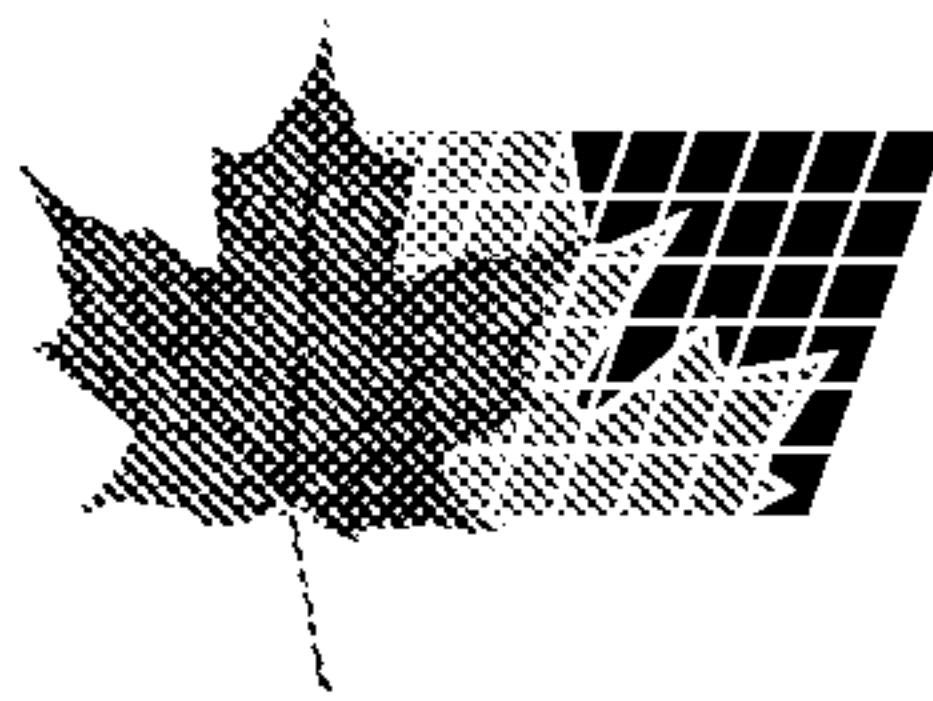




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(30) 1998/09/16 (09/153,909) US

(54) **COMBINAISON D'UN COMPOSE SULFORGANIQUE ET D'UN
MERCAPTO-ESTER DE ZINC UTILISEE COMME
STABILISANT THERMIQUE DANS LE TRAITEMENT DU
PVC**

(54) **COMBINATION OF AN ORGANOETHIO COMPOUND AND A
ZINC MERCAPTO ESTER AS HEAT STABILIZER IN PVC
PROCESSING**

(57) The zinc burn experienced during the processing of a composition comprising a halogen-containing polymer and a zinc mercaptoester is eliminated by the addition of an organothio compound. The organothio compound is selected from mercaptans and organic sulfides. Dithiodiglycol and the polyformals and polyacetals thereof are preferred as the organic sulfides. Mercaptoethanol is a preferred mercaptan.

COMBINATION OF AN ORGANOETHIO COMPOUND AND A ZINC
MERCAPTOESTER AS A HEAT STABILIZER IN PVC PROCESSING

5

ABSTRACT OF THE DISCLOSURE

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The zinc burn experienced during the processing of a composition comprising a halogen-containing polymer and a zinc mercaptoester is eliminated by the addition of an organoethio compound. The organoethio compound is selected from mercaptans and organic sulfides. Dithiodiglycol and the polyformals and polyacetals thereof are preferred as the organic sulfides. Mercaptoethanol is a preferred mercaptan.

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COMBINATION OF AN ORGANOTHIO COMPOUND AND A ZINC
MERCAPTO ESTER AS HEAT STABILIZER IN PVC PROCESSING

5 BACKGROUND OF THE INVENTION

Halogen containing polymers, especially those containing chlorine, are used widely and have great commercial significance. Polyvinyl chloride (PVC), in particular, is used in packaging, siding, pipe, and many extruded shapes. Such large scale and
10 diverse use of the halogen-containing polymers depends upon the incorporation therein of good heat and light stabilizers. PVC, for example, is known to have a tendency to degrade upon prolonged exposure to heat and light during processing and use. Darkening or other color change and the loss of tensile,
15 flexural, and impact strengths are the results of such degradation. Unless good low-cost stabilizers are available for addition to the polymer composition, the service life of articles made from the composition is limited, and its use severely restricted, as will be the conditions for making it.

20 One particularly troublesome form of degradation occurs when the polymer composition is processed into articles by methods employing heat to melt or soften the polymer. A color change can occur during the first few minutes at high temperatures (e.g., from about 175 to about 200°C) and it is commonly referred to as
25 early color or early discoloration. The avoidance of such early color is notably important in the manufacture of plastic pipe and

siding. It is, of course, also important to prevent or reduce discoloration and deterioration of the polymer during extended exposure to high temperatures, which can lead to sudden and catastrophic degradation into a pitch-like abrasive material and cause the formation of corrosive materials such as HCl inside the fabricating equipment. The inner, highly polished surfaces of the equipment can thus be rendered essentially useless. A particularly troublesome instance of such sudden degradation often occurs when zinc compounds are employed as stabilizers; the phenomenon is known as "zinc burn" in the PVC industry.

An example of zinc burn is illustrated in U. S. Patent No. 4,515,916, wherein a PVC composition containing zinc bis-(octyl thioglycolate) and a substituted dihydropyridine as a co-stabilizer showed such burn after 3 minutes on a two roll mill at 193°C. U. S. Patent No. 4,515,916 is incorporated herein by reference.

In U.S. Patent No. 3,417,039, Penneck teaches a stabilizing composition for chlorine-containing polymers which comprises a zinc salt of a carboxylic acid which may have sulfur substituents, a polyhydric alcohol, and an organic sulfur-bearing compound having the formula $R_1-S_{(1-2)}-R_2$, which is exemplified by bis-(n-dodecyloxyethyl) sulfide. The suitable salt-forming acids include benzoic, salicylic, phthalic, and maleic acid. Zinc 2-ethylhexyl maleate is a preferred salt. As shown hereinbelow, Penneck's stabilizing composition does not overcome the zinc burn problem.

Now, we have discovered that organothio compounds are superior co-stabilizers in combination with the zinc bis(mercaptoacid esters) when present during high temperature processing of halogen-containing polymers such as PVC.

SUMMARY OF THE INVENTION

It is an object of this invention to provide an improved heat stabilizer for halogen-containing polymer compositions.

It is an object of this invention to provide a halogen-containing polymer composition having improved heat stability.

It is a related object of this invention to eliminate zinc burn during the processing of PVC compositions at elevated temperatures.

These and other objects which will become apparent from the following description are achieved by a composition comprising a halogen-containing polymer and a stabilizer composition comprising:

(A) an organothio compound;

at least one zinc mercaptoester selected from the group consisting of

(B¹) a zinc mercaptoacid ester having the formula:

$\text{Zn}-[\text{S}(\text{CH}_2)_x-\text{C}(=\text{O})\text{OR}]_2$, wherein R is a hydrocarbyl radical having from 2 to about 22 carbon atoms and x is 1 or 2;

(B²) a zinc mercaptoacid ester having the formula:

$\text{Zn}-[\text{S}(\text{CHR}')_a(\text{CH}_2)_b-\text{C}(=\text{O})\text{OR}'']_2$; wherein

R' is methyl or $\text{C}(=\text{O})\text{OR}''$;

R'' is $[(\text{CH}_2-[\text{C}-(\text{R}^*)(\text{R}^{2*})]_y\text{CH}_2\text{O})_z\text{R}^{3*}]$;

R* is H, alkyl, or hydroxyalkyl;

R^{2*} is OH, hydroxy-substituted alkyl, or $\text{O}(=\text{O})\text{C}-\text{R}^{4*}$;

R^{3*} is H, $\text{O}(=\text{O})\text{C}-\text{R}^{4*}$, or alkyl,

R^{4*} is alkyl or alkenyl;

a = 0 or 1; b = 1 or 2; y = 0 or 1; and z = 1 to 4;

with the proviso that when z is greater than 1, y = 0;

and

(B³) a zinc mercaptoalkyl carboxylic acid ester having the formula:

$\text{Zn} [\text{SCH}_2(\text{CH}_2)_q\text{O}-\text{C}(=\text{O})\text{R}^{5*}]_2$; wherein

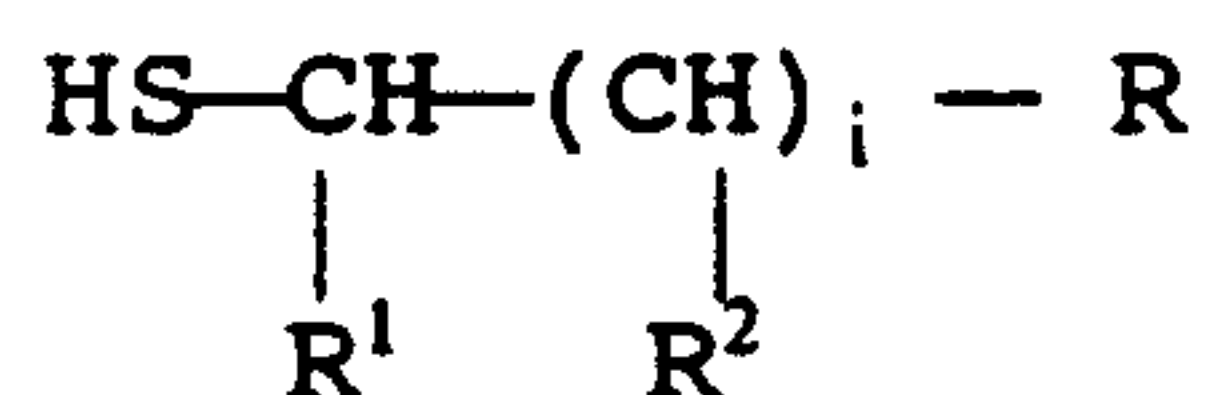
R^{5*} is an alkyl or alkenyl group having from 1 to 18 carbon atoms or an aryl group having from 6 to 12 carbon atoms, and q is from 1 to 6;

(C) from 0 to about 40 phr of a basic alkali or alkaline earth metal salt; and

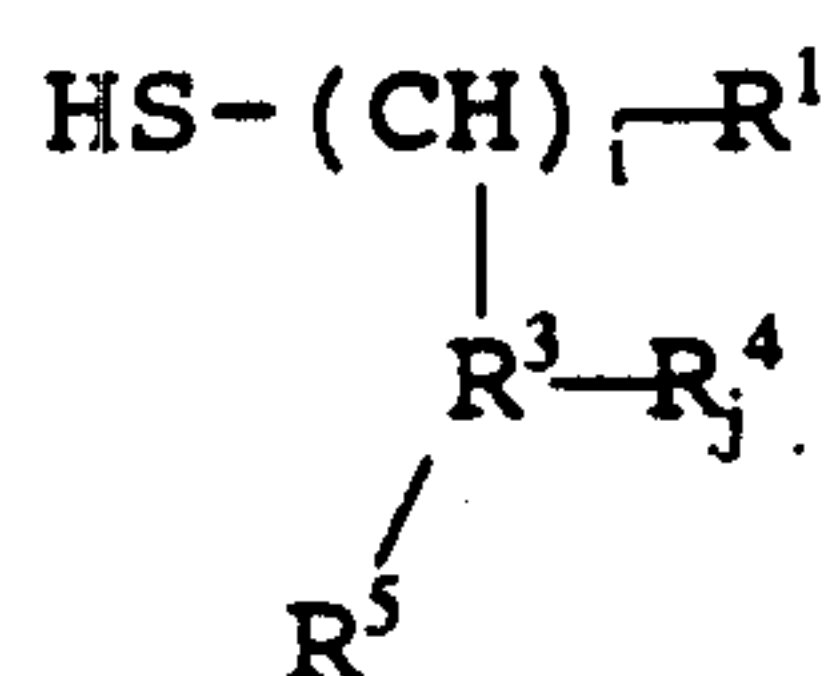
(D) from 0 to about 40 phr of a substituted dihydropyridine

DETAILED DESCRIPTION OF THE INVENTION

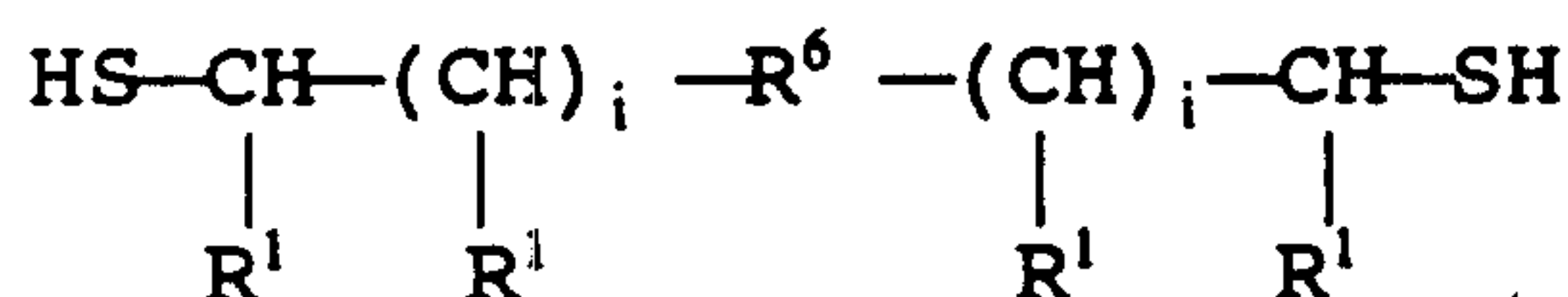
The organothio compounds that are suitable for the purposes of this invention are well-known compounds and include organic sulfides such as dithiodiglycols and polyformals of dithiodiglycols, and mercaptans such as alkyl mercaptans, mercapto esters, mercapto alcohols, thioglycerols, mercapto acids. See, for example, U.S. Patent Nos. 3, 297,629; reference. Alkyl mercaptans having from 1 to about 20 carbon atoms and from 1 to 4 mercapto groups are suitable. Among the useful mercaptan-containing organic compounds are those having structures illustrated by the following formulas:



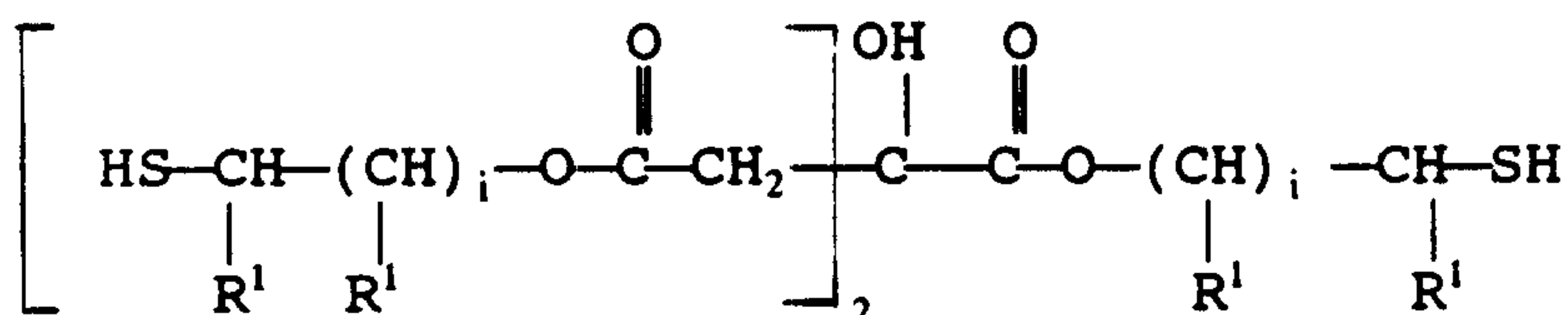
FORMULA I



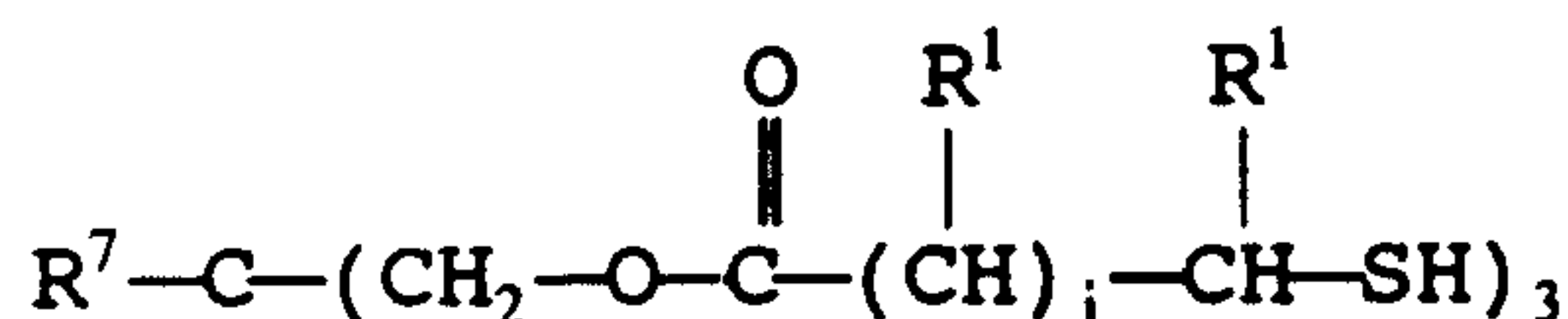
FORMULA II



FORMULA III

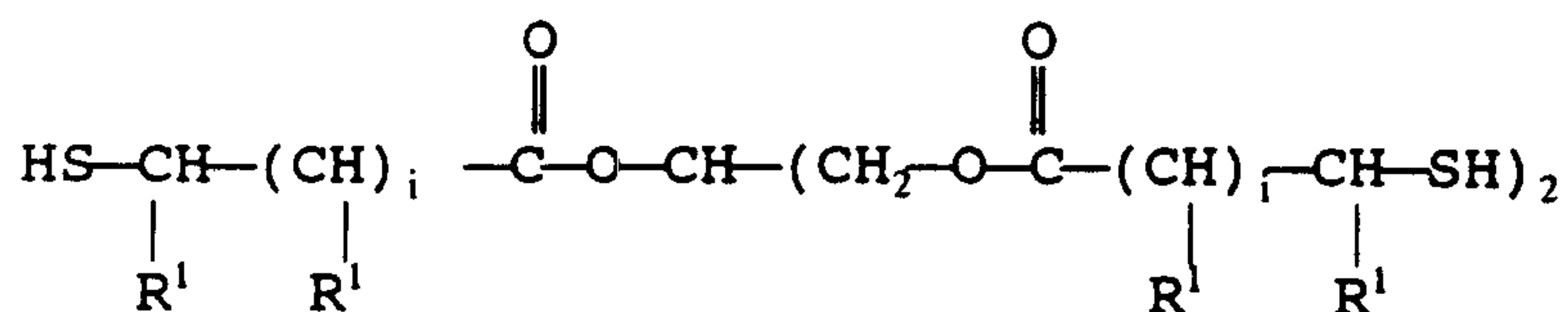


FORMULA IV



FORMULA V;

and



FORMULA VI

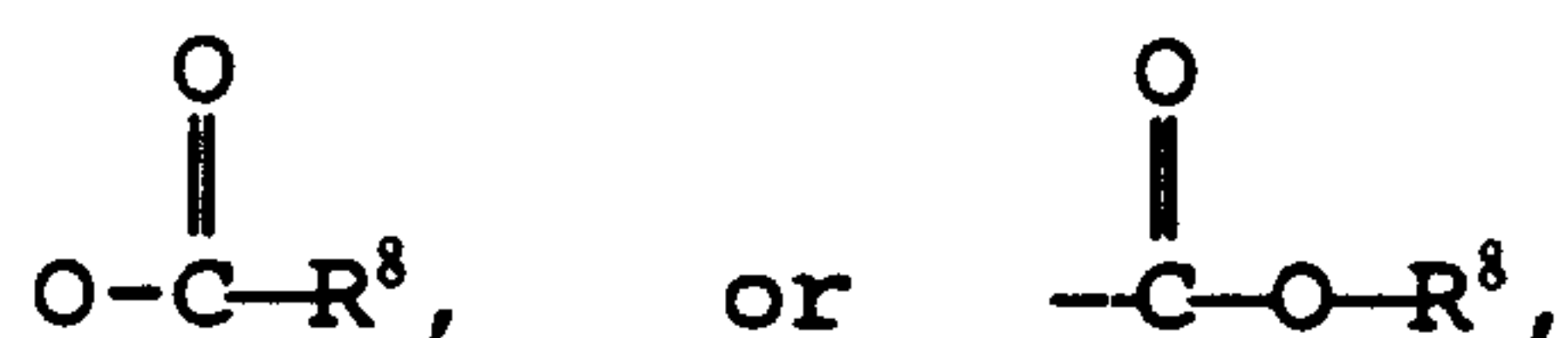
wherein R and R² are the same or different and are: -OH, -SH, aryl, C₁ to C₁₈ alkyl, -H,



R¹ is -H, aryl, or C₁ to C₁₈ alkyl;

R³ is cycloalkyl, cycloalkenyl or phenyl;

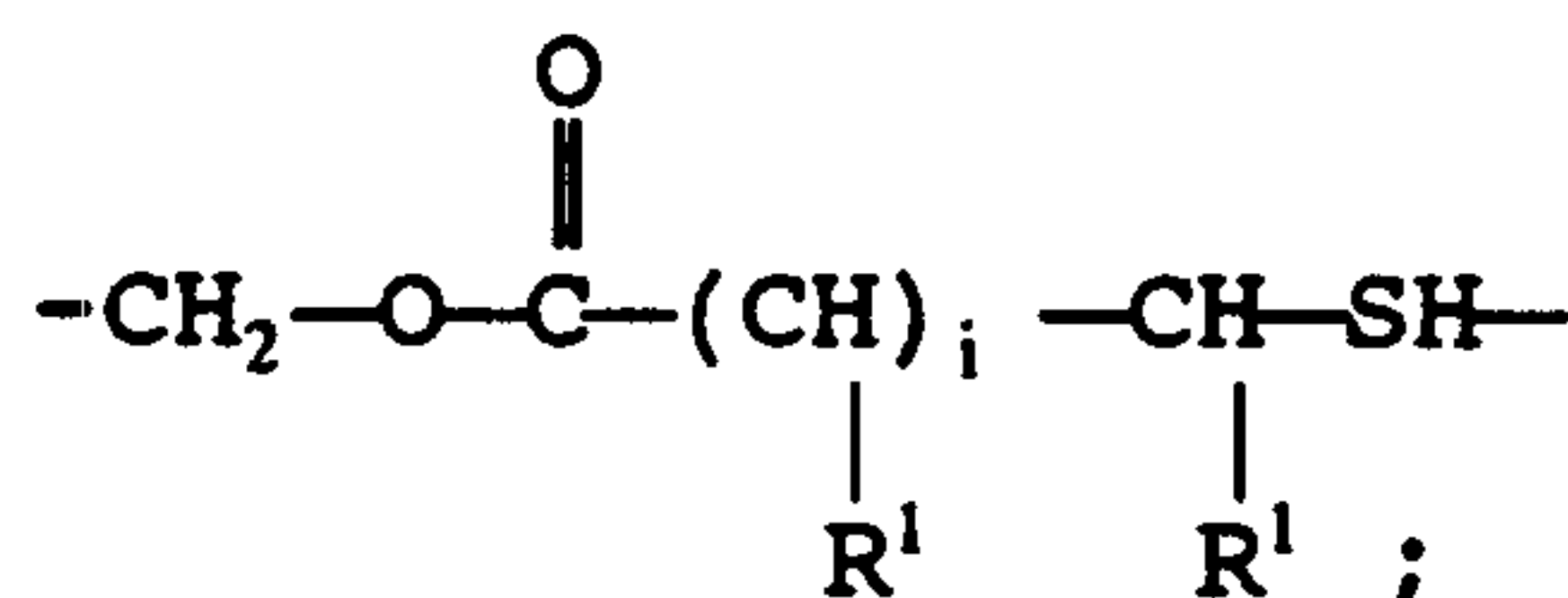
R⁴ is: -SH, aryl, C₁ to C₁₈ alkyl, -OH, -H,



with the proviso that the -SH groups are on non-adjacent carbon atoms in FORMULA II when R³ is phenyl, R⁴ is -OH and i=0;

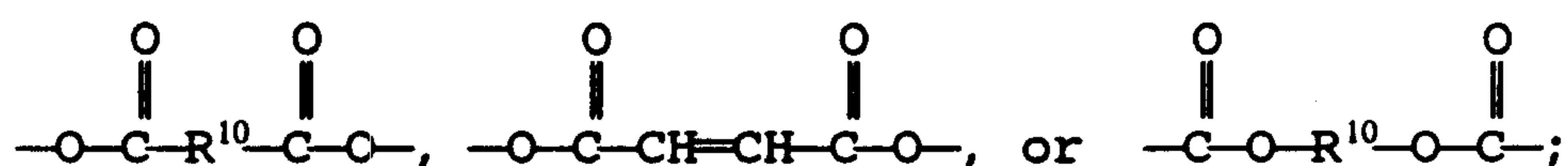
R⁵ is -H or a divalent group which may contain halogen, hydroxy, mercapto or alkyl substituents and which combines with R⁴ when R⁴ is phenyl to form a naphthalene ring;

R⁷ is -CH₃, -CH₂CH₃, or

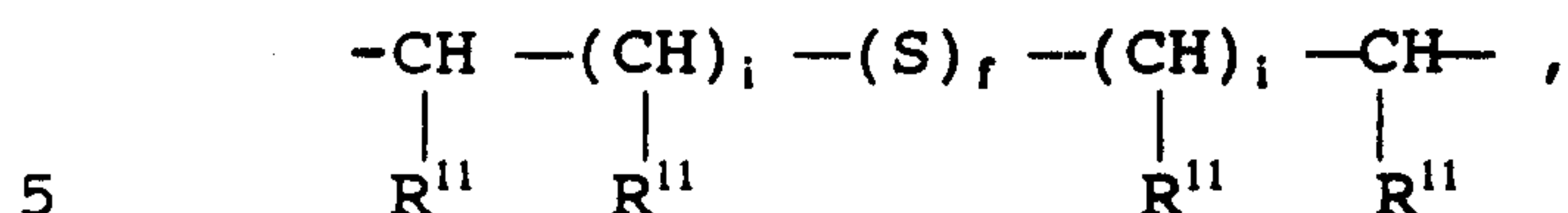


R⁸ is -H, or alkyl, alkenyl, aryl, aralkyl, alkaryl, cycloalkyl, cycloalkylenyl;

R⁹ is



wherein R^{10} is arylene, C_1 to C_8 alkylene,



or

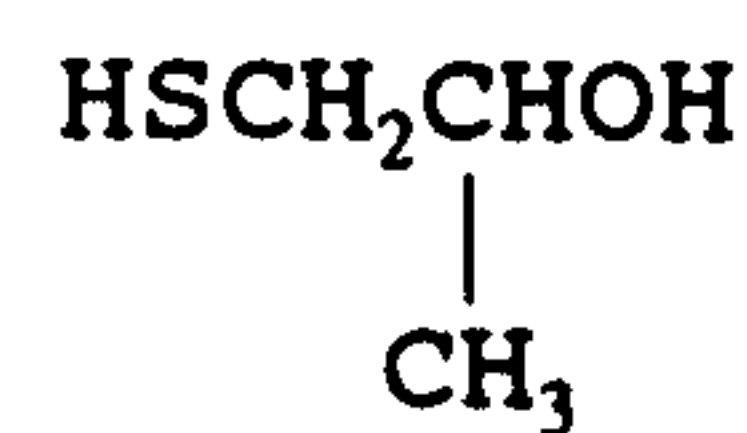
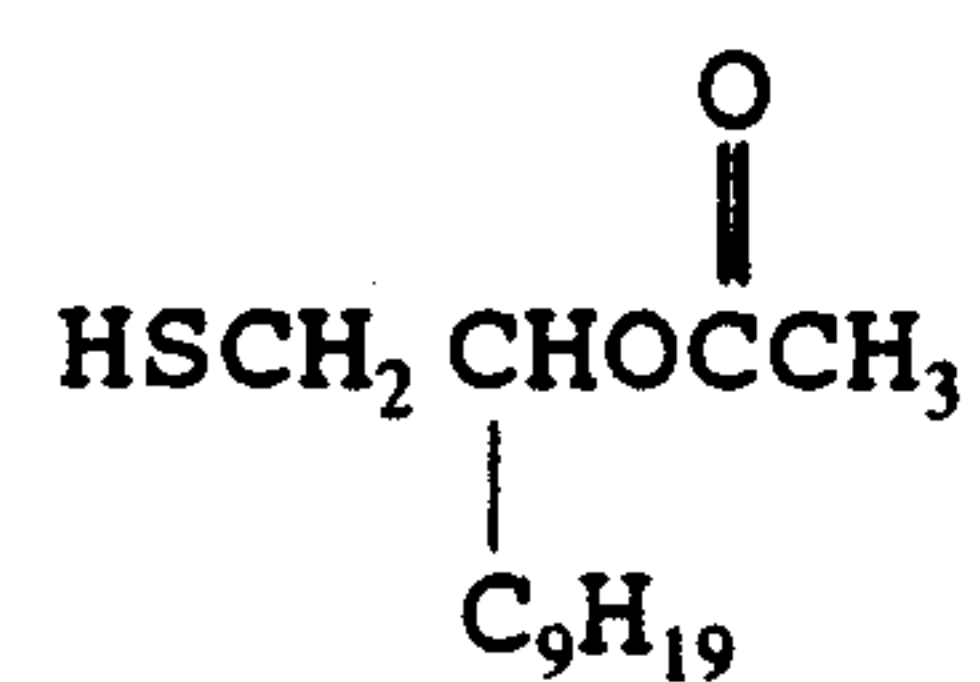
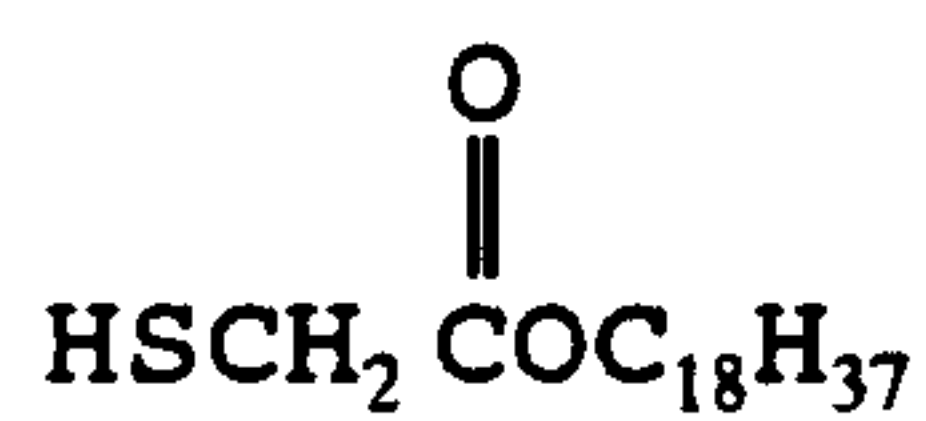
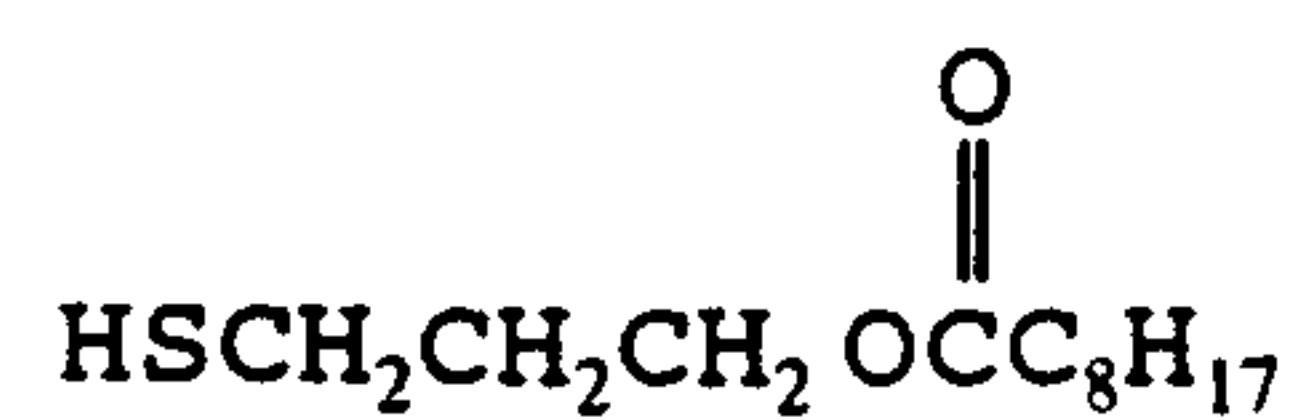
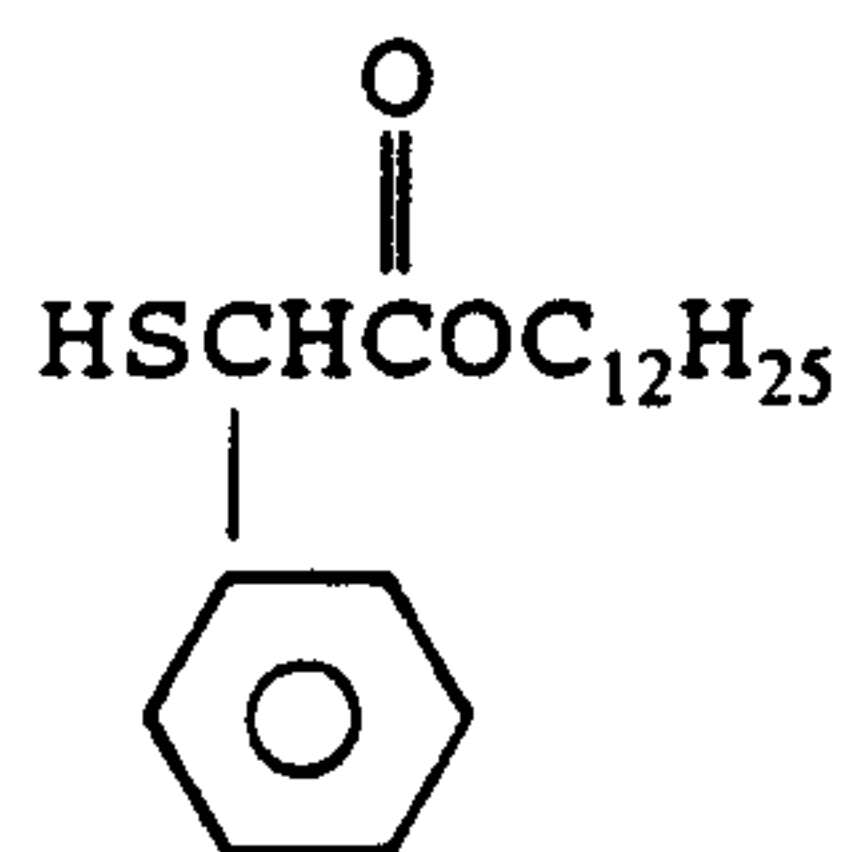


- 10 wherein b is an integer from 1 to 6;
 $i = 0$ or an integer from 1 to 6 inclusive;
 $j = 0-4$; and
 $f = 1$ or 2.

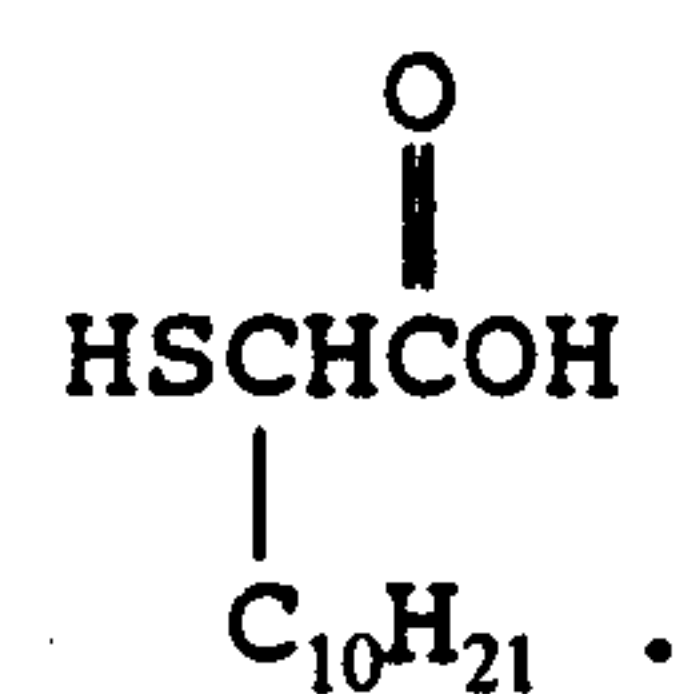
- 15 Mercaptan-containing organic compounds preferred in this invention are those compounds according to FORMULA I wherein R^1 and R^2 are $-H$, and R is OH or $-O(O=)CR^8$, and $i=1$.

- 20 Examples of the mercaptan-containing organic compounds described by FORMULA I include, but are not limited to, the following compounds:

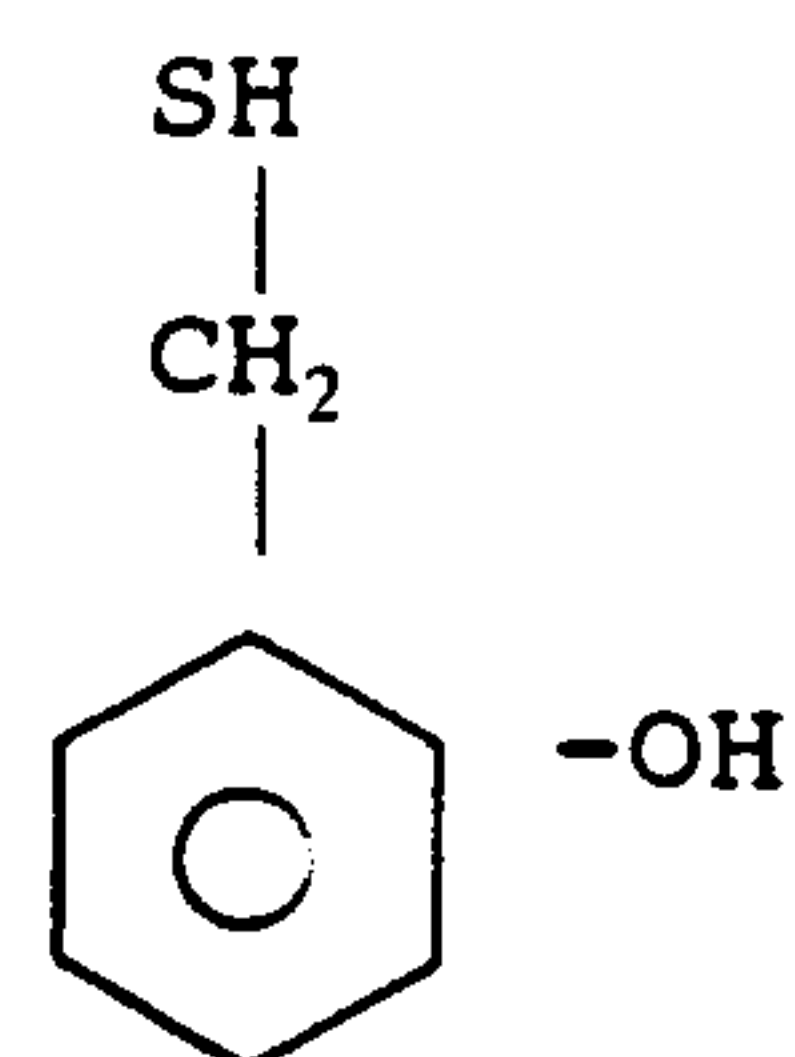
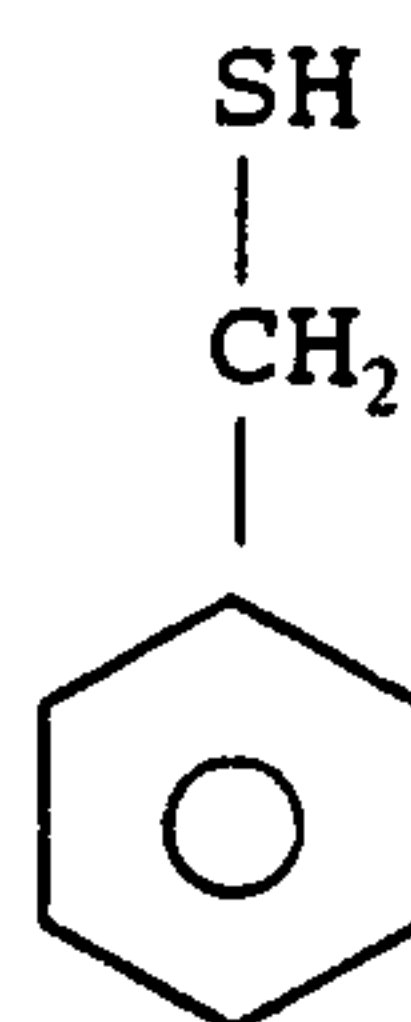
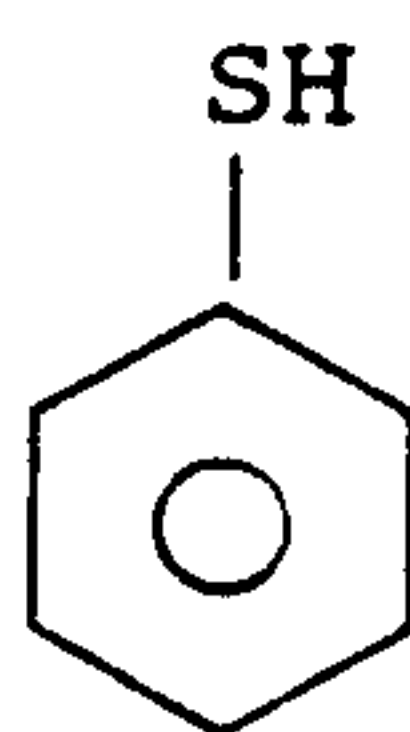




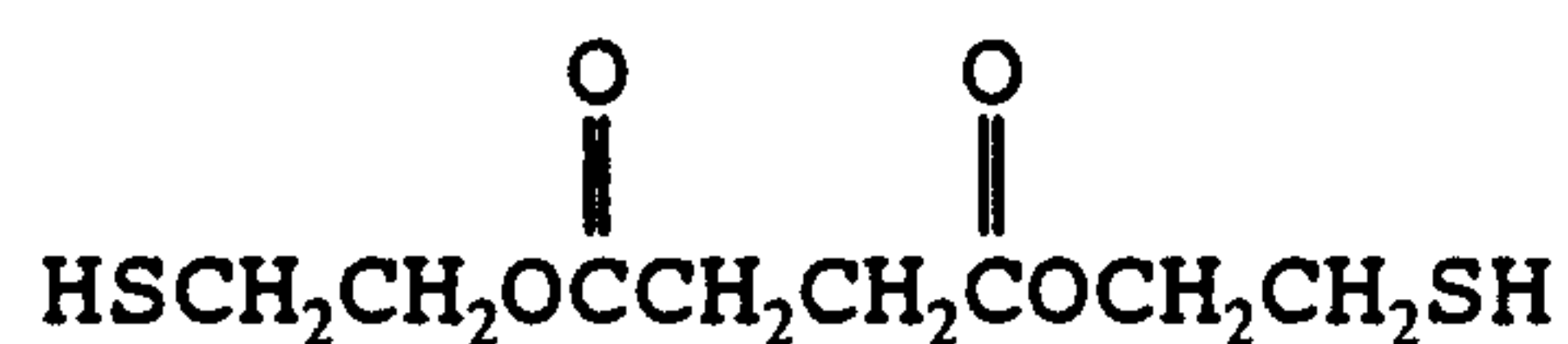
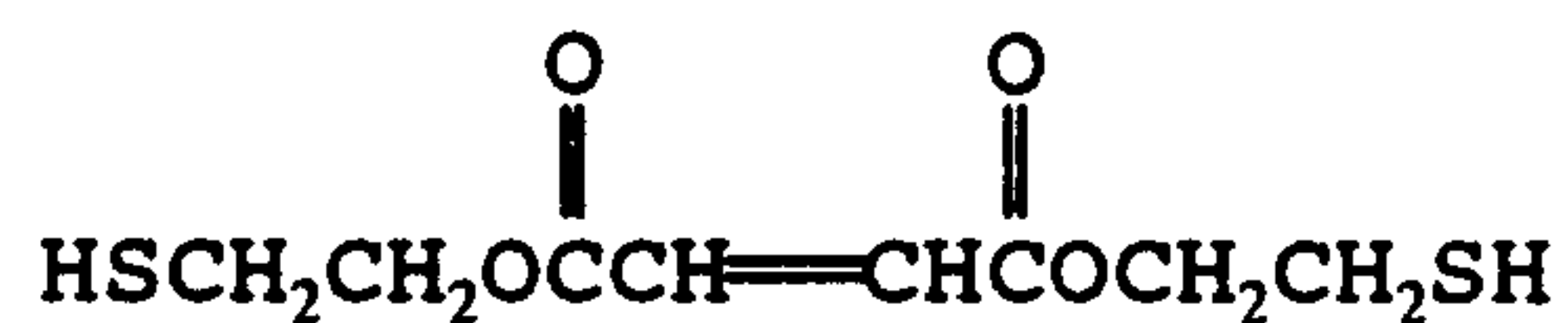
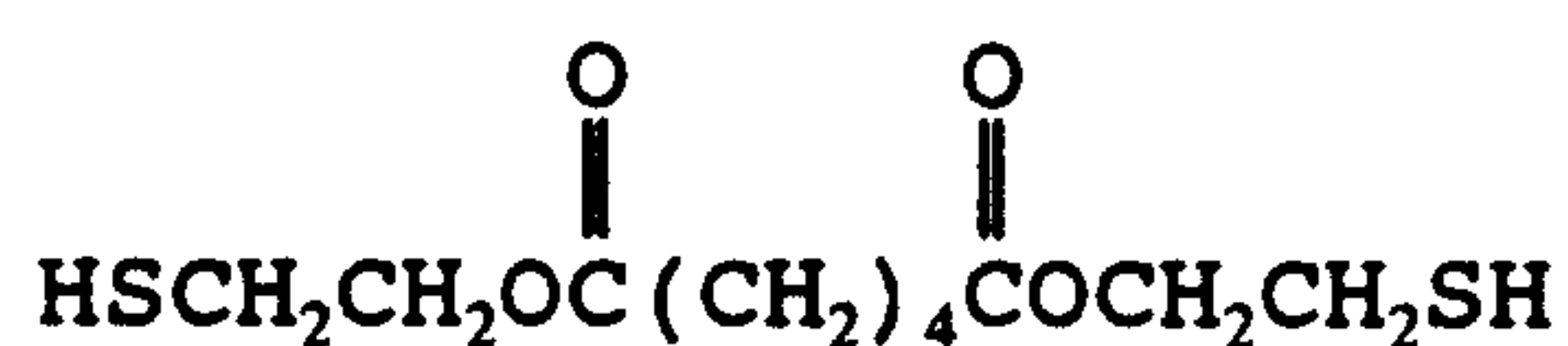
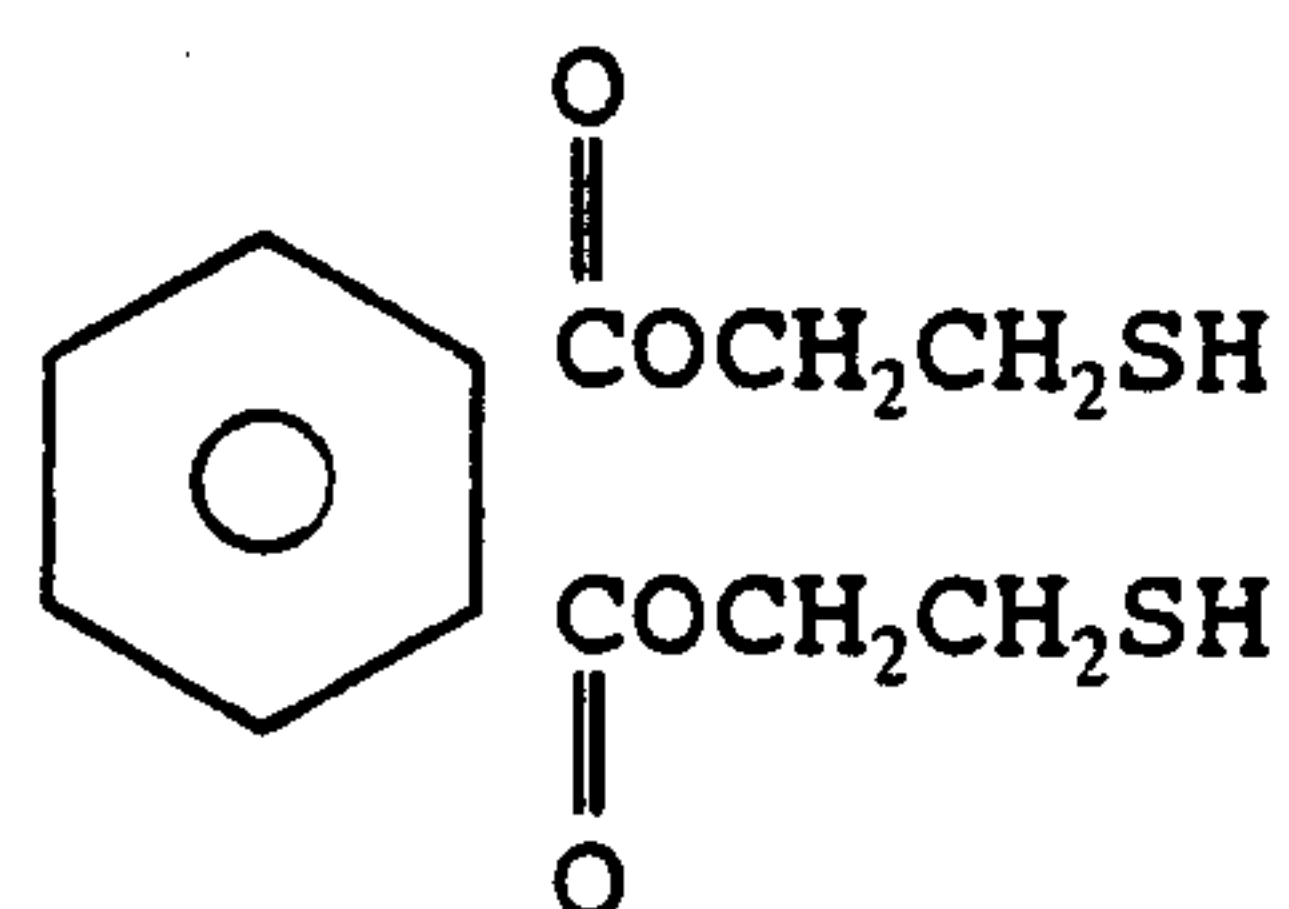
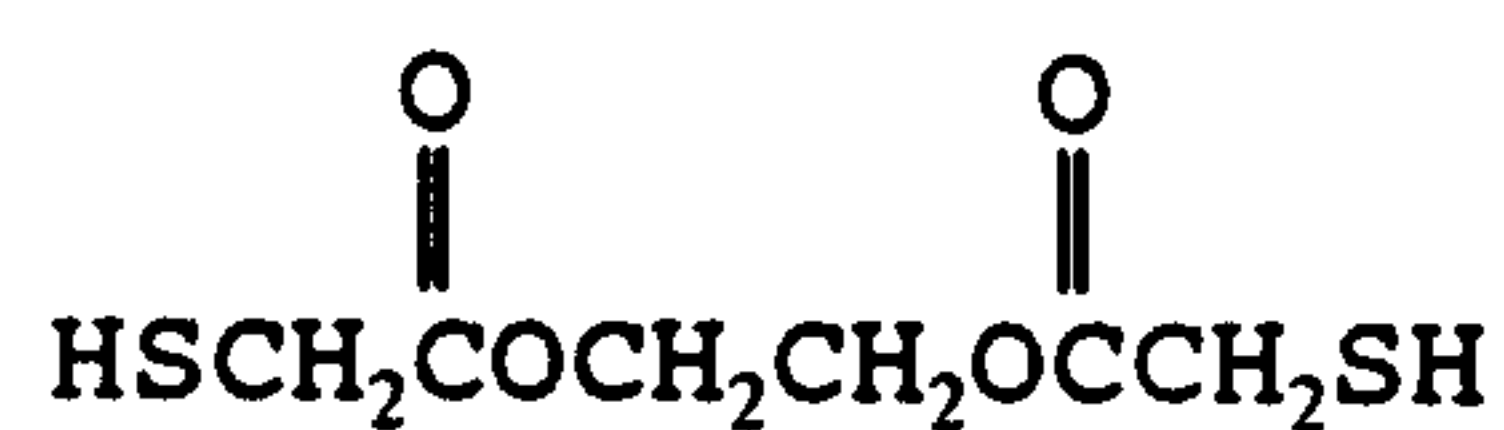
and



35 Examples of the mercaptan-containing organic compounds described by FORMULA II include, but are not limited to, the following compounds:

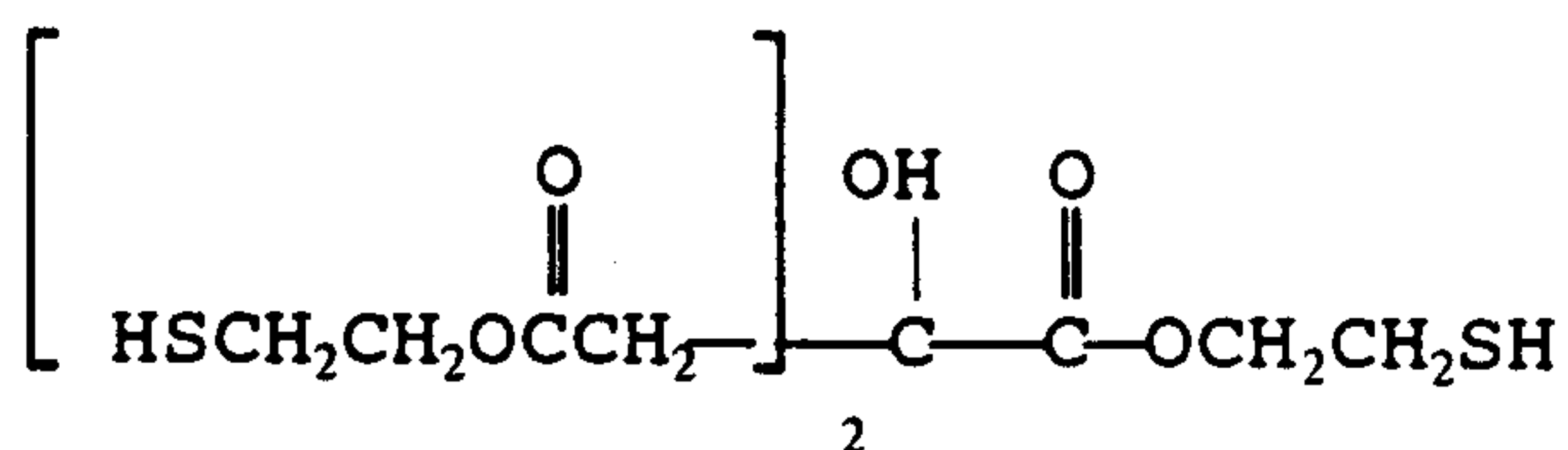


Examples of mercaptan-containing organic compounds represented by FORMULA III include, but are not limited to the following compounds:



The mercaptan-containing organic compounds described by FORMULA IV are exemplified by, but are not limited to, the following:

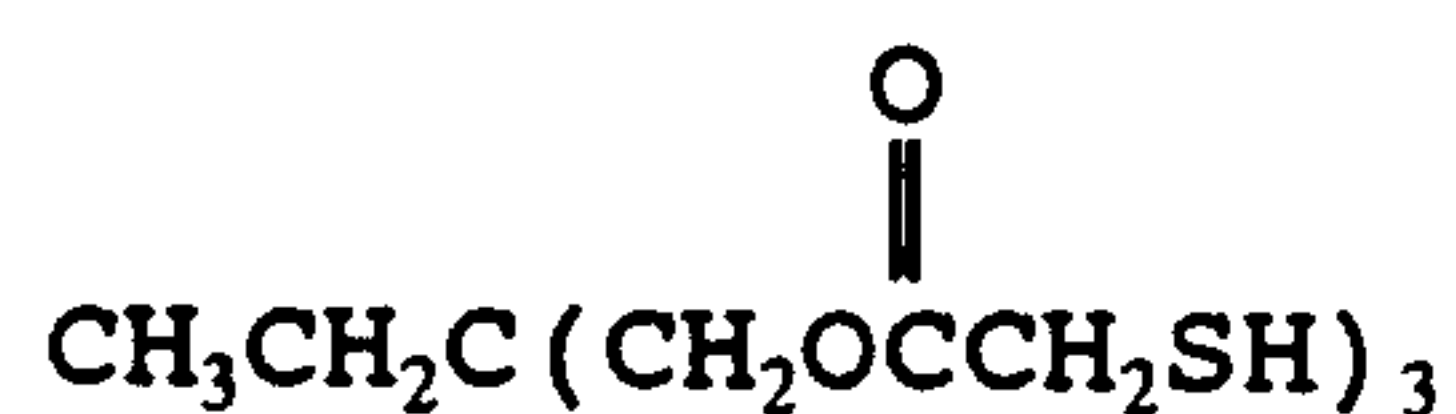
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The mercaptan-containing organic compounds represented by FORMULA V are exemplified by, but are not limited to, the following:

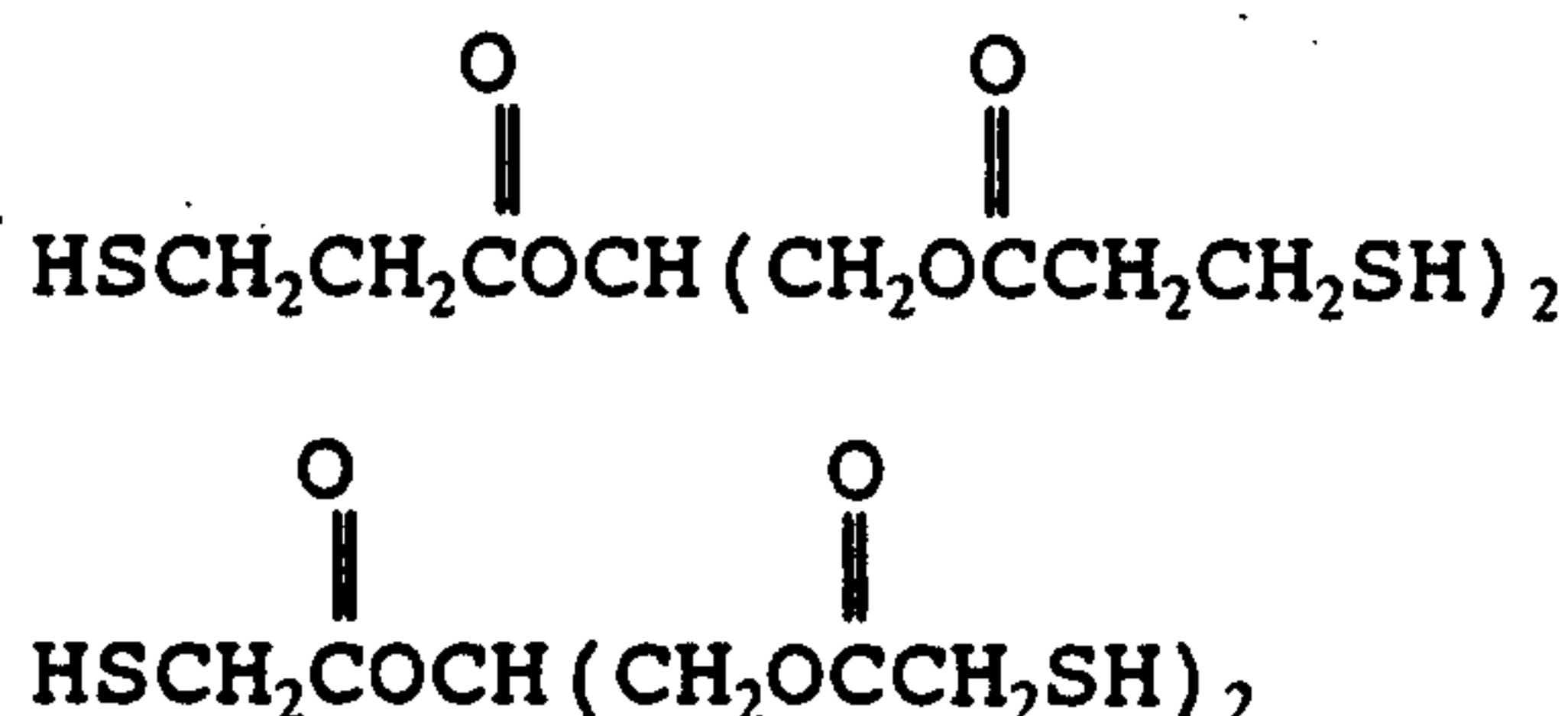
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The mercaptan-containing organic compounds represented by FORMULA VI are exemplified by, but are not limited to, the following:

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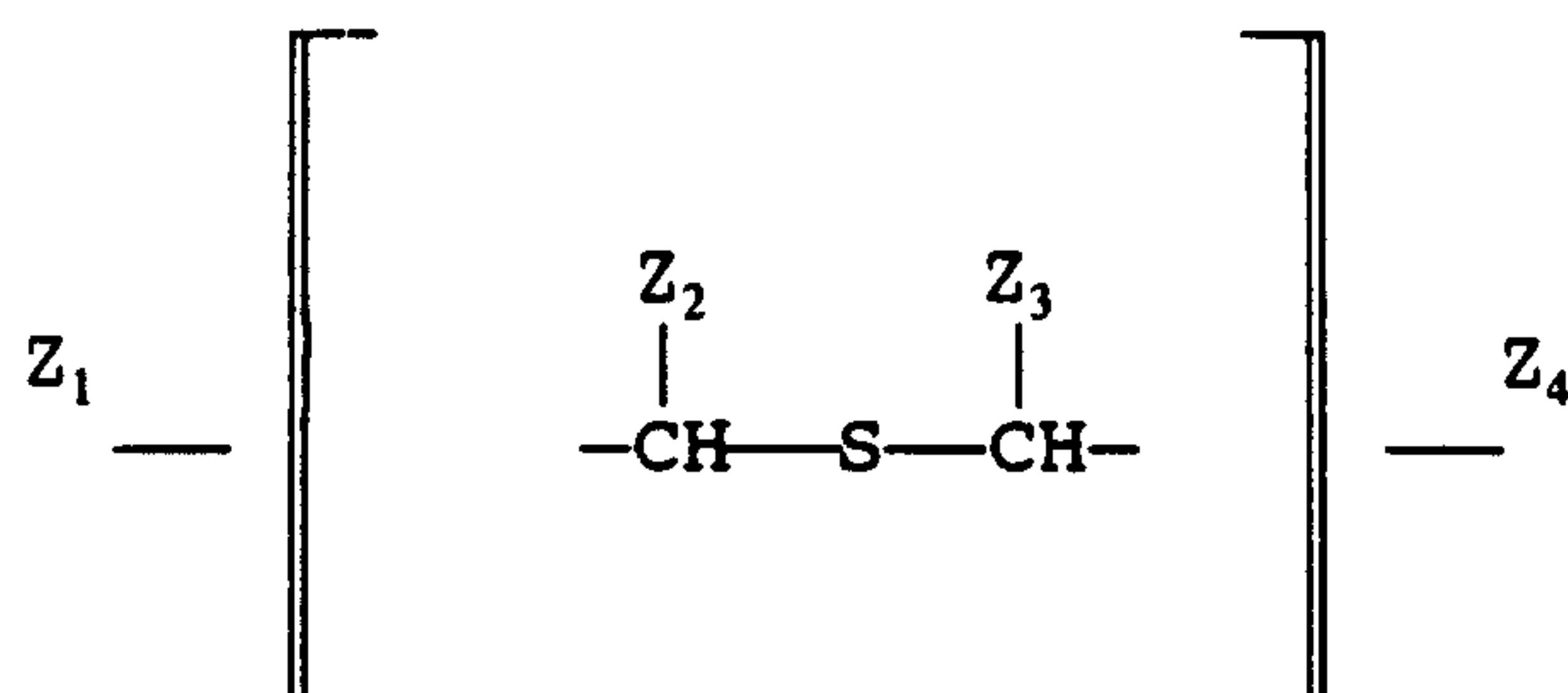


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The organic sulfides of this invention will contain the nucleus >CH-S-CH< in the molecule. This group can be attached to other structures forming saturated or unsaturated straight or branched open chain or carbocyclic or nonaromatic heterocyclic sulfides. The groups attached to the nucleus can be substituted with other groups such as aryl, carbonyl, alkoxy, aryloxy, amido, nitrile, ester, oxyether, thioether, hydroxyl and halogen groups. Such substituents are preferably at a position at least one carbon atom removed from the nucleus. Preferably, hydroxyl and halogen are at least three carbon atoms removed from the nucleus.

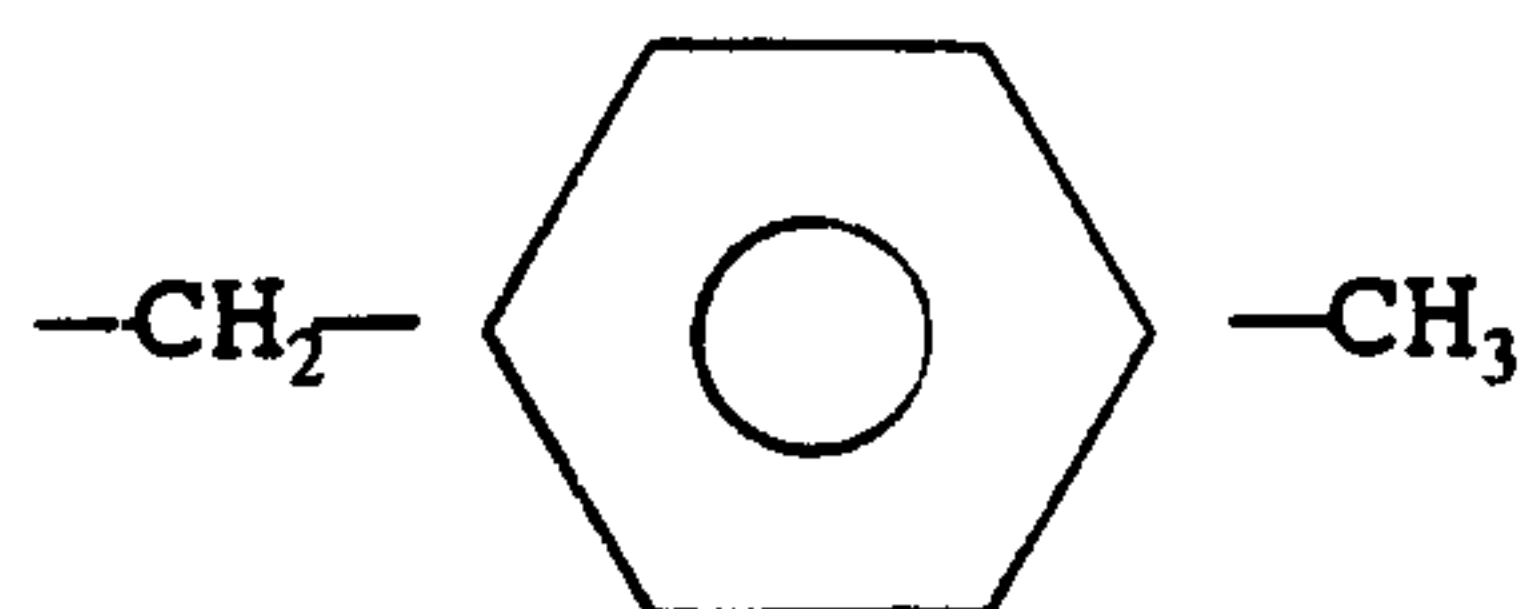
The preferred organic sulfides for use in this invention can be characterized by the formula:



in which Z_1 , Z_2 , Z_3 and Z_4 can each be hydrogen or an organic group containing from one to about thirty carbon atoms. Z_1 and Z_4 can be taken together as a heterocyclic ring including the sulfur. Z_1 , Z_2 , Z_3 and Z_4 can for example be saturated or unsaturated hydrocarbon radicals such as alkyl, alkenyl, cycloalkyl, arylalkyl and alkylarylalkyl, or radicals including oxygenated groups and/or additional oxy- and thio-carboxylic acid, oxy- and thio-carboxylic ester, hydroxyl, amido, nitrile, oxyether, thioether, and carbonyl groups and halogen atoms such as chlorine, bromine and iodine.

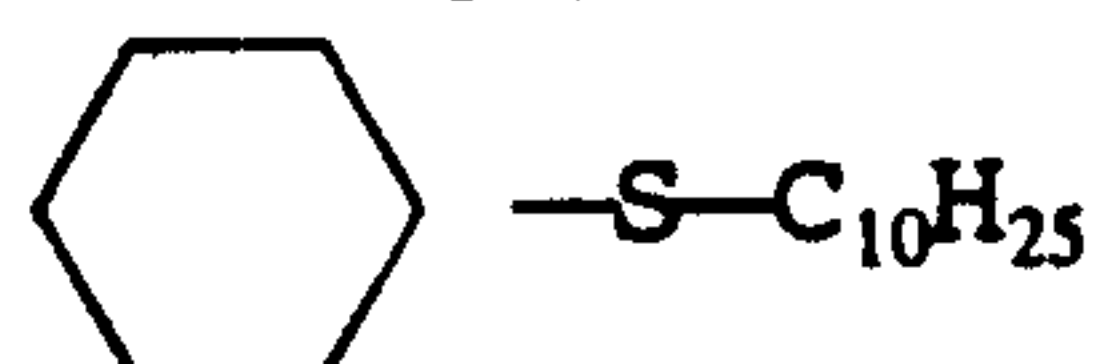
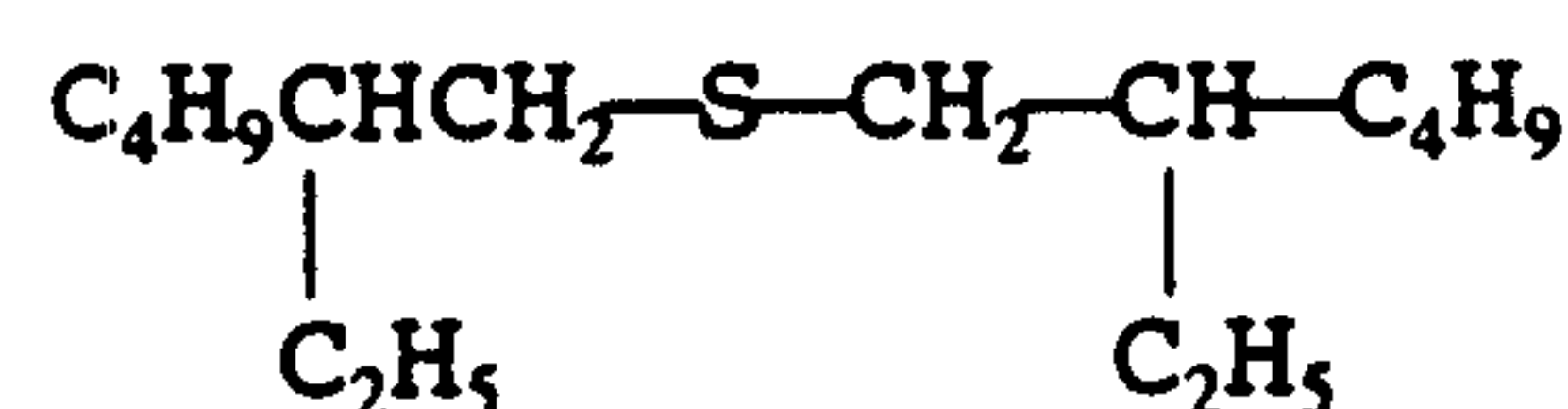
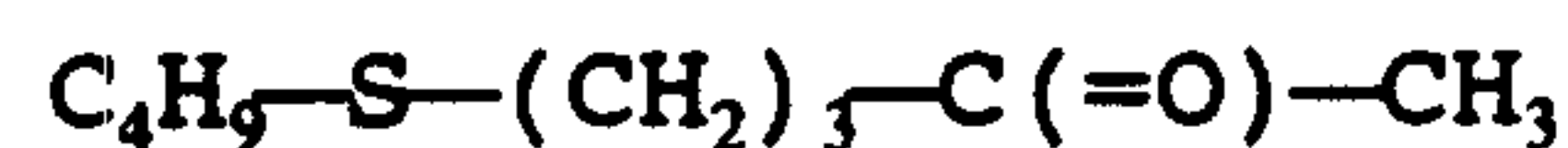
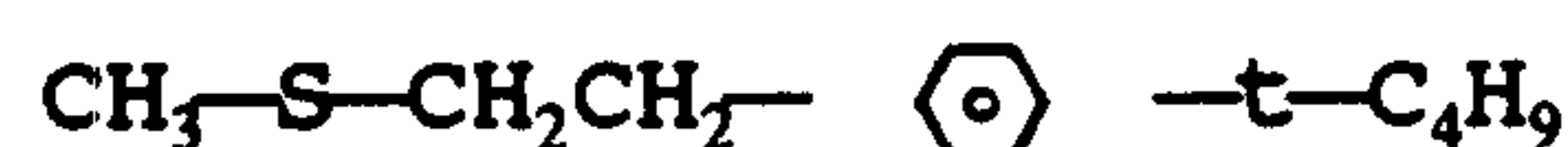
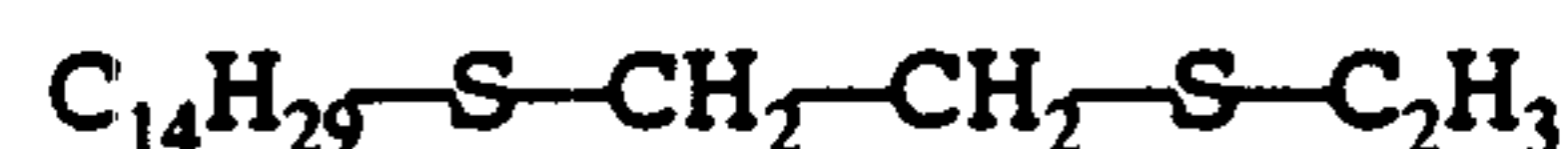
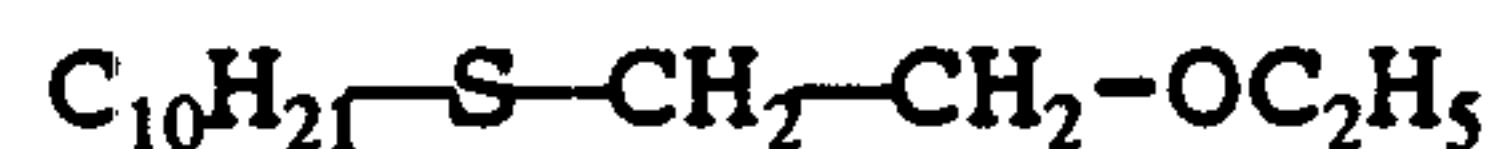
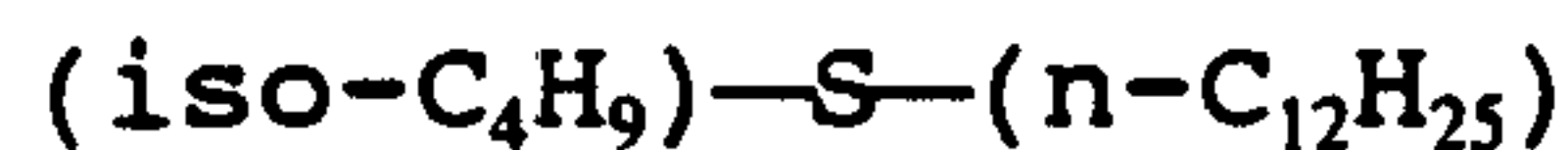
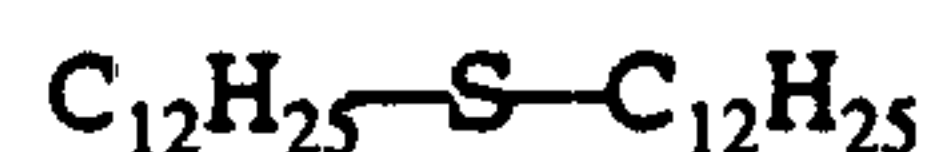
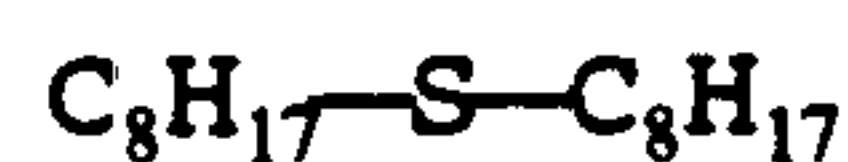
These organic sulfides should have a boiling point of at least about 175° C. to ensure nonvolatility, and preferably have a maximum molecular weight of about 800 per sulfur atom to ensure compatability with the polyvinly chloride resin compositions. The Z radicals are attached to the $>\text{CH}-\text{S}-\text{CH}<$ nucleus at any portions of the Z radical, but not through a carbonyl group or through a carbon atom or an aromatic ring. Preferably, the Z radicals do not have a hydroxyl group or halogen atom on a carbon atom alpha or beta to a thioether sulfur atom including the sulfur atom of the $>\text{CH}-\text{S}-\text{CH}<$ nucleus.

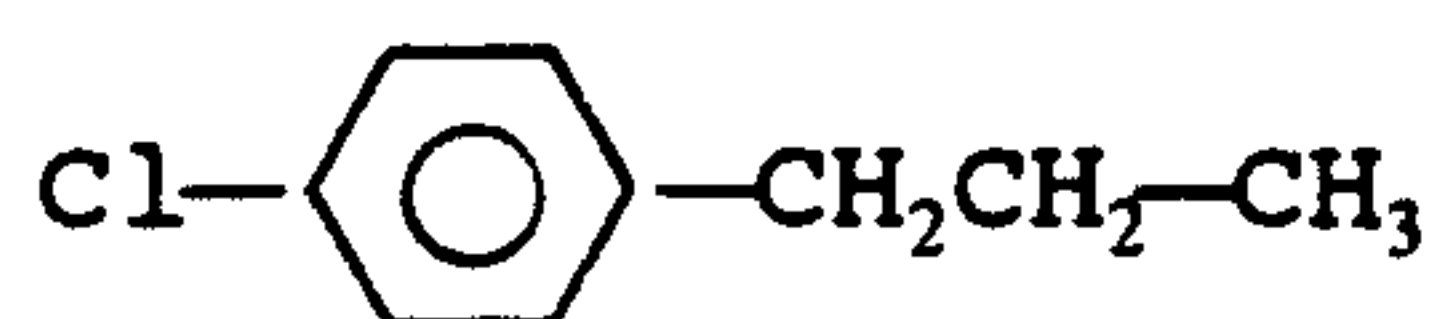
Representative Z groups include the following: methyl, ethyl, isopropyl, propyl, t-butyl, isobutyl, n-butyl, isoctyl, 2-ethylhexyl, decyl, undecyl, dodecyl, oleyl, tetra-decyl, vinyl, ethylene (as a bridge of Z_2 and Z_3), penta-methylene (as a bridge of Z_1 and Z_2), propenyl, β -phenethyl, 8-heptadecenyl, linoleyl, ethoxymethyl, butoxyethyl, ethoxyethyl, ethylthiomethyl, 3-phenylpropyl, 4-naphthylpentyl, carboxymethyl, carbomethoxyl, 11-chloroundecyl, 4-bromobutyl, p -iodo- β -phenethyl,



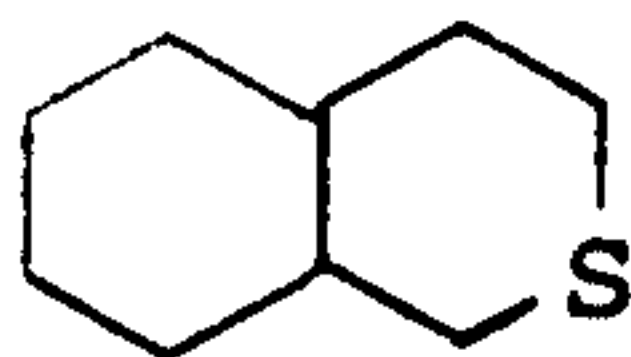
cyclopentyl, cyclohexyl, β -naphthaleneethyl, 3-hydroxypropyl, 3-carboxamidopropyl, cyanoethyl, cyanodecyl, 3-ketobutyl.

Representative organic sulfides applicable for use in this invention include the following:

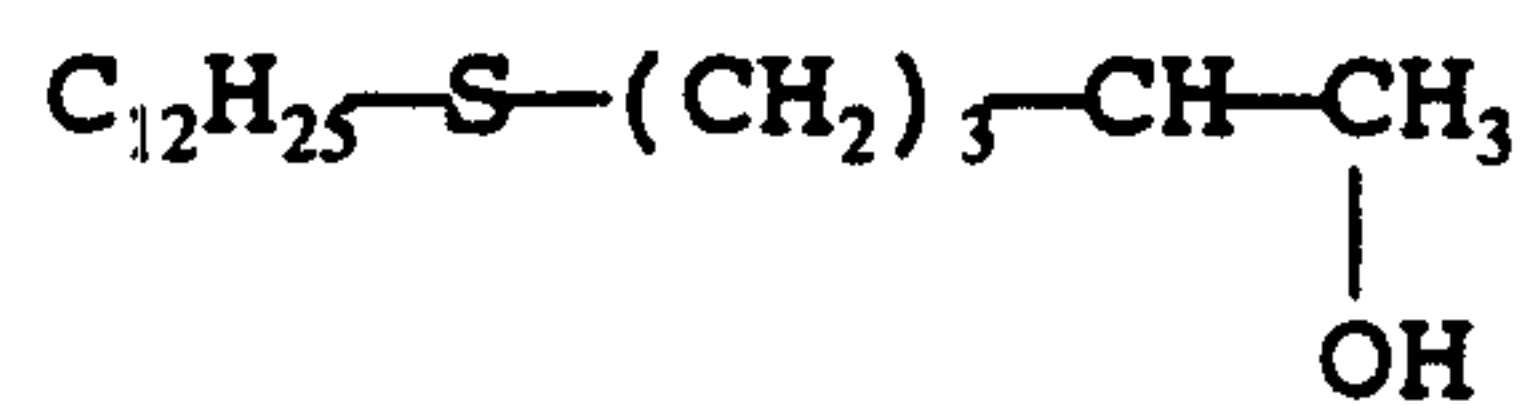




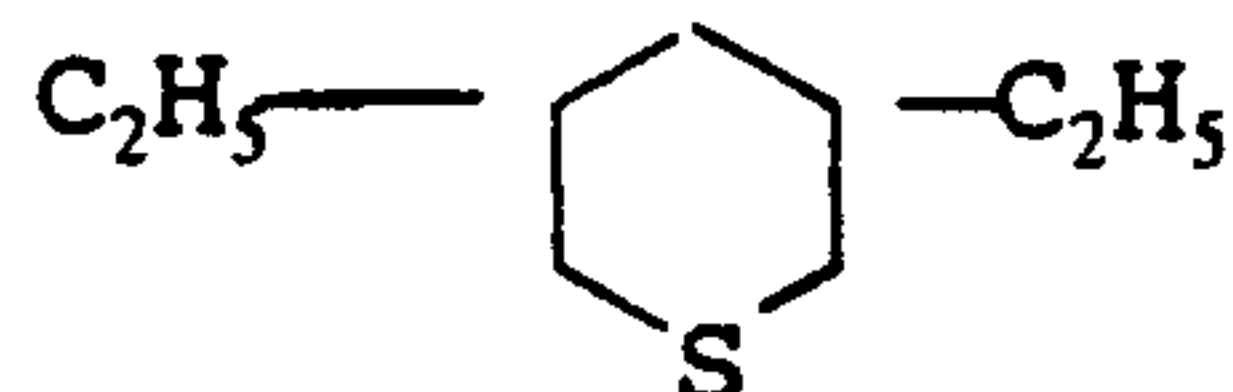
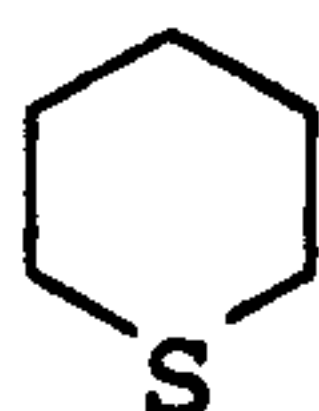
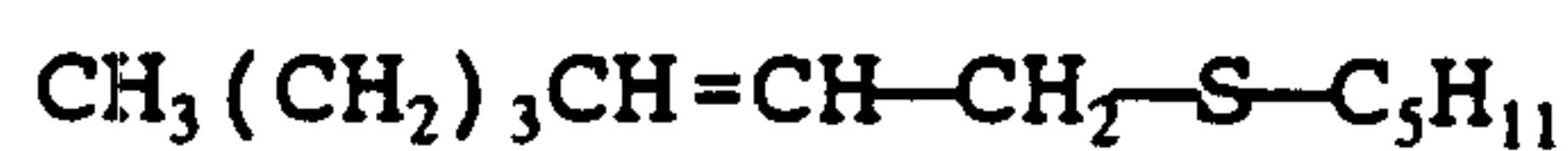
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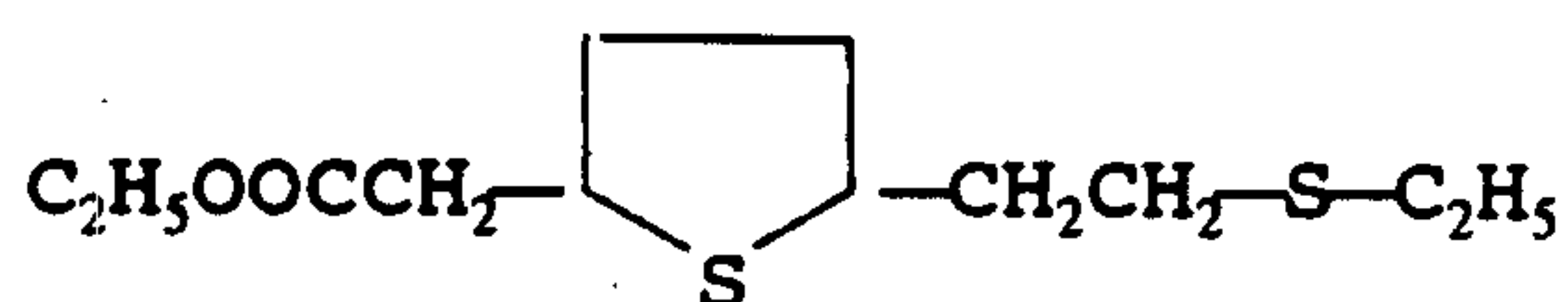
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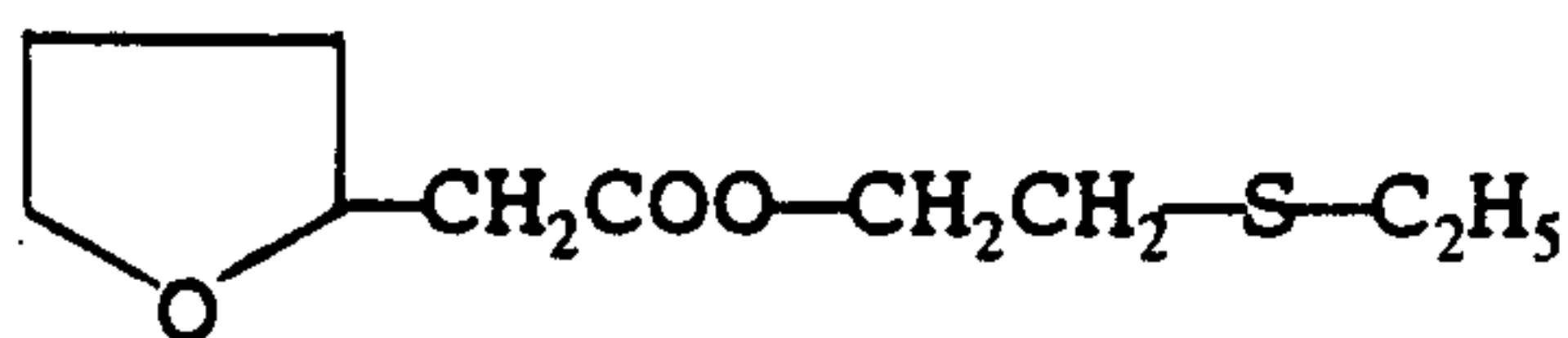
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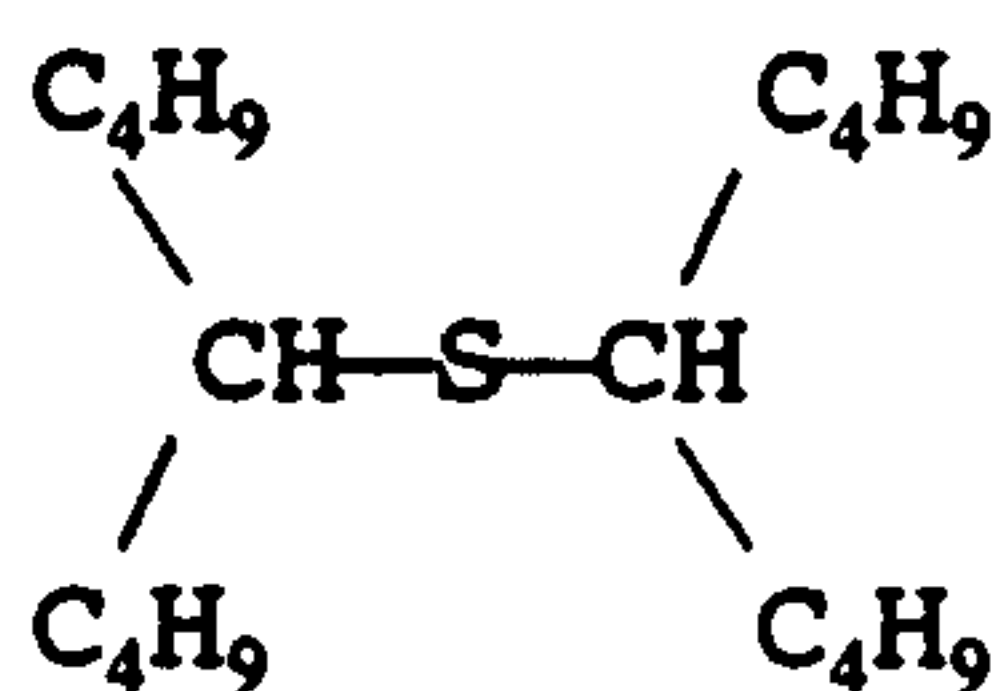
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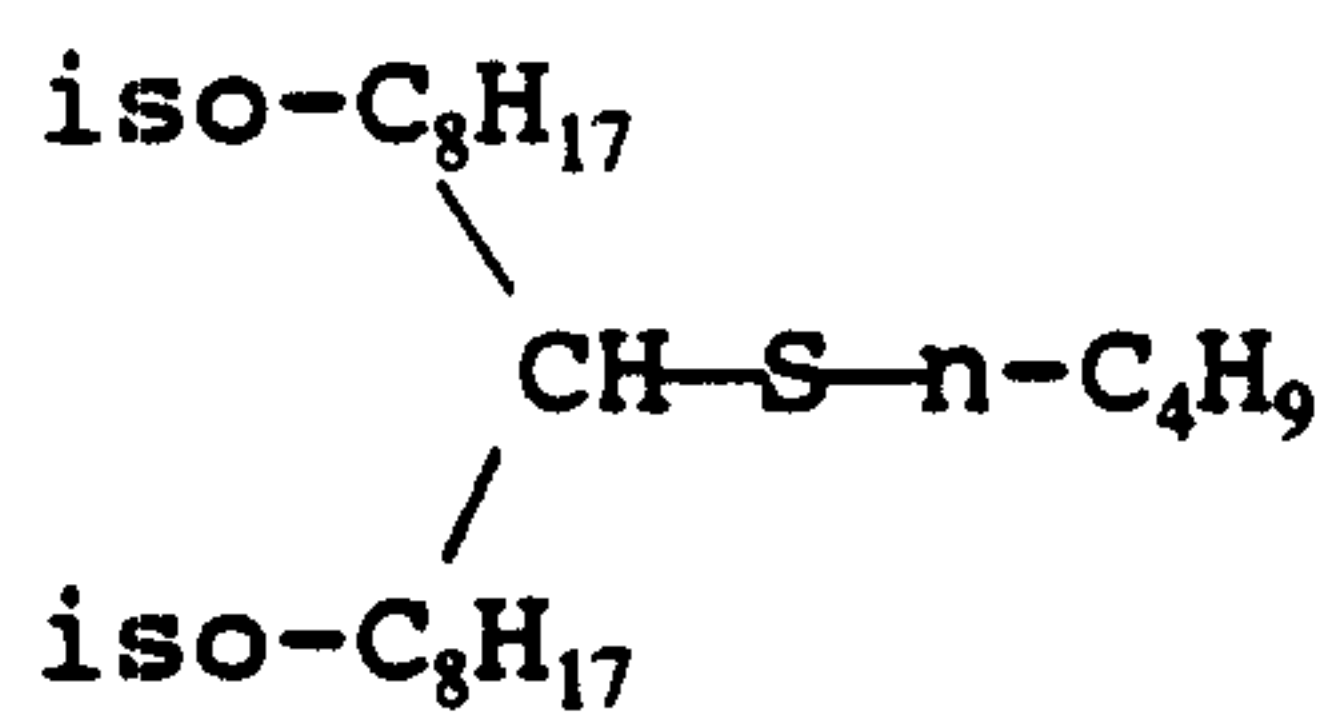
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Dithiodiglycol and the polyformals and polyacetals thereof having the formula: $\text{H}-(\text{OCH}_2\text{CH}_2\text{SSCH}_2\text{CH}_2\text{OCR}_2)_n-\text{OH}$ wherein R is

hydrogen or methyl and $n = 3-12$ are among the preferred organic sulfides for the purposes of this invention. Formation of these polymers is described in U.S. Patent Nos. 4,184,890 and 4,097,299, the teachings of which are incorporated herein by reference.

The zinc mercaptoesters of Formula B¹ are exemplified by zinc bis(2-ethylhexylthioglycolate), zinc bis(octylmercaptopropionate), zinc bis(octadecylthioglycolate), zinc bis(octadecylmercaptopropionate), and zinc bis(ethylthioglycolate). They are easily prepared by the reaction of the corresponding mercaptoacid ester with zinc chloride in the presence of a suitable hydrogen chloride scavenger such as ammonia, ammonium hydroxide, and an alkali metal hydroxide or a carbonate thereof. Another method is the condensation of the mercaptoacid ester with zinc oxide in an organic medium such as a high boiling naphtha, xylene, paraffin wax and the like. Any ratio of the zinc compound and the mercaptoester will suffice so long as the reaction conditions are such as to drive the condensation but it is preferred to use a stoichiometric ratio of the reactants. Atmospheric pressure is suitable but the reaction will proceed satisfactorily at from about 50 to about 80°C under reduced pressure. The maximum temperature is about 140-150°C.

The zinc bis-mercaptoacid ester may also be selected from among those disclosed in U.S. Patent No. 5,536,767, which is incorporated herein by reference. Such esters include the zinc bis-thioglycolate, zinc bis-mercaptopropionate, and zinc mercaptosuccinate of a polyhydric alcohol or ether, carboxylate, or ether-carboxylate thereof having at least one functional hydroxy group as exemplified by ethylene glycol, glycerol, tetraethylene glycol, trimethylolethane, pentaerythritol, glycol ethers such as tetraethylene glycol monobutyl ether, and diethylene glycol monoethyl ether, glycol mono-carboxylates such as diethylene glycol monocaprate and ethylene glycol monocaprate, and glycerol carboxylates such as glycerol monocaprate, all of which are either available commercially or are made easily by

conventional methods. The mercaptoacid esters may be made by conventional procedures wherein the mercaptoacid and the hydroxyl-group bearing compound are heated in the presence of a suitable catalyst such as methanesulfonic acid or p-toluenesulfonic acid and an azeotropic organic solvent such as toluene or heptane. Alternatively, the esterification may be conducted at reduced pressure. The reaction is continued until the acid number is reduced to about 12-15.

The acids from which the esters are derived are also generally available commercially but may be made if so desired by procedures of long-standing in the chemical arts. Mercaptoacetic acid, for example, may be made by the reaction of sodium hydro-sulfide with sodium chloroacetate and subsequent acidification. β -mercaptopropionic acid is obtained in about 80% yield from the reaction of sodium hydrosulfide with β -propiolactone in acetonitrile and subsequent acidification. Mercaptosuccinic acid may be made by adding hydrogen sulfide across the double bond of maleic anhydride followed by hydrolysis. Also suitable for the purposes of this invention are the alkyl esters of α -mercapto-propionic acid, which may be prepared from α -chloropropionic acid and sodium thiosulfate according to the procedure described in U.S. Patent No. 2,413,361, which is incorporated herein by reference.

The zinc mercaptoalkyl carboxylic acid esters of (B³) are derived from the well known "reverse esters", so called because they are the products of the reaction of mercapto alcohols and carboxylic acids instead of mercaptocarboxylic acids and alcohols. The preparation of the esters and their use as stabilizers for vinyl chloride polymers are taught in U.S. Patent No. 2,870,182, which is incorporated herein by reference. It is preferable that q is 1 or 2, and that R⁵ is preferably an alkyl group having from 7 to 17 carbon atoms or a phenyl group. They are easily prepared by the reaction of the corresponding mercaptoalkyl ester with zinc chloride in the presence of a suitable hydrogen chloride scavenger such as ammonia, ammonium hydroxide, and an alkali metal hydroxide or a carbonate thereof.

Another method is the condensation of the mercaptoalkyl ester with zinc oxide in an organic medium such as a high boiling naphtha, xylene, paraffin wax and the like. Any ratio of the zinc compound and the mercaptoalkyl ester will suffice so long as the reaction conditions are such as to drive the condensation but it is preferred to use a stoichiometric ratio of the reactants. Atmospheric pressure is suitable but the reaction will proceed satisfactorily at from about 50 to about 80°C under reduced pressure. The maximum temperature is about 140-150°C.

The halogen containing polymers which are stabilized by the stabilizer compositions of this invention and which are useful in the polymer compositions of this invention include, for example, halogenated polyolefin homopolymers, halogenated polyolefin copolymers, polymer blends containing a halogenated polyolefin homopolymer or copolymer, vinyl halide homopolymers, vinyl halide copolymers and polymer blends containing vinyl halide homopolymer or copolymers. As vinyl halide homopolymers, vinyl halide copolymers and polymer blends containing vinyl halide homopolymers or vinyl halide copolymers usable in the practice of this invention there, for example, may be used (1) polyvinyl chloride, polyvinylidene chloride, polyvinyl bromide, polyvinyl fluoride, polyvinylidene fluoride, (2) copolymers of vinyl chloride with a copolymerizable ethylenically unsaturated monomer such as vinylidene chloride, vinyl acetate, vinyl butyrate, vinyl benzoate, diethyl fumarate, diethyl maleate, other alkyl fumarates and maleates, vinyl propionate methyl acrylate, 2-ethylhexyl acrylate, butyl acrylate, ethyl acrylate, and other alkyl acrylates, methyl methacrylate, ethyl methacrylate, butyl methacrylate, hydroxyethyl methacrylate and other alkyl methacrylates, methyl alpha chloracrylate, styrene, vinyl ethers such as vinyl ethyl ether, vinyl chloroethyl ether, vinyl phenyl ether, vinyl ketones such as vinyl methyl ketone, vinyl phenyl ketone, 1 fluoro-1-chloroethelene, acrylonitrile, chloroacrylonitrile, allylidene diacetate, chloroallylidene diacetate, ethylene and propylene, and (3) polymer blends such as blends of polyvinyl chloride and polyethylene, polyvinyl

chloride and chlorinated polyethylene, polyvinyl chloride and polymethyl methacrylate, polyvinyl chloride and polybutylemethacrylate, polyvinyl chloride and polystyrene, polyvinyl chloride and acrylonitrile-butadiene-styrene copolymer, and polyvinyl chloride and polyethylene and polymethyl methacrylate. Typical vinyl halide copolymers usable in this invention include vinyl chloride-vinyl acetate (87:13), vinyl chloride-vinylidene chloride (95:5), vinyl chloride-trichloroethylene (95:5) and vinyl chloride-2-ethylhexyl acrylate (80:20). The polymer blends usable in the practice of this invention comprise physical blends of at least two distinct polymeric species and contain from 25 to 95 weight percent of vinyl halide homopolymer.

The term basic alkali or alkaline earth metal compound, as used herein, means compounds selected from the group consisting of oxides, hydroxides, sulfides, silicates, phosphates, borates, and carbonates of alkali metals and alkaline earth metals. Preferably, the alkali metals are lithium, sodium, and potassium, and the alkaline earth metals are magnesium, calcium, strontium, and barium. Examples of basic alkali or alkaline earth metal compounds include but are not limited to calcium hydroxide, magnesium hydroxide, lithium hydroxide, sodium borate, and sodium silicate.

The amount of each component in the stabilizer compositions of this invention may vary over a wide range but they will generally comprise, by weight, from about 5 to about 85 %, preferably from about 20 to about 50 %, by weight of the zinc mercaptoester, and from about 20 % to about 60%, preferably from about 20 to about 40 %, by weight of the organothio compound. The stabilizer may also contain from 0 to about 40 %, preferably about 5 to about 30 % of a basic alkali or alkaline earth compound. Although it has been discovered that the stabilizer composition of this invention is superior to one in which the organothio compound is replaced by a substituted dihydropyridine, a stabilizer composition of this invention which comprises a combination of the organothio compound and the substituted

5 dihydropyridine provides both exceptional early- and long term color hold. Thus, stabilizer compositions of this invention contain from 0 to about 40 % of the substituted dihydropyridine of U.S. 4,515,916. When used, a preferable amount of said dihydropyridine is from 5 to about 30 % of the total weight of the stabilizer composition.

10 Lubricants are optionally present in the stabilizer composition of this invention because of their important effect of reducing the temperature of the polymer compositions during mastication and extrusion.. When employed, the stabilizer composition contains up to about 75 %, preferably about 60% by weight or more, of a lubricant such as paraffin wax, calcium stearate, ethylene bis-stearamide, stearyl stearate, cetyl palmitate, and other ester waxes may be used. From 0 to about 15 % of a partially oxidized polyethylene such as Allied Chemical's AC629A product may be used as an additional lubricant in the stabilizer compositions of this invention.

20 It will be readily apparent to one of ordinary skill in the art, that the precise amount of stabilizer composition used will depend upon several factors, including, but not limited to, the particular halogen-containing organic polymer employed, the temperature to which the polymer will be subjected, and the possible presence of other stabilizing compounds. In general, the more severe the conditions to which the halogen-containing organic polymer is subjected, and the longer the term required for resisting degradation, the greater will be the amount of stabilizer composition required. In general, the effective amount of a preferred stabilizer, i.e., one containing a lubricant and a substituted dihydropyridine, may be as little as 25 about 2.0 parts by weight, or less, per hundred parts by weight of the polymer (phr) of the halogen-containing polymer. Without the lubricant and substituted dihydropyridine, the amount may be 30 about 0.6 phr or less. While there is no critical upper limit on the amount of stabilizer composition, amounts in excess of 3.5 phr of the preferred stabilizer (2 phr of stabilizer without lubricant or substituted dihydropyridine), based on the weight 35

of the halogen-containing polymer, do not yield a commensurate increase in effectiveness. More preferably, the stabilizer compositions containing both lubricant and substituted dihydropyridine are employed in amounts ranging from about 2.0 to about 3.0 phr by weight of the halogen-containing polymer. The preferred amount of stabilizer without lubricant and substituted dihydropyridine is from about 0.6 to about 1.0 phr.

The organothio compounds and the zinc mercaptoesters are preferably employed in the polymer compositions of this invention in the least amount that is sufficient to impart the desired resistance to heat deterioration to the halogen-containing organic polymers. The halogen-containing organic polymer compositions of this invention comprise from 0.1 to about 1.2 phr, preferably from about 0.2 to about 0.4 phr, of the organothio compound and from about 0.2 phr to about 1.7 phr, preferably from about 0.4 to about 0.8 phr, of the zinc mercaptoester by weight of the polymer composition. Preferably, the polymer compositions comprise from about 0.1 to about 0.8 phr of a basic alkali or alkaline earth compound and from about 0.1 to about 0.8 phr by weight of the substituted dihydropyridine.

In addition to the halogen-containing polymer and the stabilizer composition, the polymer composition of this invention may contain conventional additives such as fillers, pigments, plasticizers, dyes, antioxidants, and ultraviolet light stabilizers. Materials such as calcined clays, calcium carbonate, and talcs may be used as fillers. Suitable pigments include titanium dioxide, carbon black, and iron oxide. Phthalates, sebacates, adipates, phosphates, and fatty esters having between 16 and 150 carbon atoms are representative of well known plasticizers suitable for the compositions of this invention. Suitable antioxidants include tricresyl phosphite; 2,6-di-t-butyl-4-methyl phenol; 2,6-di-t-butyl-4-decyloxy phenol; and 2-t-butyl-4-octadecyloxy phenol.

The polymer composition of this invention may be prepared by methods well known in the art and by the use of conventional equipment. The stabilizer composition may be added to the

halogen-containing polymer with continuous blending in a high intensity mixer such as a Henschel blender. The important consideration is that the stabilizer composition and the halogen-containing polymer be thoroughly blended.

5 The stabilized halogen-containing polymer compositions of this invention may be used to form articles of manufacture such as pipe. A variety of conventional molding techniques may be employed to form the stabilized compositions into any desired shape.

10 The following examples illustrate the invention.

EXAMPLES 1-3 AND COMPARATIVE EXAMPLE 1

A PVC pipe composition containing:

	<u>INGREDIENT</u>	<u>AMOUNT</u>
15	PVC resin (k=67)	100.0 parts
	Calcium carbonate	5.00 phr
	Titanium dioxide	1.0 "
	Calcium stearate	0.45 "
	Paraffin wax	1.2 "
20	Oxidized polyethylene	0.15 "
	Calcium hydroxide	0.3
	Zinc bis-(2- ethylhexylthioglycolate)	0.4

was modified as shown in Table I and the resulting compositions
25 were processed on a standard horizontal two-roll mill (roll speeds 30F/40R) at 390°F with chips taken at one minute intervals to a maximum of 12 minutes. The color properties of the chips were measured using a Hunter Labs Colorimeter (L, a, b) and the total color change (ΔE) was selected as the measurement for
30 comparison in Table II. The dynamic thermal stability (DTS) of the compositions was measured on a Brabender Plasti-Corder PL-2000 at 190°C/60rpm with No.6 roller blades and an electric head. The DTS, shown in Table III, was recorded as the time in minutes before a sharp upturn in the torque curve during processing was
35 observed.

Table I

Example Use Level, phr	Co-Stabilizer	
1	Dithiodiglycol	0.30
2	2-mercaptoethanol	0.30
3	Dithiodiglycol polyformal	0.30
Comp. Ex. 1	1,6-dimethyl-2,5-dicarboxyethyl-1,4-dihydropyridine	0.30

Table II

PVC Color Hold (ΔE) During Processing by Two-Roll Mill @ 390°F												
min/ex	1	2	3	4	5	6	7	8	9	10	11	12
1	5.2	6.9	8.9	10.4	11.1	12.4	13.2	14.3	15.6	16.7	17.8	19.8
2	4.0	4.7	5.7	6.7	7.7	8.6	10.0	12.1	14.8	18.3	20.6	36.8
3	4.8	5.5	5.9	7.0	11.5	16.5	19.5	21.8	23.2	23.7	24.2	35.0
CE 1	2.8	2.7	3.0	3.6	4.7	7.7	24.2	56.8	-	-	-	-

Table III

PVC Dynamic Thermal Stability by Brabender @190°C	
Example	Minutes
1	12.8
2	11.2
3	9.0
CE 1	8.6

EXAMPLE 4 AND COMPARATIVE EXAMPLE 2

A PVC pipe composition containing:

5	<u>INGREDIENT</u>	<u>AMOUNT</u>
	PVC resin (k =65)	100.0 parts
	Calcium carbonate	5.00 phr
	Titanium dioxide	1.0 "
10	Calcium stearate	0.60 "
	Paraffin wax	1.2 "
	Oxidized polyethylene	0.15 "

15 was modified as shown in Table IV and the resulting compositions were processed on a standard horizontal two-roll mill (roll speeds 30F/40R) at 390°F (199°C) with chips taken at one minute intervals. The color properties of the chips were measured using a Hunter Labs Colorimeter (L, a, b) and the whiteness index (WI) was selected as the measurement for comparison in Table V. The DTS, measured as described above but at 190°C and at 60 RPM, is shown in Table VI. The composition in Comparative Example 2 is similar to that of Example 13 in U.S. Patent No. 3,417,039 (Penneck).

Table IV

25	Example	Co-stabilizers	phr
	4	Zinc bis-(2-ethylhexylthioglycolate) Dithiodiglycol polyformal (n = 5) Calcium hydroxide	0.40 0.30 0.30
	CE 2	Zinc Bis-(2-ethylhexyl maleate) Bis-(n-decyloxyethyl) sulfide (b.p. > 200 °C) 2,2-dimethyl-1,3-propanediol	1.00 0.50 2.00

Table V

30

Table V

PVC Color Hold (ΔE) During Processing by Two-Roll Mill @ 390°F White Tile Standard												
min/ex	1	2	3	4	5	6	7	8	9	10	11	12
4	11.4	17.0	20.9	21.0	22.0	23.0	23.8	23.9	24.5	25.1	25.3	25.8
CE 2	2.6	3.6	11.3	44.7	—	char						

Table VI

PVC Dynamic Thermal Stability by Brabender @190°C				
Example	Fusion Time Minutes	Stability Time Minutes	Min. Torque g.m	Max. Torque g.m
4	1.9	19.0	1275	2500
CE 2	2.5	4.5	1900	2000

EXAMPLE 5 AND COMPARATIVE EXAMPLES 3 & 4

A PVC pipe composition containing:

INGREDIENTAMOUNT

PVC resin (k =65)	100.0 parts
Calcium carbonate	5.00 phr
Titanium dioxide	1.0 "
Calcium stearate	0.60 "
Paraffin wax	1.2 "
Oxidized polyethylene	0.20 "

was modified as shown in Table VII and the resulting compositions were processed on a standard horizontal two-roll mill (roll speeds 30F/40R) at 390°F (199°C) with chips taken at one minute intervals. The color properties of the chips were measured using a Hunter Labs Colorimeter (L, a, b) and the total energy (ΔE) was selected as the measurement for comparison in Table VIII.

Table VII

Example	Co-stabilizers	phr
5	Zinc bis-(2-ethylhexylthioglycolate) Dithiodiglycol Calcium hydroxide	0.40 0.30 0.30
CE 3	Zinc Bis-(2-ethylhexyl maleate) 2,2-dimethyl-1,3-propanediol Dithiodiglycol	0.50 0.25 0.30
CE 4	Zinc Bis-(2-ethylhexyl maleate) Dithiodiglycol	0.50 0.30

Table VIII

PVC Color Hold (ΔE) During Processing by Two-Roll Mill @ 390°F White Tile Standard												
min/ex	1	2	3	4	5	6	7	8	9	10	11	12
5	6.3	10.9	14.6	15.7	16.9	17.8	19.0	19.6	21.0	21.7	23.0	23.9
CE 3	4.8	66.4	8.7	9.2	9.9	11.7	char					
CE 4	5.4	7.8	9.6	10.0	10.4	14.2	char					

Table IX

PVC Dynamic Thermal Stability by Brabender @190°C		
Example	Min. Torque g.m	Max. Torque g.m
5	1375	2425
CE 3	1600	1800
CE 4	1625	1825

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A heat stabilizer composition comprising:

(A) an organothio compound;

at least one zinc mercaptoester selected from the group consisting of

(B¹) a zinc mercaptoacid ester having the formula:

$$\text{Zn} - [\text{S}(\text{CH}_2)_x - \text{C}(=\text{O})\text{OR}]_2$$
, wherein R is a hydrocarbyl radical having from 2 to about 22 carbon atoms and x is 1 or 2;

(B²) a zinc mercaptoacid ester having the formula:

$$\text{Zn} - [\text{S}(\text{CHR})_a (\text{CH}_2)_b - [\text{C}(=\text{O})\text{O}]\text{R}']_2$$
; wherein:

R' is methyl or C(=O)OR";

R" is $(\text{CH}_2 - [\text{C} - (\text{R}^*)(\text{R}^{2*})]_y \text{CH}_2\text{O})_z \text{R}^{3*}$;

R* is H, alkyl, or hydroxyalkyl;

R^{2*} is OH, hydroxy-substituted alkyl, or O(O=)

C-R^{4*};

R^{3*} is H, (O=)C-R^{4*}, or alkyl,

R^{4*} is alkyl or alkenyl;

a = 0 or 1; B = 1 or 2; y = 0 or 1; and z

= 1 to 4; with the proviso that when z is

greater than 1, y = 0;

and

(B³) a zinc mercaptoalkyl carboxylic acid ester having the formula:

$$\text{Zn} [\text{SCH}_2 (\text{CH}_2)_q \text{O} - \text{C}(=\text{O})\text{R}^{5*}]_2$$
; wherein

R^{5*} is an alkyl or alkenyl group having from 1 to 18 carbon atoms or an aryl group having

from 6 to 12 carbon atoms, and q is from 1 to 6;

(C) from 0 to about 20% of a basic alkali or alkaline earth metal compound; and

(D) from 0 to about 10% by weight of a substituted dihydropyridine.

2. The composition of claim 1 wherein the organothio compound is a mercaptan.

3. The composition of claim 1 wherein the organothio compound is dithiodiglycol.

4. The composition of claim 1 wherein the organothio compound is dithiodiglycol polyformal.

5. The composition of claim 1 wherein the zinc mercaptoester is the zinc mercaptoacid ester of B¹.

6. The composition of claim 1 wherein the zinc mercaptoester is the zinc mercaptoacid ester of B².

7. The composition of claim 1 wherein the zinc mercaptoester is the zinc mercaptoalkyl ester of B³.

8. The composition of claim 5 wherein x is 1 and R has 8 carbon atoms.

9. The composition of claim 6 wherein z = 2 and R³ is alkyl...

10. The composition of claim 6 wherein z = 1, y = 1, and R² is OH.

11. The composition of claim 6 wherein Z = 1, R³ is (O=)C-R⁴, and R⁴ is alkyl.

12. The composition of claim 6 wherein Z = 1, y = 1, R¹ is alkyl, and R² is hydroxyalkyl.

13. The composition of claim 7 wherein q is 1 and R^{5*} is an alkyl group having from 1 to 7 carbon atoms.

14. The composition of claim 1 wherein a substituted dihydropyridine constitutes from about 5% to about 20% of the total weight.

15. The composition of claim 1 wherein a basic alkali or alkaline earth metal compound constitutes from about 10% to about 15% of the total weight.

16. A polymer composition stabilized against the deteriorative effects of heat comprising a halogen-containing polymer and a stabilizer composition comprising;

(A) an organothio compound;

at least one zinc mercaptoester selected from the group consisting of

(B¹) a zinc mercaptoacid ester having the formula:

$$\text{Zn} - [\text{S}(\text{CH}_2)_x - \text{C}(=\text{O})\text{OR}]_2$$
, wherein R is a hydrocarbyl radical having from 2 to about 22 carbon atoms and x is 1 or 2;

(B²) a zinc mercaptoacid ester having the formula:

$$\text{Zn} - [\text{S}(\text{CHR})_a (\text{CH}_2)_b - [\text{C}(=\text{O})\text{O}] \text{R}']_2$$
; wherein:

R' is methyl or C(=O)OR'';

R'' is $[(\text{CH}_2 - [\text{C} - (\text{R}^*) (\text{R}^{2*})]_y \text{CH}_2\text{O})_2 \text{R}^{3*}]$;

R* is H, alkyl, or hydroxyalkyl;

R^{2*} is OH, hydroxy-substituted alkyl, or

O(O=)C-R^{4*};

R^{3*} is H, (O=)C-R^{4*}, or alkyl,

R^{4*} is alkyl or alkenyl;

a = 0 or 1; b = 1 or 2; y = 0 or 1; and z = 1 to 4; with the proviso that when z is greater than 1, y = 0;

and

(B³) a zinc mercaptoalkyl carboxylic acid ester having the formula:

$$\text{Zn} [\text{SCH}_2 (\text{CH}_2)_q \text{O} - \text{C}(=\text{O})\text{R}^{5*}]_2$$
; wherein R^{5*} is an alkyl or alkenyl group having from 1 to 18 carbon atoms or an aryl group having from 6 to 12 carbon atoms, and q is from 1 to 6;

(C) from 0 to about 20% of a basic alkali or alkaline earth metal compound; and

(D) from 0 to about 10% by weight of a substituted dihydropyridine.

17. The polymer composition of claim 16 wherein the amount of stabilizer composition is from about 0.4 to about 2.0% of the total weight.

18. An article fabricated from a polymer composition stabilized against the deteriorative effects of heat comprising a halogen-containing polymer and a stabilizer composition comprising:

(A) an organothio compound;

at least one zinc mercaptoester selected from the group consisting of

(B¹) a zinc mercaptoacid ester having the formula:

$$\text{Zn} - [\text{S}(\text{CH}_2)_x - \text{C}(=\text{O})\text{OR}]_2$$
, wherein R is a hydrocarbyl radical having from 2 to about 22 carbon atoms and x is 1 or 2;

(B²) a zinc mercaptoacid ester having the formula:

$$\text{Zn} - [\text{S}(\text{CHR})_a (\text{CH}_2)_b - [\text{C}(=\text{O})\text{O}]\text{R}']_2$$
; wherein:

R' is methyl or C(=O)OR";

R" is $[(\text{CH}_2 - [\text{C} - (\text{R}^*) (\text{R}^{2*})]_y \text{CH}_2\text{O})_2 \text{R}^{3*}]$;

R* is H, alkyl, or hydroxyalkyl;

R^{2*} is OH, hydroxy-substituted alkyl, or
 $O(O=)C-R^{4*}$;

R^{3*} is H, $(O=)C-R^{4*}$, or alkyl,

R^{4*} is alkyl or alkenyl;

5 $a = 0$ or 1 ; $b = 1$ or 2 ; $y = 0$ or 1 ; and $z = 1$
to 4 ; with the proviso that when z is greater
than 1 , $y = 0$;

and

10 (B³) a zinc mercaptoalkyl carboxylic acid ester
having the formula:

$Zn [SCH_2 (CH_2)_q O-C(=O)R^{5*}]_2$; wherein

R^{5*} is an alkyl or alkenyl group having from 6
to 12 carbon atoms, and q is from 1 to 6 ;

15 (C) from 0 to about 20% of a basic alkali or
alkaline earth metal compound; and

(D) from 0 to about 10% by weight of a substituted
dihydropyridine.