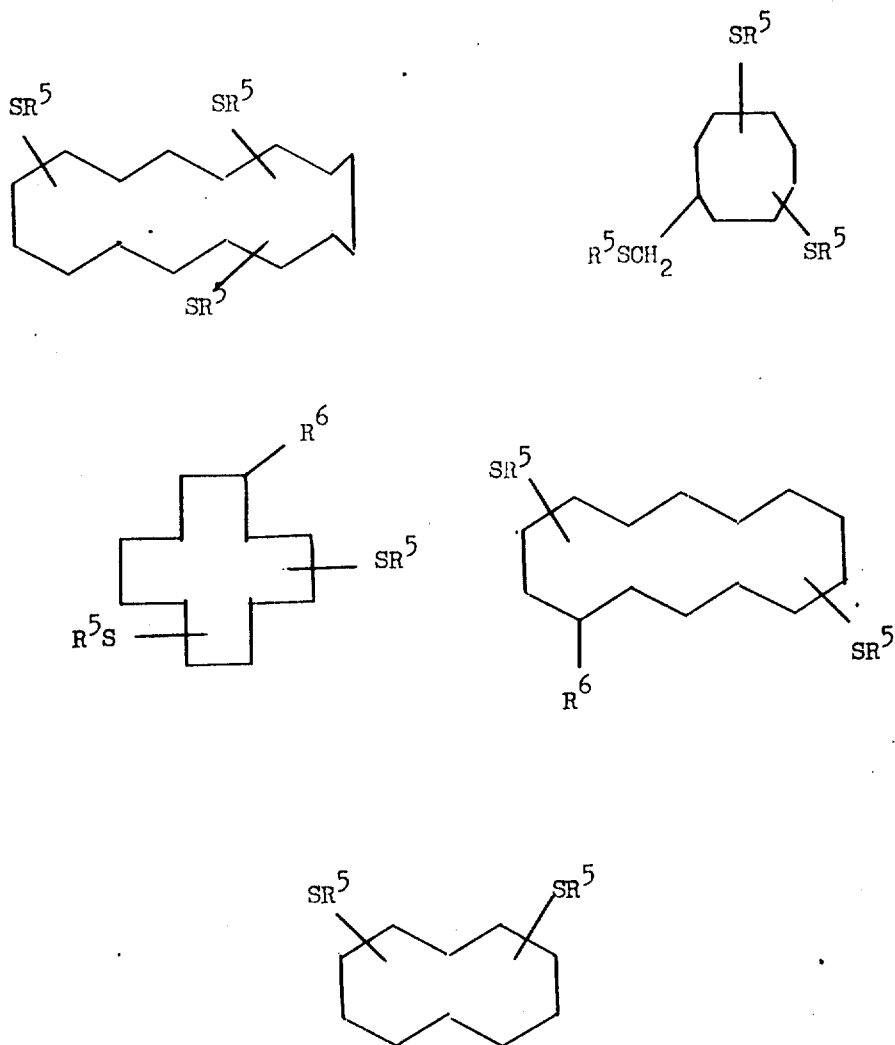






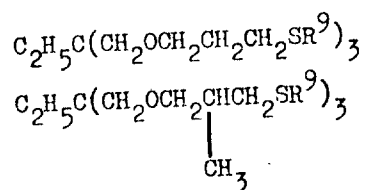
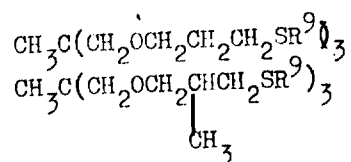
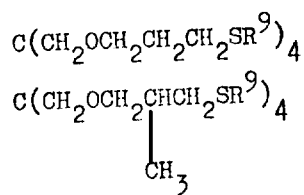
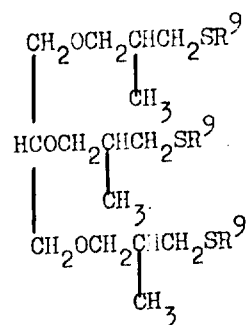
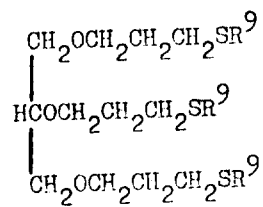


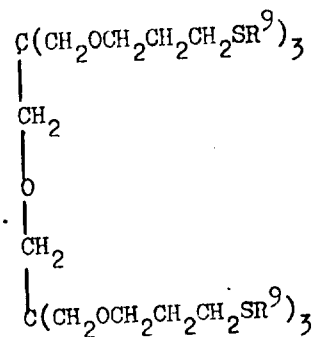
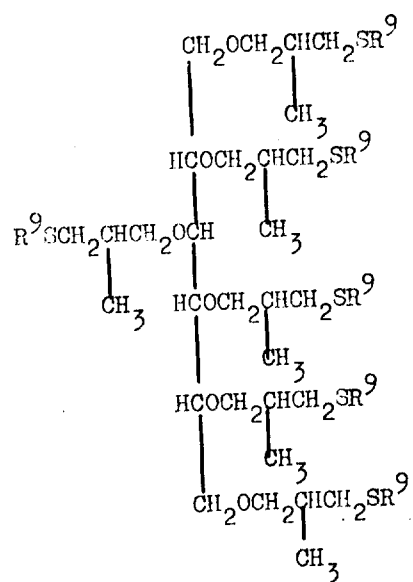
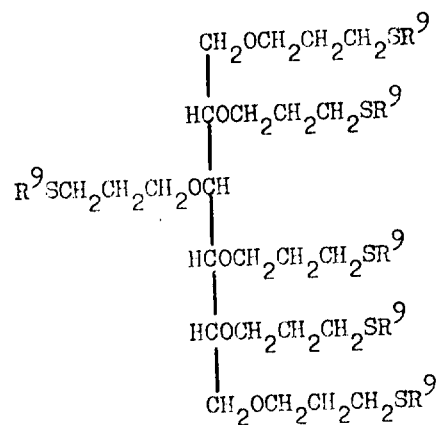


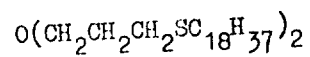
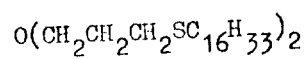
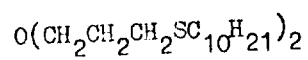
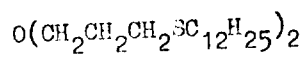
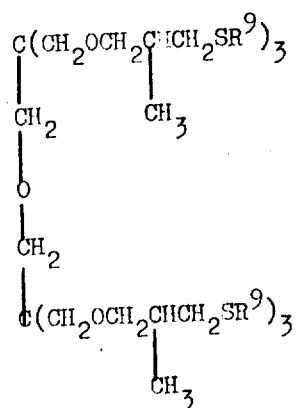
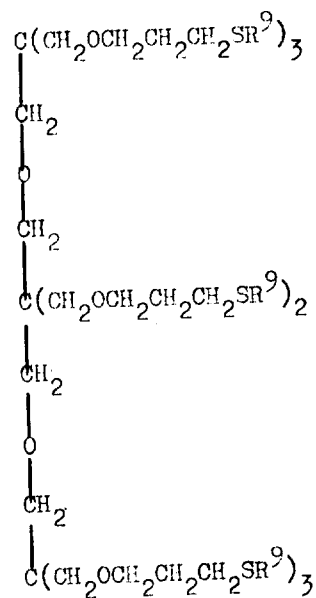


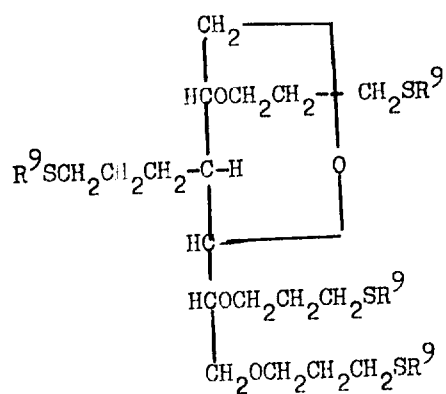
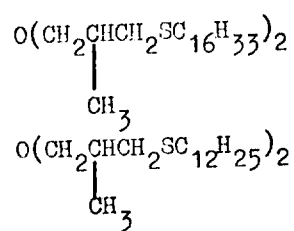
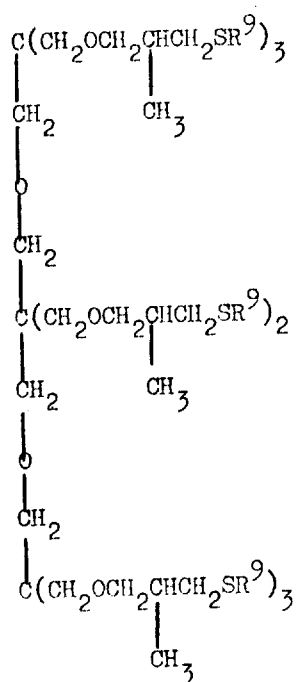
R^5 in the formulas set forth above represents an alkyl group of 8 to 24 carbon atoms and R^6 represents an alkyl group of 1 to 7 carbon atoms.

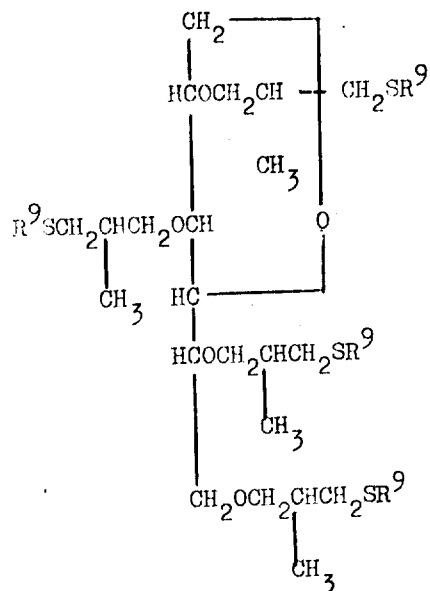
5 Non-limiting examples of preferred organic sulfide antioxidants useful in the present invention include, e.g.,



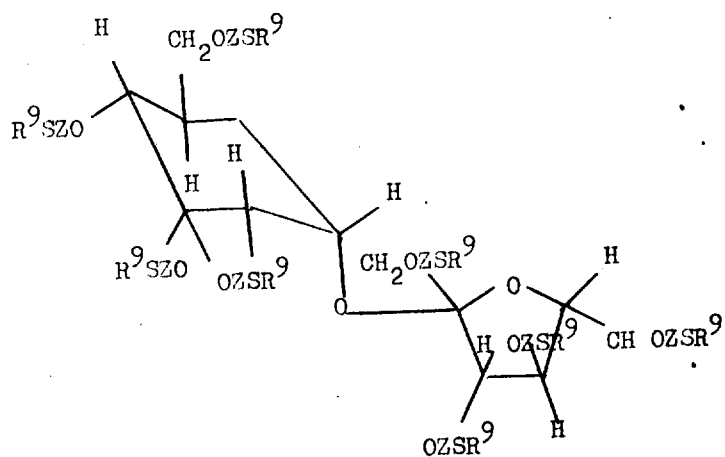


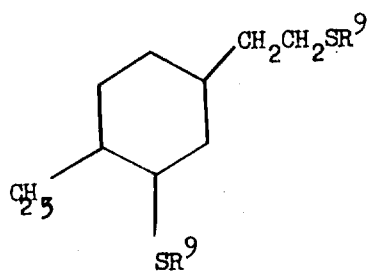
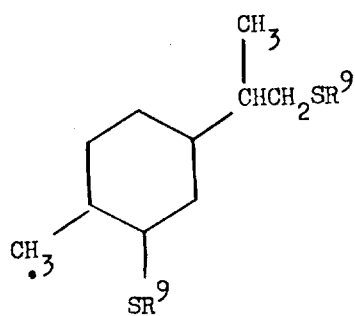
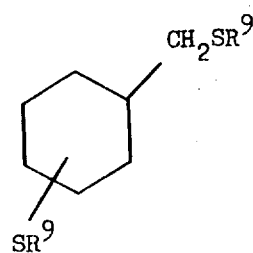
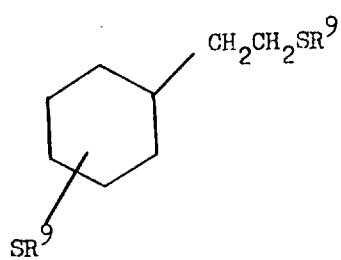
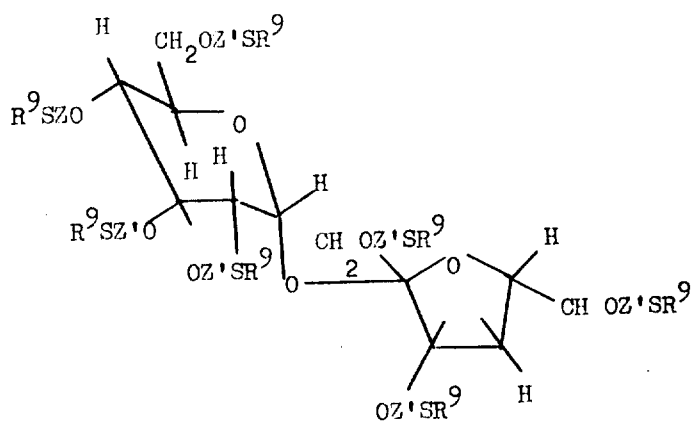


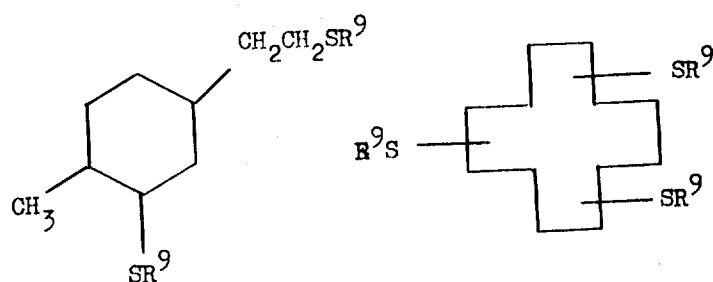
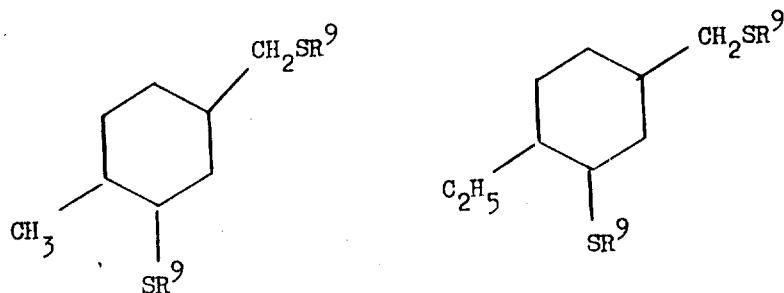
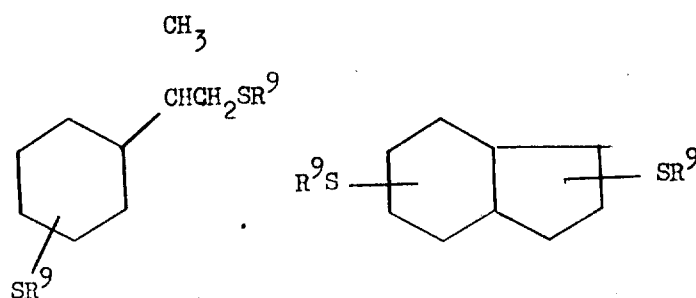




(plus other isomers of sorbitan)



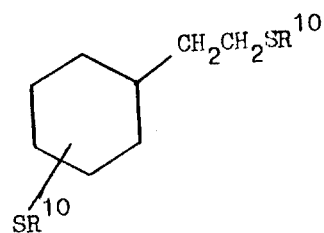
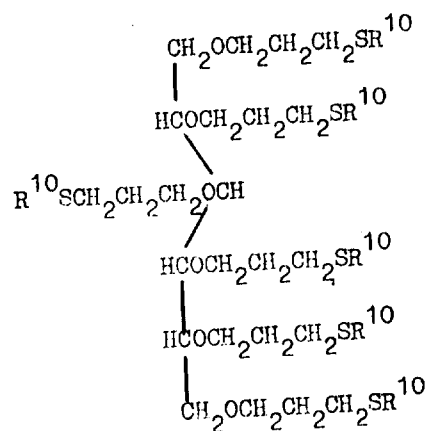
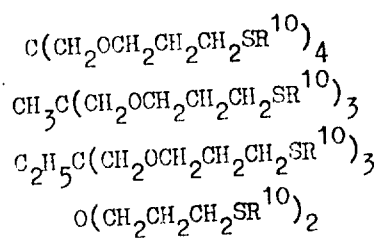
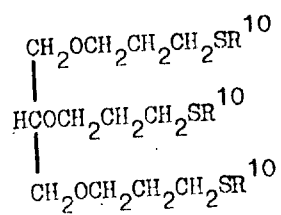


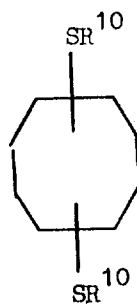
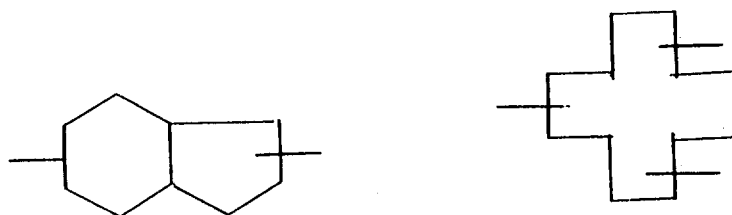
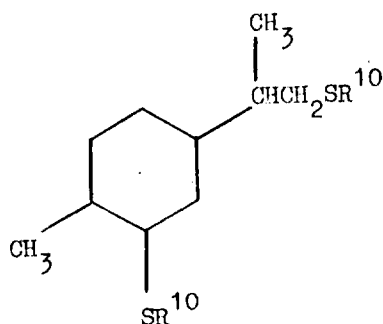


wherein R^9 represents an alkyl group of 10-18 carbons;
 R^6 is $-H$, $-CH_3$ or $-C_2H_5$ and Z ; and Z' are as defined above.

Non-limiting examples of the most preferred organic

sulfide antioxidants useful in the compositions of the present invention include, e.g.,





wherein R^{10} represents an alkyl group of 12-18 carbons.

Compounds of Formula I may be prepared, e.g., by first reacting a polypl (with two or more hydroxyl groups

per molecules) with an allylic or substituted allylic halide (chloride, bromide, or iodide) in the presence of a base, such as sodium or potassium hydroxide, for example. The amount
5 of base used should be an amount sufficient to remove by product hydrogen halide and to form the corresponding polyallylic ether. Water or an inert solvent may be used if necessary to facilitate the separation of the by-product
10 metal halide from the polyallytic ether.

Next, a mercaptan is added to the resultant polyallylic ether of the above reaction, under free radical conditions (i.e., in the presence of peroxides, azo compounds, ultra-violet
15 light, etc.), in order to form the antioxidant compounds of this invention. The number of moles of mercaptan employed in this reaction is an amount at least equal to the number of double bonds in the polyallylic ether.

20 Compounds of Formula II and III may be prepared by adding a mercaptan to either a diallyl ether or an olefin, respectively, by



the method described above for compounds represented by Formula I. Other appropriate methods for preparing compounds represented by Formula II or III of the present invention and
5 will be apparent to one skilled in the art based upon the present disclosure.

Non-limiting examples of preferred organic sulfide antioxidants useful in the present compositions include 2,9-bis(octadecylthio)-p-
10 menthane; beta(alkylthio)ethyl-3-(alkylthio)cyclohexane; beta(alkylthio)ethyl-4-(alkylthio)cyclohexane; beta(n-octadecylthio)ethyl-3-(n-octadecylthio)cyclohexane, beta(n-octadecylthio)ethyl-4-(n-octadecylthio)cyclohexane, which are all
15 usually prepared as a mixture of isomers and referred to hereinafter as "beta(alkylthio)ethyl-3 and 4-(alkylthio)cyclohexane", and equivalent terms;
20 1,5,9-tris(hexadecylthio)cyclododecane, 1,5,8-tris(hexadecylthio)cyclododecane, 1,4,8-

tria(hexadecylthio)cyclododecane, which are
 usually prepared as a mixture of isomers and
 referred to hereinafter as "1,4(or 5), 8(or 9)-
 tris(hexadecylthio)cyclododecane", and
 5 equivalent terms; 2,9-bis(alkylthio)-p-
 menthane; 3,3'-bis (alkylthiopropyl) ether;
 1,4,8-tris(alkylthio)cyclododecane; 1,5,8-
 tris(alkylthio)cyclododecane and 1,5,9-
 tris(alkylthio)cyclododecane, which are all
 10 usually prepared as a mixture of isomers and
 referred to hereinafter as "1,4(or 5), 8(or 9)-
 tris(alkylthio)cyclododecane" and equivalent
 terms; pentaerythritol tetrakis(n-
 octadecylthiopropyl) ether; pentaerythritol
 15 tris(n-octadecylthiopropyl) ether;
 pentaerythritol tetrakis(n-dodecylthiopropyl)
 ether; pentaerythritol tris(n-
 dodecylthiopropyl) ether; trimethylolpropane
 tris(n-octadecylthiopropyl) ether;
 20 trimethylolpropane tris(n-hexyldecylthiopropyl)
 ether; dipentaerythritol hexakis(n-
 dodecylthiopropyl) ether dipentaerythritol
 hexakis(n-hexadecylthiopropyl) ether. The

alkylthio group in each of the above classes of compounds contains about 2 to about 38 carbons and preferably, about 8 to about 20 carbons.

Polyolefin resins which may be crosslinked
5 with peroxide crosslinked inducing agents or high energy radiation and stabilized with the organic sulfide antioxidants of the present invention include, e.g., linear low density polyethylenes, low density polyethylenes, high
10 density polyethylenes, ethylene-propylene copolymers, ethylene-vinyl acetate copolymers, ethyleneacrylate ester copolymers, chlorosulfonated polyethylenes, polypropylenes, polybutene-1, polyisobutylenes, poly-4-
15 methylpentene-1, poly-methylbutene-1, poly-4,4-dimethylpentene-1, polydecene-1, polydodecene-1, ethylenepropylene-butadiene terpolymers, ethylene-propylenedicyclopentadiene terpolymers, polybutadiene, ethylene-
20 propylenenorbornadiene terpolymers, cis-1,4-polyisoprenes, styrene-butadiene copolymers, silicone rubbers, and mixtures thereof.

Preferred polyolefins resins useful in the present invention are those which contain ethylenes, such as low density polyethylenes, linear low density polyethylene and high
5 density polyethylenes, ethylene-propylene copolymers, ethylene-vinyl acetate, ethylene-acrylate ester copolymers, ethylene-propylene-butadiene terpolymers, ethylene-propylene-dicyclopentadiene terpolymers,
10 ethylene,propylene-norbornadiene terpolymers, chlorosulfonated opolyethylene and blends thereof.

The polyolefin resins useful in the present invention may be crosslinked through the
15 addition of peroxide crosslinking agents or by high doses of high energy radiation.

The appropriate peroxide crosslinking agents which may be used in the compositions of the present invention are any of those peroxide
20 crosslinking agents which are compatible with the organic sulfide antioxidants used in a

particular composition according to the present invention.

Exemplary of the peroxide crosslinking agents useful in the present composition are

5 di-t-butyl peroxide, dicumyl peroxide, benzoyl peroxide, t-butyl cumyl peroxide, 2,5-dimethyl-1,2,5-di(t-butylperoxy)hexyne-3, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, a , a- bis(t-butylperoxy)diisopropylbenzene, n-butyl-4,4-

10 bis(t-butylperoxy) valerate, 1,1-di(t-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-di(t-butylperoxy)cyclohexane, ethyl-3,3-di(t-butylperoxy)butyrate, 2,2-di(t-amylperoxy)propane, ethyl-3,3-di(t-amylperoxy)butyrate, as well as

15 t-alkyl; alkylcarbonate and benzoate diperoxy derivatives of 3-hexyne, 4-octyne, and 3,5-octadiyne. The use of additional peroxide crosslinking agents will be evident to one skilled in the art based on the present

20 disclosure.

Moreover, the polyolefin resins useful in the present compositions may be crosslinked by

subjecting the composition to the appropriate dose of high energy radiation, such as electron beam radiation, gamma radiation, ultraviolet radiation, microwave radiation, etc. Other
5 types of high energy radiation which may be
b types of high energy radiation which may be useful to crosslink the polyolefin resin compositions of the present invention will be evident to one of ordinary skill in the art based upon the present disclosure.

10 The compositions of the present invention may further comprise auxiliary antioxidants in synergistic combination with the organic sulfide antioxidants. For example, phosphite, phenolic and arylamine antioxidants may be
15 added to the present compositions in order to provide enhanced antioxidant and stabilizing effects.

Moreover, additives, such as talc, metal deactivators, calcium carbonate, calcium
20 sterate, UV stabilizers (e.g., benzophenones, salicylic acid esters, hindered amines and

benzotriazoles), etc., may also optionally be included in the compositions of the present invention. Other additives which may be included in the present compositions will be
5 evident to one of ordinary skill in the art based upon the present disclosure.

In the compositions according to the present invention, the organic sulfide antioxidants are contained in a weight ratio of
10 about 1:10,000 to about 1:20, and preferably about 1:2,000 to about 7:1,000 (organic sulfide antioxidant to polyolefin resin). If used, the auxiliary antioxidant may be contained in the present compositions in a weight ratio of about
15 10:1 to 1:10 and preferably, about 1:2 to about 1:4 (auxiliary antioxidant to organic sulfide antioxidant). The weight ratio of the peroxide crosslinking agent to the organic sulfide antioxidant is from about 100:1 to about 1:100
20 and preferably, about 50:1 to about 5:1.

The present compositions may be prepared in any manner generally known to those skilled in

the art. For example, the polyolefin resins may be crosslinked with either peroxide crosslinking agents or high energy radiation. The organic sulfide antioxidants may be added to the polyolefin resins prior to crosslinking in any conventional manner, such as by blending, extruding, kneading etc., known in the art in order to produce compositions which are uniform in their constitution.

10 If an auxiliary antioxidant, such as a known phenolic antioxidant or arylamine antioxidant, is to be added to the polyolefin resin, it will be added at the same time as the organic sulfide antioxidant. Other additives, 15 such as talc, metal deactivators, calcium carbonate, calcium stearate, etc., may also be added to the composition at this point.

Although the method for the preparations of the present compositions is not limited, 20 generally, the peroxide crosslinking agent, if used, is added to the polymeric resin after the

addition of the other ingredients. Likewise,
if the resin is to be crosslinked with a high
energy radiation, the resin will be subjected
to the high energy radiation after the addition
5 of the ingredients. Other appropriate methods
for preparing the present compositions will be
evident to one skilled in the art based upon
the present disclosure.

The present invention will now be
10 illustrated in more detail by reference to the
following examples.

EXAMPLES 1-6

In the following examples, the improvement
in the oxidative and thermal stability of
15 crosslinked low density polyethylene due to
presence of the organic sulfide antioxidants of
this invention are demonstrated.

The compositions were prepared in the
following manner. The bowl of a Brabender

Torque Rheometer was preheated to 125°C, and the mixing blades were set to rotate at 50 to 60 rpm. The resin was added first and maintained at 125°C, until it fluxed (approximately five minutes). The organic sulfide antioxidant and the auxiliary phenolic antioxidant, as well as the calcium stearate additive, were then added to the resin simultaneously and mixed for an additional five minutes. The dicumyl peroxide crosslinking agent was then added to the mixture. This resulting mixture was further mixed for an additional five minutes for a total mixing time of 15 minutes. During this period, the bowl temperature was maintained at a temperature of no higher than 145°C.

The resultant polymer blends were then pressed into plaques in a cold press for three minutes at 30,000 psi. These plaques were then crosslinked by placing them into a heated Carver Press for five minutes at 120°C, and 150 psi. The pressure was then raised to 20,000

psi for two minutes and the temperature was raised to 175°C. This temperature and pressure were maintained for 15 minutes. The plaques were then cut into Tensile Bars in accordance with ASTM Procedure No. 4. The tensile bars were suspended in-a forced air oven at 150°C.

Every seven days, the samples were removed from the oven for a determination of the tensile strength and percent elongation according to the ASTM D638 test procedure. The tests were continued for 21 days or until either the tensile strength or percent elongation of the specimens reached 50% of its original value, at which time the samples were considered to have "failed". In the Tables below the "% Tensile Strength" is defined as follows:

$$\frac{(\text{Tensile Strength})_x}{(\text{Tensile Strength})_o} \times 100$$

wherein (Tensile Strength)_x is the tensile strength of the sample after "x" days in the 150°C. oven and (Tensile Strength)₀ is the initial tensile strength before the samples were oven-aged (i.e., day zero).

In a similar manner, the "% (% Elongation)" is defined as follows:

$$\frac{(\% \text{ Elongation})_x}{(\% \text{ Elongation})_0} \times 100$$

wherein (% Elongation)_x is the % elongation of the sample after "x" days in the 150°C. oven and (% Elongation)₀ is the initial % elongation before the samples were oven-aged (i.e., day zero).

In Examples 1 to 6, the following materials were used:

LDPE - Low Density Polyethylene

CaSt - Calcium Stearate

PAO-1 - Phenolic Antioxidant

- PAO-2 - Phenolic Antioxidant
OTEOTC - beta-(octadecylthio)ethyl-3(4)-
octadecylthiocyclohexane
DSTDP - Distearyl Thiodipropionate
5 DICUP - Dicumyl Peroxide
MD - Meal Deactivator

The results set forth in Table 1 demonstrate the improved oxidative and thermal stability of the crosslinked low density
10 polyethylene compositions containing the organic sulfide antioxidants of the present invention as compared to those containing the conventional sulfide antioxidant, DSTDP, regardless of which primary phenolic
15 antioxidant was used.

A comparison of Example 1 vs. Example 1 and Example 3 vs. Example 4 demonstrate that the compositions containing the compounds of the instant invention, OTEOTC, did not fail until
20 21 days of oven-aging. In contrast, corresponding compositions containing the

conventional sulfide antioxidant failed after
14 days. In addition, in a comparison of
Example 5 vs. Example 6, wherein both the
compositions containing DSTDP and OTEOTC failed
5 after 21 days, the composition containing the
present antioxidant (Example 6) failed only the
% (% Elongation), whereas the corresponding
DSTDP composition (Example 5) failed both thr %
Tensile Strength and the % (%Elongation) tests.

TABLE 1

Example No	1	2	3	4	5	6
LDPE ^(a)	98.55	98.55	97.8	97.8	98.55	98.55
PAO-1 ^(b)	0.2	0.2				
PAO-2 ^(c)			0.2	0.2	0.2	0.2
CaSt	0.1	0.1	0.1	0.1	0.1	0.1
DSDP	0.4		0.4		0.4	
OTEOTC		0.4		0.4		0.4
DicuP ^(d)	0.75	0.75	1.5	1.5	0.75	0.75
0 Days						
Tensile Strength (psi) ^(e)	2740	2340	1460	1350	2500	1900
% Elongation	1060	876	492	428	1146	784
7 Days						
Tensile Strength (psi) ^(e)	1740	2610	2340	2000	2730	2870
%Tensile Strength	78	112	160	154	106	210

TABLE 1 -continued

Example No	1	2	3	4	5	6
% Elongation	614	1010	724	684	1110	1152
X (% Elongation)	58	113	148	160	97	147
14 Days						
Tensile Strength (psi) ^(e)	680	1830	840	1250	1580	2250
X Tensile Strength	Failed	78	58	93	61	114
X Elongation	31	629	71	234	612	920
X (% Elongation)	Failed	70	Failed	55	53	117
21 Days						
Tensile Strength (psi) ^(e)	-	950	-	870	520	990
X Tensile Strength	-	Failed	-	65	Failed	61
X Elongation	-	41	-	61	48	50
X (% Elongation)	-	Failed	-	Failed	Failed	Failed

(a) Union Carbide Corp's DYNA (R) - 1

(b) Ciba-Geigy's Irganox (R) 1010

(c) Ciba-Geigy's Irganox (R) 1035

(d) Lucidol Division of Pennwalt Corp's Lupersol (R) 500R

(e) At break

EXAMPLES 7-18

In Examples 7-18, the improvement in the oxidative and thermal stability of crosslinked, low density polyethylene containing a metal deactivator through the incorporation of the compounds of the present invention are demonstrated.

The preparation of Examples 7-18 is the same as that described for Examples 1-6 above. In addition, a metal deactivator was added to the mixture simultaneously with the antioxidants and calcium stearate.

The results set forth in Table II further demonstrate the improved oxidative and thermal stability of the crosslinked low density polyethylene compositions containing the organic sulfide antioxidants of the present invention as compared to those containing conventional sulfide antioxidants, i.e., DSTDP.

A comparison of Example 7 vs. Example 8 and

Example 9 vs. Example 10, demonstrates that the compositions according to the instant-invention containing the present organic sulfide antioxidants did not fail until 21 days of
5 oven-aging, while those containing the conventional sulfide antioxidant failed after 14 days.

Moreover, the 14-day sample containing the DSTDP (i.e., Example 9) was discolored. Such
10 discoloration is a drawback in commercial situation wherein color retention is an important consideration.

Although both Examples 11 and 12 (containing DSTDP and OTEOTC, respectively)
15 failed after 21 days, the samples containing the DSTDP were discolored while those containing the antioxidants of the present invention were not. Also, the samples containing the sulfide antioxidant of the
20 instant invention had generally higher % Tensile Strength and %(% Elongation) values.

Examples 14 did not fail even after 21 days, in contrast to Example 13 which failed at 21 days.

5 In Examples 15 through 18, none of the compositions failed at 21 days. However, those containing the compound of this invention (i.e., Examples 16 and 18) had significantly higher % TensileStrength and % (% Elongation) values.

TABLE II

Example No	7	8	9	10	11	12	13	14	15	16	17	18
LDPE (a)	97.8	97.8	97.3	97.8	97.7	97.7	97.7	98.45	98.45	98.45	98.45	98.45
PAO-1(b)	0.2	0.2					0.2	0.2	0.2	0.2		
PAO-2(c)			0.2	0.2	0.2	0.2				0.2	0.2	
Cast	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
HD(d)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
DSTD	0.3		0.3		0.4	0.4	0.4		0.3		0.4	
OTB07C		0.3		0.3		0.4		0.4		0.3		0.4
DICUP(e)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	0.75	0.75	0.75	0.75
0 Days												
Tensile Strength (psi)(f)	1140	1130	1060	1130	1060	1030	1030	1150	1110	1070	1090	1090
% Elongation	182	184	147	196	124	147	130	168	181	162	237	184
7 Days												
Tensile Strength (psi)(f)	1650	2150	1810	1990	1670(f)	2170	2030	2160	2110	2180	2200	2290
% Tensile Strength	145	190	171	176	158	211	186	188	190	204	202	210
% Elongation	533	800	712	706	627	777	186	832	950	833	1036	978
% (% Elongation)	293	435	484	360	506	529	617	495	525	514	437	532
14 Days												

TABLE II- continued

Sample No	7	8	-	9	10	11	12	13	14	15	16	17	18
Tensile Strength (psi) ^(f)	570	1800		390 ^(f)	1020	1030	1870	1270	2230	2190	1970	2100	1990
% Tensile Strength	50	166		31	90	98	177	117	194	198	184	193	183
% Elongation	44	670		66	144	137	732	290	820	981	778	932	795
% (% Elongation)	Failed	364		Failed	73	159	498	223	488	542	480	393	432
21 Days													
Tensile Strength (psi) ^(f)	-	710	-	-	660	660	920	760	1030	1000	1320	1340	2010
% Tensile Strength	-	63	-	-	58	62	89	70	90	90	170	169	184
% Elongation	-	40	-	-	30	58	68	55	164	203	648	866	862
% (% Elongation)	-	Failed	-	Failed	Failed	Failed	Failed	Failed	93	112	400	365	468

(a) Union Carbide Corp's DYNA (R) - 1

(b) Ciba-Geigy's Irganox (R) 1010

(c) Ciba-Geigy's Irganox (R) 1035

(d) Ciba-Geigy's MD 1024 (R)

(e) Lucidol Division of Pennwalt Corp's Lupersol (R) 500R

(f) At break

EXAMPLES 19-28

In Examples 19-28, improvements are demonstrated in the oxidative and thermal stability of crosslinked ethylene-vinyl acetate (82:18) copolymers (EVA) due to the incorporation therein of the organic sulfide antioxidant compounds of the present invention. The preparation of these compositions is the same as that described for Examples 1-6. The results set forth in Table III clearly demonstrate the improved oxidative and thermal stability of crosslinked ethylene-vinyl acetate copolymers containing the organic sulfide antioxidant compounds of the present invention in comparison to those containing a conventional antioxidant (DSTDP).

In Example 19 vs. Example 20, Examples 21 vs. Example 22, Example 23 vs. Example 24 and Example 25 vs. Example 26, the compositions containing the organic sulfide antioxidant compounds of the instant invention (OTEOTC) (i.e., Examples 20, 22, 24 and 26) outperform

those containing a conventional antioxidant (DSTDF) (i.e., Examples 19, 21, 23 and 25). Specifically, the time required for the samples containing the present antioxidants to fail was
5 at least 7 days longer than those containing the DSTDF antioxidant.

Only for Examples 27 and 28 did the composition containing the conventional antioxidant fail at the same time as that
10 containing the present antioxidant (21 days). However, even this case, the Example containing the organic sulfide antioxidants according to the present invention (i.e., Example 28) had
higher % Tensile Strength and % (% Elongation)
15 values than the composition comprising the conventional antioxidant.

TABLE III

Example No.	19	20	21	22	23	24	25	26	27	28
EVA(a)	97.0	97.0	96.75	96.75	97.0	97.0	96.5	96.5	96.75	96.75
PAO-1(b)	0.5	0.5	0.5	0.5						
PAO-2(c)					0.5	0.5	0.5	0.5	0.5	0.5
Cast	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
DSTOP	0.5		0.75		0.5		1.0		0.75	
OTEDTC		0.5		0.75		0.5		1.0		0.75
DICUP(d)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
0 Days										
Tensile Strength (psi)(e)	2425	1990	1871	1707	2377	2115	2139	1559	2356	1946
% Elongation	882	752	616	633	1006	860	971	701	940	562
7 Days										

TABLE III - continued

Example No.	19	20	21	22	23	24	25	26	27	28
Tensile Strength (psi) (e)	378	1983	2020	1869	1339	2181	2839	2804	3211	2947
% Tensile Strength	Failed	99.7	108	110	56	103	133	129	136	151
% Elongation	64	722	788	678	512	795	1089	791	1239	1172
% (% Elongation)	Failed	96	117	107	51	92	125	113	132	236
14 Days										
Tensile Strength (psi) (e)		785	420	2559	334	1330	2210	1980	1840	2240
% Tensile Strength		Failed	Failed	149	Failed	63	183	127	78	115
% Elongation		205	80	332	51	429	946	754	739	859
% (% Elongation)		Failed	Failed	147	Failed	58	109	108	79	99
21 Days										
Tensile Strength (psi) (e)				807		341	428	1710	314	839
% Tensile Strength				47		Failed	Failed	110	Failed	Failed
% Elongation				279		61	81	794	13	302
% (% Elongation)				Failed		Failed	Failed	113	Failed	Failed

(a) Du Pont's Elvex (R) 470

(b) Ciba-Geigy's Irganox (R) 1010

(c) Ciba-Geigy's Irganox (R) 1035

(c) Lucidol Div. of Pennwalt Corp. Lupersol (R) 500R,

(e) At break

EXAMPLES 29-32

The compositions were prepared by the following procedure. The resin was first added to a two-roll mill at 120°C. and milled for 5 minutes until it fluxed. The additives were then added to the resin and milling was continued for an additional 8 minutes, in order to uniformly mix the additives into the resin. The sheet of material was then placed in a Carver Press at a temperature of 185°C. for 8 1/2 minutes at a pressure of 20,000 psi. The resulting plaques were then cut into Tensile Bars in accordance with ASTM Procedure No. 4 and suspended in a forced air oven at 150°C. Samples were then removed at 6 and 8 week intervals and the tensile strength measured according to ASTM Test Procedure D638. The % Tensile Strength was calculated by the method described above.

The following materials were used in Examples 29-32:

THDTCD - 1,5 (or 6), 9(or 10)-

Tris(hexadecylthio)cyclododecane.

BOTM - 2,9-Bis(Octadecylthio)-p-methane

TBCP - t-butyl Cumyl Peroxide

The data set forth in Table IV clearly
5 demonstrates the improved oxidative and thermal
stability of the crosslinked low density
polyethylene compositions containing organic
sulfide antioxidant the compounds of the
present invention compared to those containing
10 a conventional antioxidant.

After six weeks, the % retention of tensile
strength was much greater for the compositions
according to the present invention compared to
the sample containing the conventional
15 antioxidant. This improvement ranged from 11%
to 34%. Furthermore, the composition
containing the present compounds retained 96%
of its original tensile strength, while that
containing the conventional antioxidant
20 compound dropped below 50%, the point at which
a sample is normally considered to have failed.

TABLE IV

Example No.	29	30	31	32
LDPE ^(a)	100.0	100.0	100.0	100.0
PAO-2 ^(b)	0.2	0.2	0.2	0.2
TBCP ^(c)	1.5	1.5	1.5	1.5
BOTH	0.3			
THDYCD		0.3		
OTKOTC			0.3	
DSYDP				0.3
Tensile Strength (psi) (initial)	2750	2520	2570	2560
X Tensile Strength Retention (6 wks)	91	110	98	82
X Tensile Strength Retention (8 wks)		96		<50

(a) Union Carbide's DYNH (R) -1

(b) Ciba-Geigy's Irganox (R) 1035

(c) Lucidol division of Pennwalt Corporation Lupersol (R) 801.

EXAMPLES 33-41

Examples 33-41 further illustrate the greater stabilizing and antioxidizing effect of the organic sulfide antioxidants of the present invention.

Small samples (i.e., 10-25 mg) were heated in platinum boats at a rate 10°C. per minute. The temperature for a weight loss of 5% was then determined. The gas flow (nitrogen or air) was 200 cc per minute into a DuPont Model 9900 Thermogravimetric Analyzer.

The antioxidants used in Examples 33-37 and set forth below, are conventional antioxidants used in the plastics industry.

- 15 DLTDP - Dilauryl Thiodipropionate
- DSPDPH - Distearyl Pentaerythritol
Diphosphite
- TBPPH - Tetrakis(2,4-di-t-butylphenyl)-
4,4'-biphenylenediphosphonite
- 20 TBPP - Tris(2,5-di-tbutylphenyl)Phosphite

PETAE - A 40:60 mixture of-Pentaerythritol
Tetrakis(3-hexadecylthiopropyl)
Ether and Pentaerythritol Tris (3-
hexadecylthiopropyl) Ether

5 The results set forth in Table V
demonstrate the temperature at which a 5%
weight loss occurs for a series of
antioxidants. Examples 38-41 are the sulfide
antioxidants according to the present
10 invention. As can be seen from this data, the
temperature at which a 5% weight loss occurs is
considerably greater for the compounds of the
present invention as compared to conventional
antioxidants. These results are similar
15 whether conducted in air or nitrogen.

TABLE V

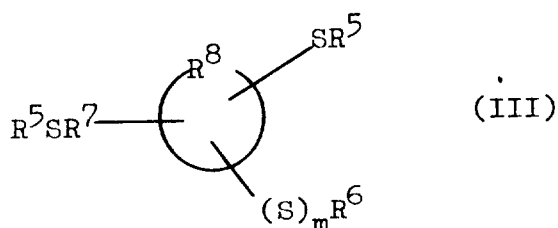
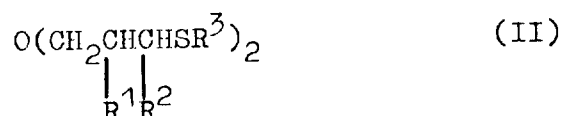
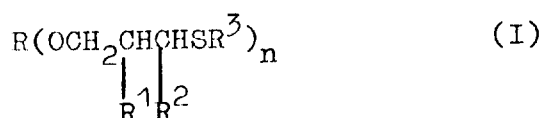
<u>Thermogravimetric Analysis</u>			
Example No.	Compound	5 % Weight	
		<u>Loss ($^{\circ}\text{C}$)</u>	
		Nitrogen	Air
33	DSTDP	271	266
34	DLTDP	308	259
35	DSPDFH	252	259
36	TBPRFH	171	160
37	TBPP	291	280
38	OTEDTC	354	315
39	BOTH	340	308
40	THDTCD	342	312
41	PETAE	359	314

The present invention may be embodied in other specific forms without departing from the spirit or essential attributes thereof and, accordingly, reference should be made to the
5 appended claims, rather than to the foregoing specification as indicating the scope of the invention.

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We Claim:

1. A composition comprising a crosslinked polyolefin resin and an amount of organic sulfide antioxidant sufficient to stabilize the resin against thermal or oxidative degradation, wherein the organic sulfide antioxidant is represented by Formula I, II or III;



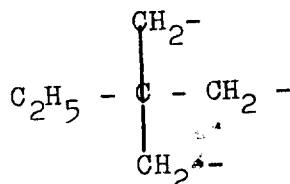
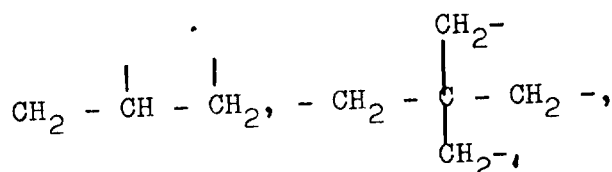
wherein:

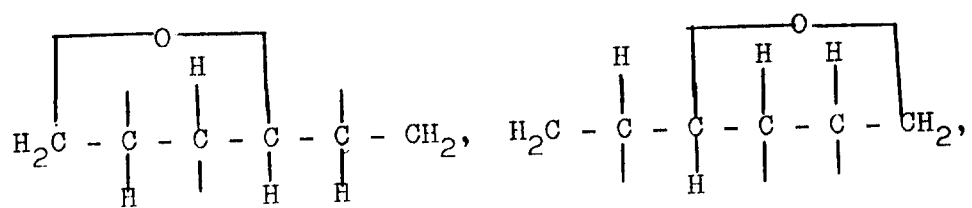
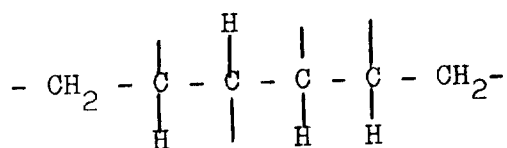
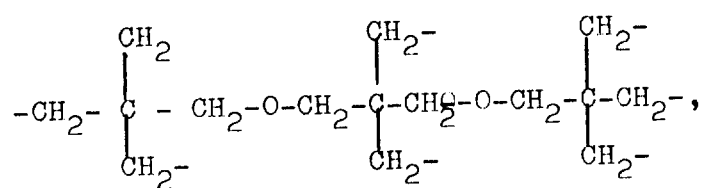
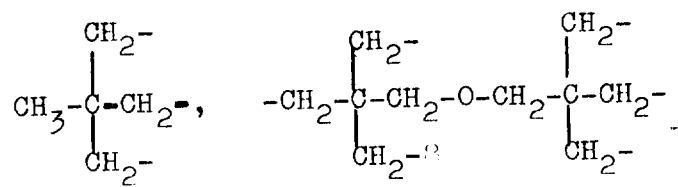
- 10 m is 0 or 1;
n is an integer of 2 to 15;
R is a substituted or unsubstituted

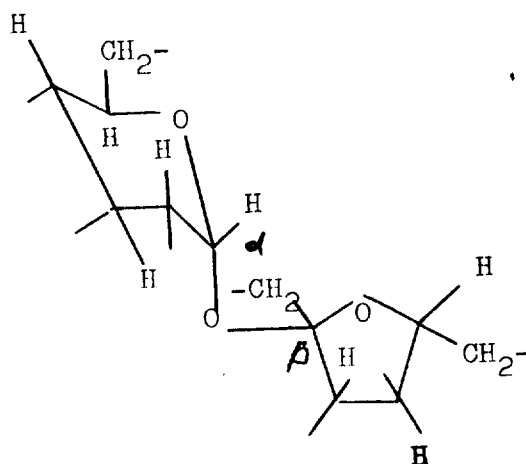
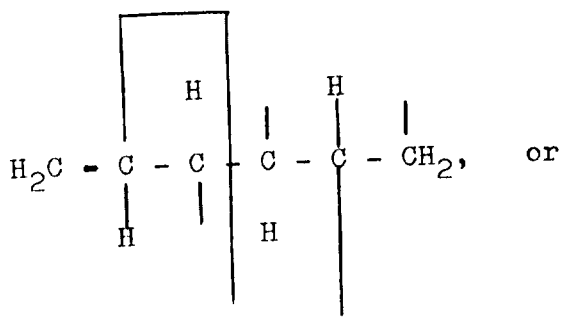
multivalent alkyl group of 2 to 30
 carbons, or a substituted or
 unsubstituted multivalent cycloalkyl
 group of 5 to 20 carbons, a substituted
 5 or unsubstituted multivalent alkyl group
 of 2 to 30 carbons where any of up to 6
 carbon atoms are replaced with an O or S
 heteroatom, a substituted or
 unsubstituted multivalent cycloalkyl
 10 group of 5 to 20 carbons where any of up
 to 6 carbon atoms are replaced with an O
 heteroatom, with the proviso that the
 heteroatoms must be separated from each
 other and from the portion of the
 15 compound to which the R group is bonded
 by at least one carbon atom, the
 substituents for R being -OH, -SR⁴ or -
 -OR⁴, wherein R⁴ is an alkyl group of 1
 to 30 carbon or cycloalkyl group of 5 to
 20 20 carbons;
 R¹ and R² are independently H or an alkyl
 group of 1 to 4 carbons;
 R³ is an alkyl group of 1 to 24 carbons or a

- cycloalkyl group of 5 to 20 carbons;
- R⁵ is an alkyl group of 1 to 24 carbons;
- R⁶ is H or an alkyl group of 1 to 24 carbon, with the proviso that when m = 0, R⁶ is H or an alkyl group of 1 to 7 carbons and when m = 1, R⁶ is an alkyl group of 1 to 24 carbons;
- R₇ is a direct bond or an alkylene group of 1 to 4 carbons; and
- R₈ is a monocyclic, bicyclic or tricyclic cycloalkyl group of 5 to 16 carbons.

2. A composition as in claim 1 wherein the organic sulfide antioxidant is represented by Formula I or II, wherein R is:







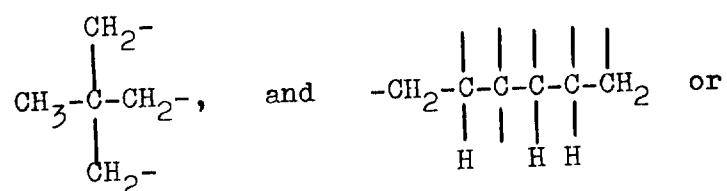
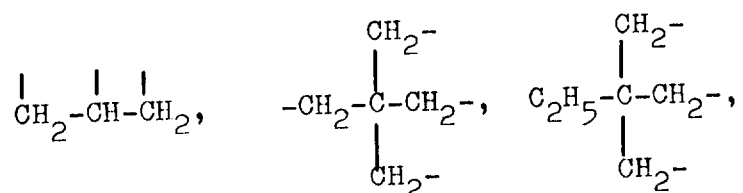
wherein α and β are the types of linkages;
and wherein

R^1 is H or $-\text{CH}_3$;

R^2 is H; and

R^3 is an alkyl group of 10 to 18 carbons,

3. A composition as in claim 2, wherein R
is:

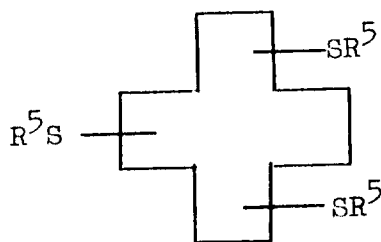
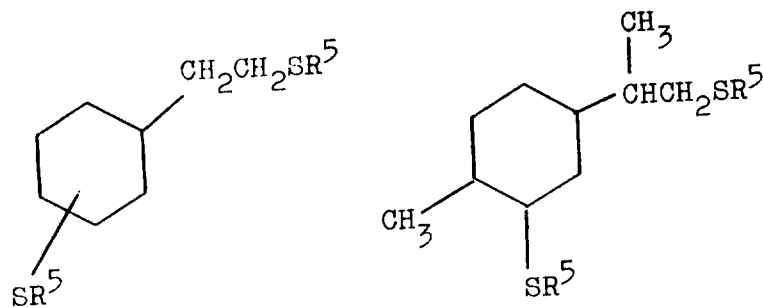


wherein

R^1 and R^2 are H; and

R^3 is an alkyl group of 12 to 18 carbons.

4. A composition as in claim 1, wherein the organic sulfide antioxidant is represented by Formula III and has one of the following structures:



3. A composition as in claim 1, wherein the cross-linked polyolefin resin is at least one of linear low density polyethylenes, low density polyethylenes, high density polyethylenes, ethylene-propylene copolymers, ethylene-vinyl acetate copolymers, ethylene-acrylate ester copolymers, chlorosulfonated polyethylenes, polypropylenes, polybutene-1,

polyisobutylene, poly-4-methylpentene-1, poly-
 methylbutene-1, poly-4,4-dimethyl-pentene-1-
 polydecene-1, polydodecene-1, ethylene-
 propylene-butadiene terpolymers,
 5 ethylenepropylene-dicyclopentadiene
 terpolymers, polybutadiene, ethylene-propylene-
 norbornadiene and copolymers, cis-1,4-
 polyisoprene, styrene-butadiene copolymers,
 silicone rubbers, and mixtures thereof.

10 6. A composition according to claim 1,
 further comprising a peroxide crosslinking
 agent.

7. A composition as in claim 6, wherein
 the peroxide crosslinking agent is di-t-butyl
 15 peroxide, di-cumyl peroxide, benzoyl peroxide,
 t-butyl cumyl peroxide, 2,5-dimethyl-2,5-di(t-
 butylperoxy)hexyne-3, 2,5-dimethyl-2,5-di(t-
 butylperoxy)hexyne, $\mathcal{L}$, $\mathcal{L}$, -bis(t-
 butylperoxy)diisopropylbenzene, n-butyl-4,4-
 20 bis(t-butylperoxy) valerate, 1,1-di(t-butyl-
 peroxy)-3,3,5-trimethylcyclohexane, 1,1-di(t-

butylperoxy)cyclohexane, ethyl-3,3-di(tbutyl-
peroxy)-butyrate, 2,2-di(t-amylperoxy) propane,
ethyl-3,3-di(t-amylperoxy)butyrate or t-alkyl,
alkylcarbonate or benzoate diperoxy derivatives
5 of 3-hexyne, 4-octyne, or 3,5-octadiyne.

8. A composition as in claim 1, wherein
the composition is crosslinked with high energy
radiation.

9. A composition as in claim 1, further
10 comprising an auxiliary antioxidant.

10. A composition as in claim 9, wherein
the auxiliary antioxidant is at least one
phosphite, phenolic or arylamine antioxidant.

11. A composition as in claim 1, further
15 comprising at least one additive to facilitate
processing.

12. A composition as in claim 11, wherein
said additive is a metal deactivator, talc,

calcium carbonate, calcium ^asterate or UV
stabilizer.

13. A composition as in claim 1, wherein
the weight ratio of the organic sulfide
5 antioxidant to the cross-linked polyolefin
resin is about 10,000 to about 1:20.

14. A composition as in claim 13, wherein
the weight ratio of the sulfide antioxidant to
the crosslinked polyolefin resin is about
10 1:2000 to about 7:1000.

15. A composition as in claim 6, wherein
the weight ratio of the peroxide crosslinking
agent to the organic sulfide antioxidant is
about 100:1 to about 1:100.

15 16. A composition as in claim 15, wherein
the weight ratio of the peroxide crosslinking
agent to the organic sulfide antioxidant is
about 50:1 to about 5:1.

17. A composition as in claim 9, wherein the weight ratio of the auxiliary antioxidant to the organic sulfide antioxidant is about 10:1 to about 1:10.

5 18. A composition as in claim 17, wherein the weight ratio of the auxiliary antioxidant to the organic sulfide antioxidant is about 1:2 to about 1:4.

10 19. A composition as in claim 1, wherein the organic sulfide antioxidant is beta(n-octadecylthio)ethyl-3(4)-n-octadecylthiocyclohexane.

20. A composition as in claim 1, wherein the organic sulfide antioxidant is 1,4(~~5~~), 8(9) tris(hexadecylthio)cyclododecane.
15

21. A composition as in claim 1, wherein the organic sulfide antioxidant is pentaerythritol tetrakis(3-hexadecylthiopropyl)ether.

22. A composition as in claim 1, wherein
the organic sulfide antioxidant is
pentaerythritol tris(3-
hexadecylthiopropyl)ether.

5 23. A composition as in claim 1, wherein
the organic sulfide antioxidant is
pentaerythritol, tetrakis(n-
octadecylthiopropyl)ester.

24. A composition as in claim 1, wherein
10 the organic sulfide antioxidant is
pentaerythritol tris(n-octadecylthiopropyl)
ether.

25. a composition as in claim 1, wherein
the organic sulfide antioxidant is
15 pentaerythritol tetrakis(n-dodecylthiopropyl)
ether.

26. A composition as in claim 1, wherein
the organic sulfide antioxidant is
pentaerythritol tris(n-dodecylthiopropyl)ether.

27. A composition as in claim 1, wherein
the organic sulfide antioxidant is
trimethylolpropane tris(n-
octadecylthiopropyl)ether.

5 28. A composition as in claim 1, wherein
the organic sulfide antioxidant is
trimethylolpropane tris(n-
hexyldecylthiopropyl)ether.

29. A composition as in claim 1, wherein
10 the organic sulfide antioxidant is
dipentaerythritol hexakis(n-octylthiopropyl)
ether.

30. A composition as in claim 1, wherein
the organic sulfide antioxidant is
15 dipentaerythritol hex^aakis(n-dodecylthiopropyl)
ether.

31. A composition as in claim 1, wherein
the organic sulfide antioxidant is
dipentaerythritol hexakis(n-
20 hexyldecylthiopropyl)ether.

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James L. Reilly

Inventors