



(72) SCHOLL, THOMAS, DE

(71) BAYER AKTIENGESELLSCHAFT, DE

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(54) **PROCESSUS DE SYNTHÈSE D'ACIDES
POLYTHIO-POLYCARBOXYLIQUES**

(54) **PROCESS FOR THE PREPARATION OF
POLYTHIOPOLYCARBOXYLIC ACIDS**

(57) Polythiopolycarboxylic acids with a relatively high content of bonded sulfur can be prepared in a high purity by a simple process, without undesirable waste products, such as hydrochloric acid and sodium chloride, being obtained, by reacting mercaptoalkylcarboxylic acids with sulfur at elevated temperature.

**PROCESS FOR THE PREPARATION OF POLYTHIOPOLYCARBOXYLIC
ACIDS**

ABSTRACT OF THE DISCLOSURE

Polythiopolycarboxylic acids with a relatively high content of bonded sulfur can be prepared in a high purity by a simple process, without undesirable waste products, such as hydrochloric acid and sodium chloride, being obtained, by reacting mercaptoalkylcarboxylic acids with sulfur at elevated temperature.

PROCESS FOR THE PREPARATION OF POLYTHIOPOLYCARBOXYLIC ACIDS

5 FIELD OF THE INVENTION

The present invention relates to a process for the preparation of polythio-
polycarboxylic acids which is based on the reaction of mercaptoalkylcarboxylic acids
with sulfur at elevated temperature. The polythiocarboxylic acids prepared in this
10 manner have a high content of bonded sulfur in the form of a polysulfidic distribution
and are suitable, for example, for the preparation of rubber mixtures and rubber
vulcanization products.

BACKGROUND OF THE INVENTION

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Polythiodicarboxylic acids of the structure $R^1-(S)_n-R^2$ are known from U.S. Patent
No. 5,130,363 and are suitable e.g. for the production of rubber vulcanization
products with improved hysteresis properties. These compounds were prepared by
the reaction of mercaptoalkylcarboxylic acids with sulfur chlorides, such as sulfur
20 dichloride or disulfur chloride. A disadvantage here is the handling of the corrosive
sulfur chlorides and of the by-product hydrogen chloride.

EP-A 0,780,429 describes a preparation process for a mixture of di-, tri- and tetra-
thiodipropionic acid starting from 3-chloropropionic acid and sodium polysulfide in
25 water. In addition to the formation of amounts of NaCl as a waste product, a further
disadvantage of this process is that the content of bonded sulfur is narrowly limited
and a mixture which comprises dithiodipropionic acid to the extent of approx. 70%
and tri- and tetrathiodipropionic acid only to the extent of approx. 30% is therefore
formed.

30

U.S. Patent No. 4,119,549 discloses a process for the preparation of sulfurized
compounds by reaction of olefins with hydrogen sulfide and sulfur. The process

leads to non-uniform products if the olefin components employed are those with double bonds which readily undergo polymerization, in particular α,β -unsaturated carboxylic acids.

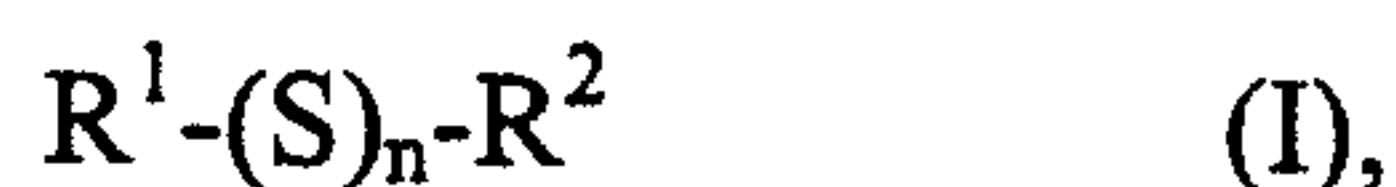
5 SUMMARY OF THE INVENTION

Therefore, the object of the present invention is a preparation process for particularly pure polythiopolycarboxylic acids which allows the preparation of relatively high contents of bonded sulfur and gives no hydrochloric acid and sodium chloride as
10 undesirable waste products.

It has now been found that polythiopolycarboxylic acids can be obtained in a high purity and with a high content of bonded sulfur and without sodium chloride or hydrogen chloride as a waste product by a simple route by heating mercapto-
15 alkylcarboxylic acids with sulfur.

DETAILED DESCRIPTION OF THE INVENTION

Therefore, the present invention provides a process for the preparation of
20 polythiopolycarboxylic acids of the formula



wherein

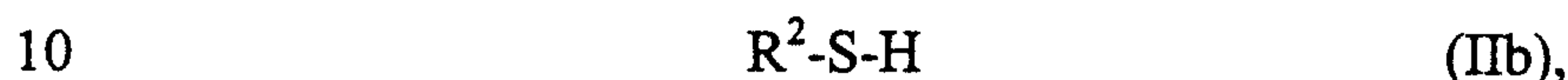
25 R^1 and R^2 are identical or different and represent a linear or branched C_1 - C_{36} -alkyl radical, preferably C_1 - C_{12} -alkyl radical, or a C_5 - C_{18} -, preferably C_5 - C_{12} -cycloalkyl radical, wherein the alkyl radical and the cycloalkyl radical are substituted by 1 to 4, preferably 1 to 2, carboxyl or carboxylate groups and wherein, in the case of a carboxylate group, an ammonium group, a C_1 - C_{18} -
30 mono-, -di- or -trialkylammonium group, a C_6 - C_{18} -mono-, -di- or

-triarylammonium group, a C₇-C₂₁-mono-, -di- or -trialkylarylammonium group or a 1- to 4-valent metal ion is present as the cation, and

n represents an integer from 2 to 14,

5

wherein mercaptoalkylcarboxylic acids of the formulae



wherein

R¹ and R² have the above meaning,

15

or mixtures of corresponding mercaptoalkylcarboxylic acids are reacted with sulfur in a molar ratio of 1:0.25 to 1:5, preferably 1:0.5 to 1:3, more preferably 1:1 to 1:2.5, at temperatures of 70 to 220°C, preferably 100 to 170°C, optionally in the presence of acid or alkaline catalysts and optionally in the presence of an inert solvent.

20

Possible radicals R¹ and R² are, for example:

-CH₂COOH, -CH₂CH₂COOH, -CH(CH₃)COOH, -CH(COOH)CH₂COOH,
-cyclohexyl-COOH.

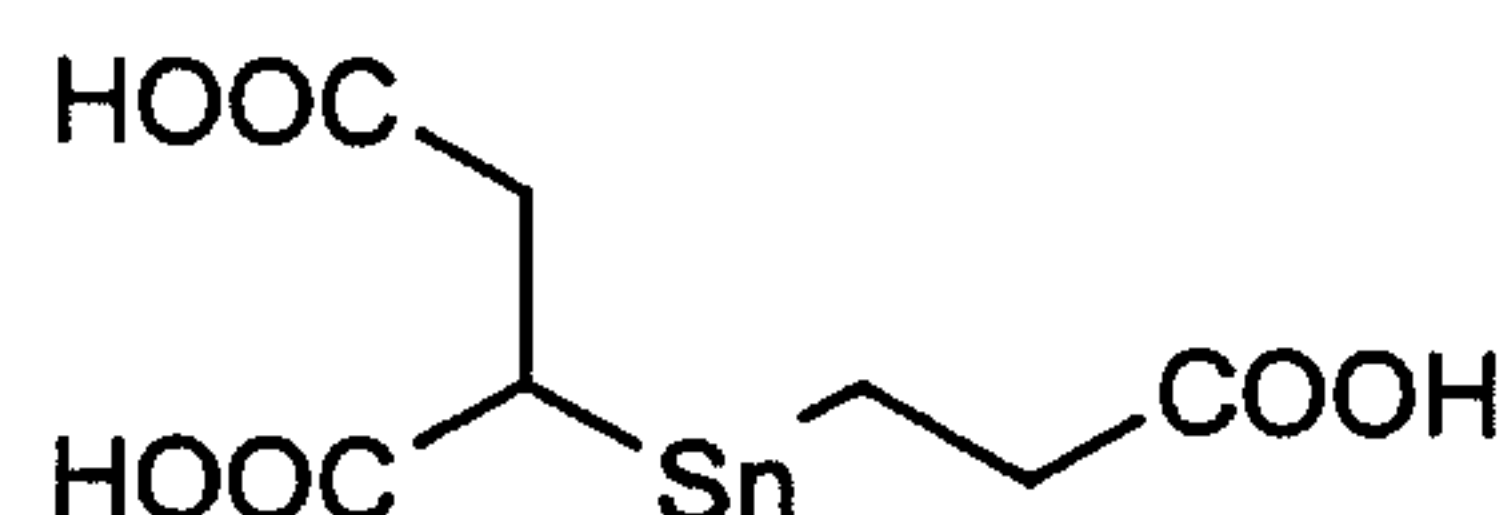
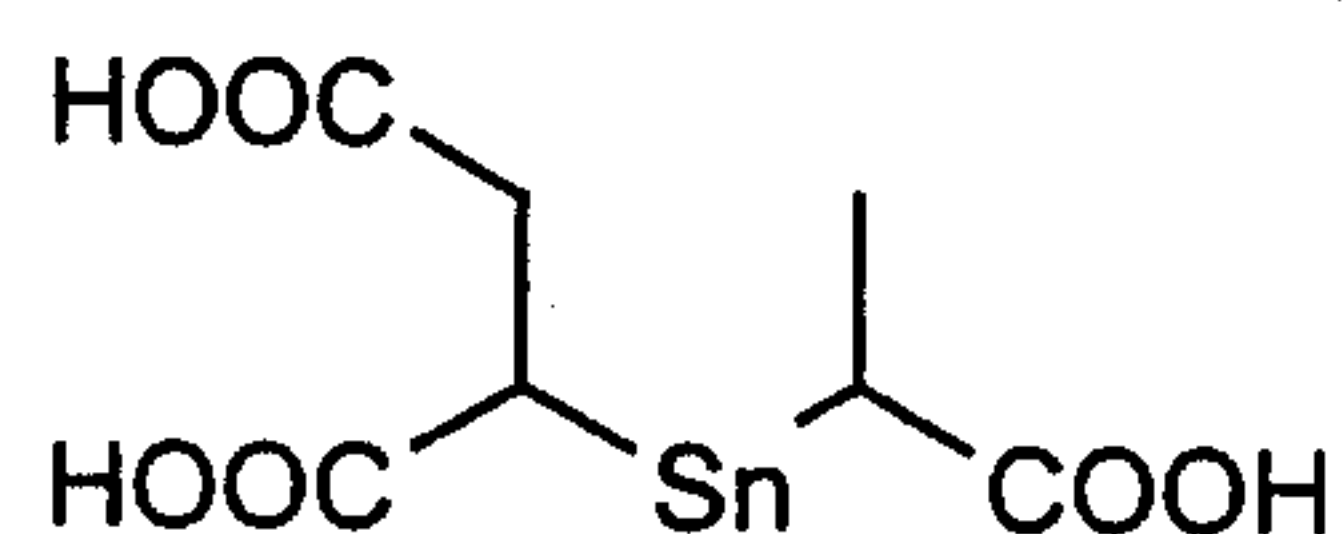
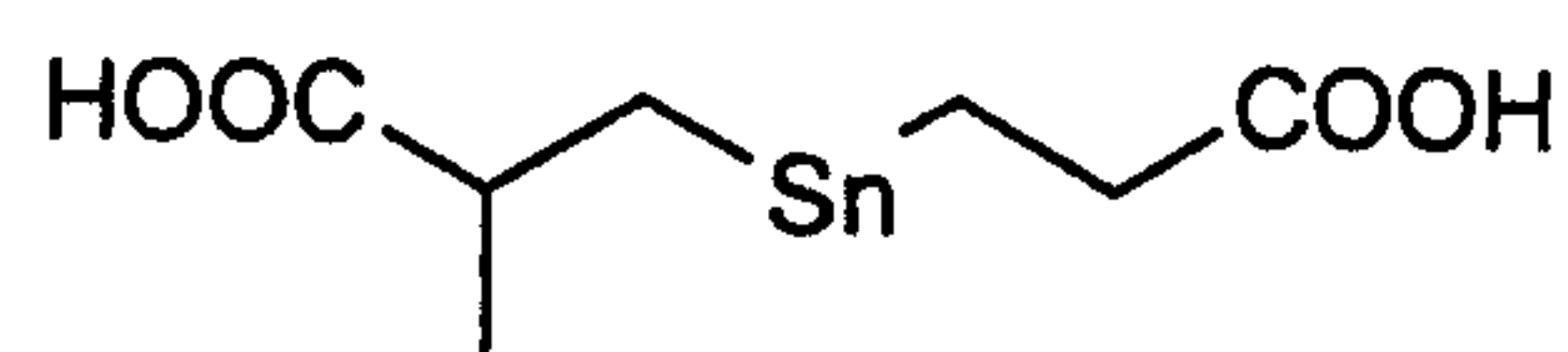
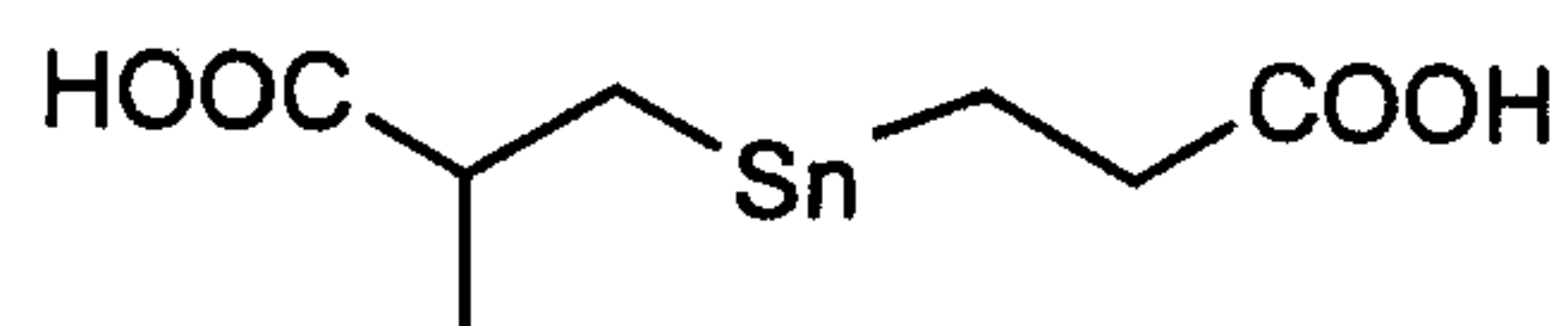
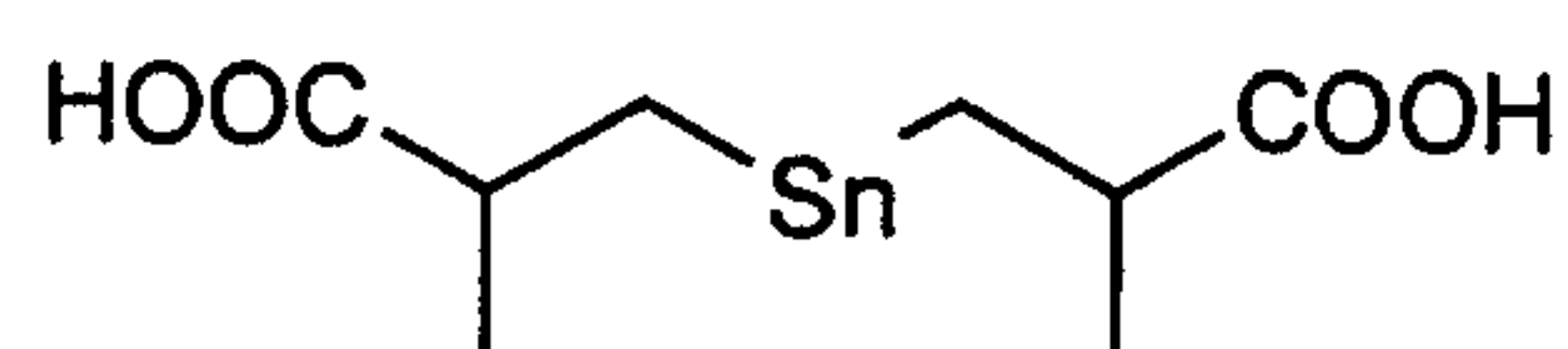
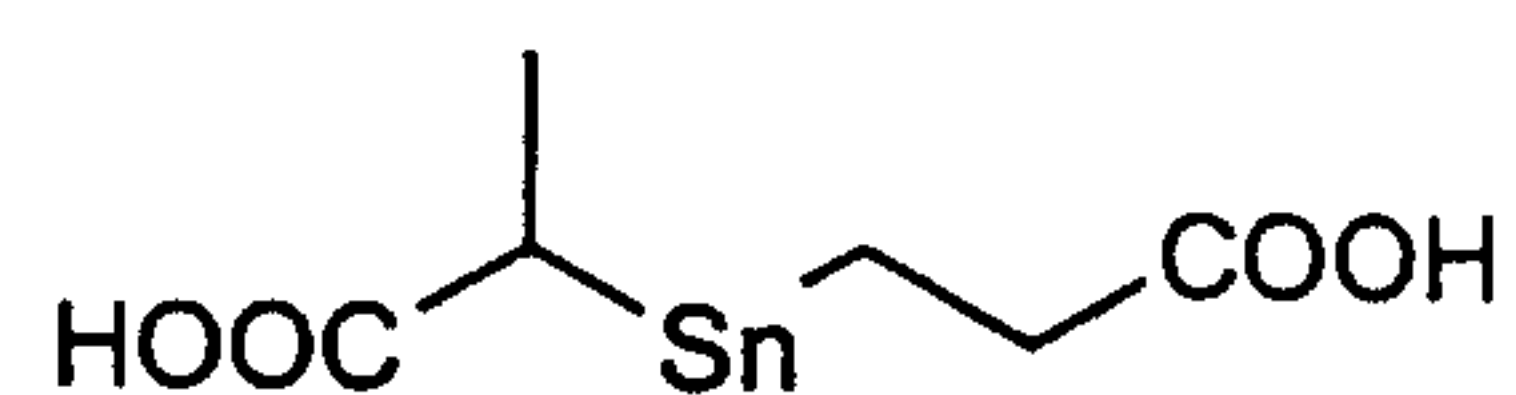
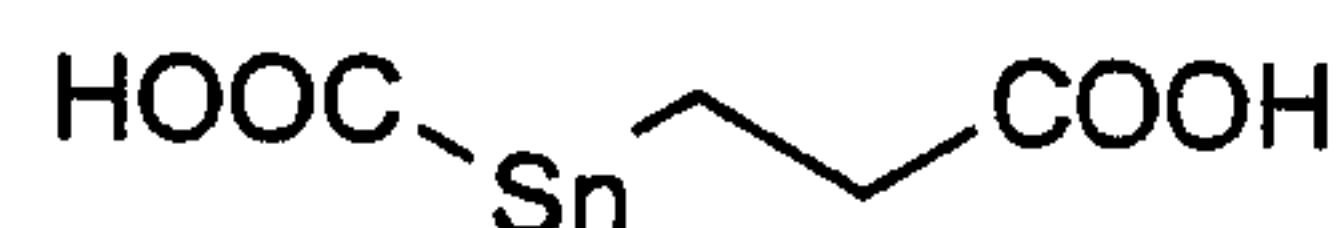
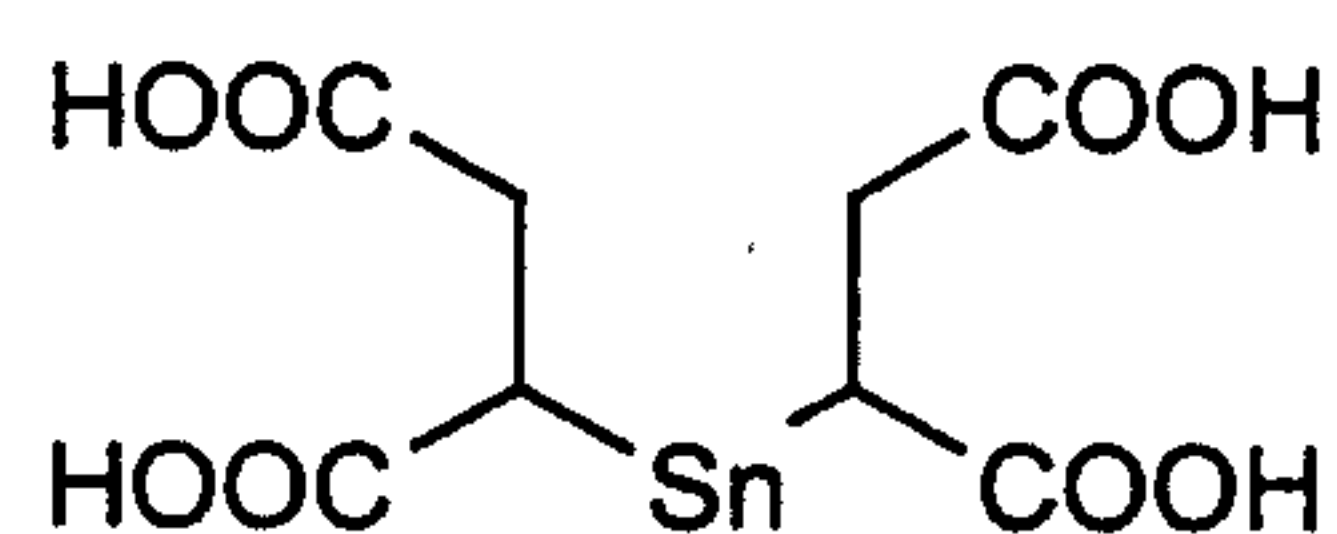
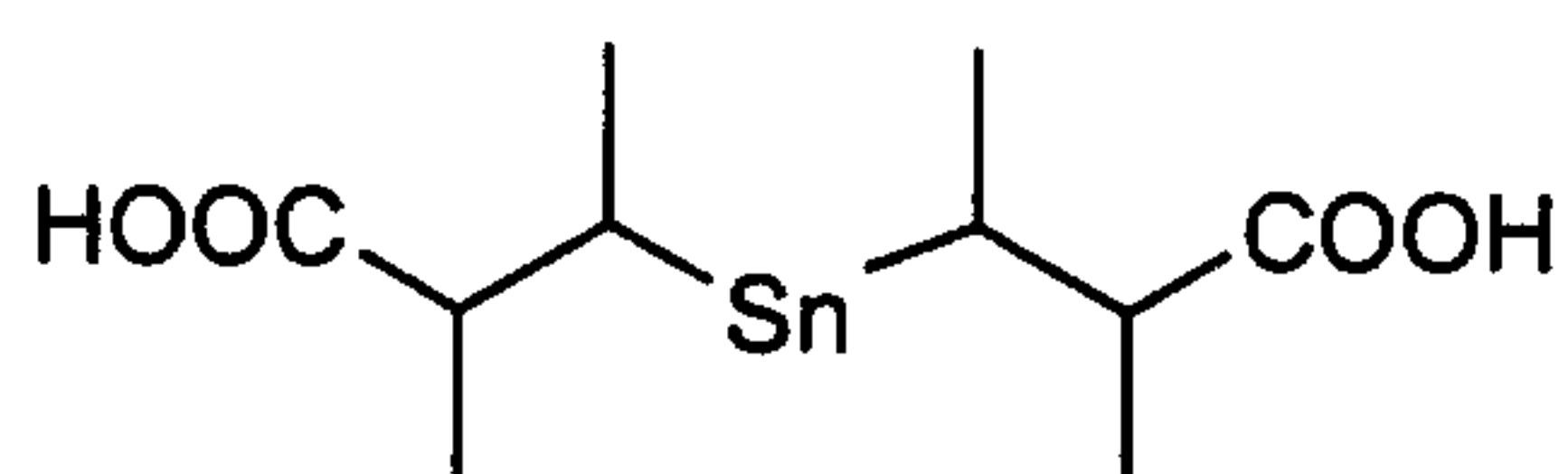
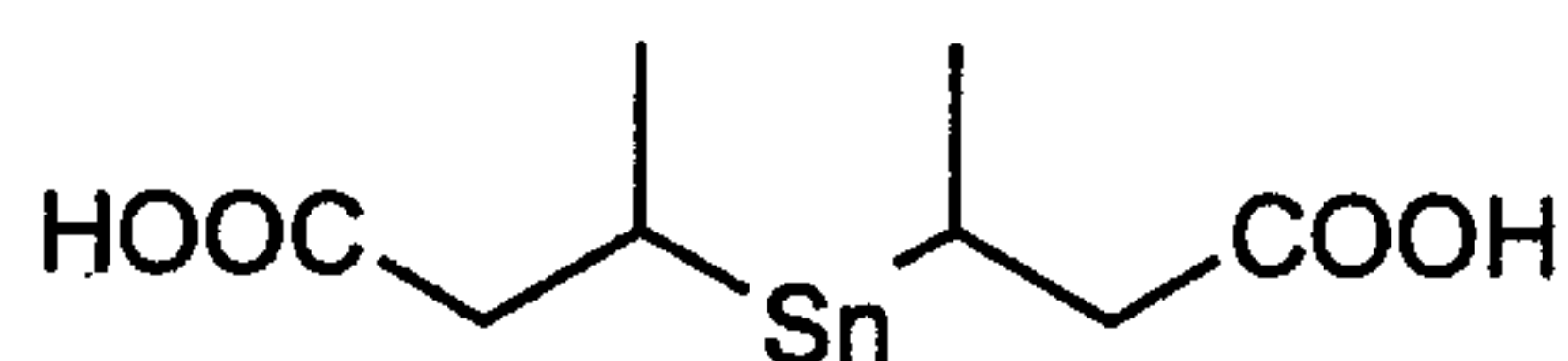
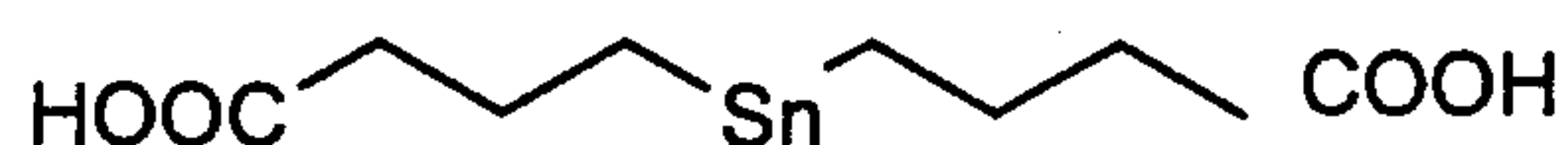
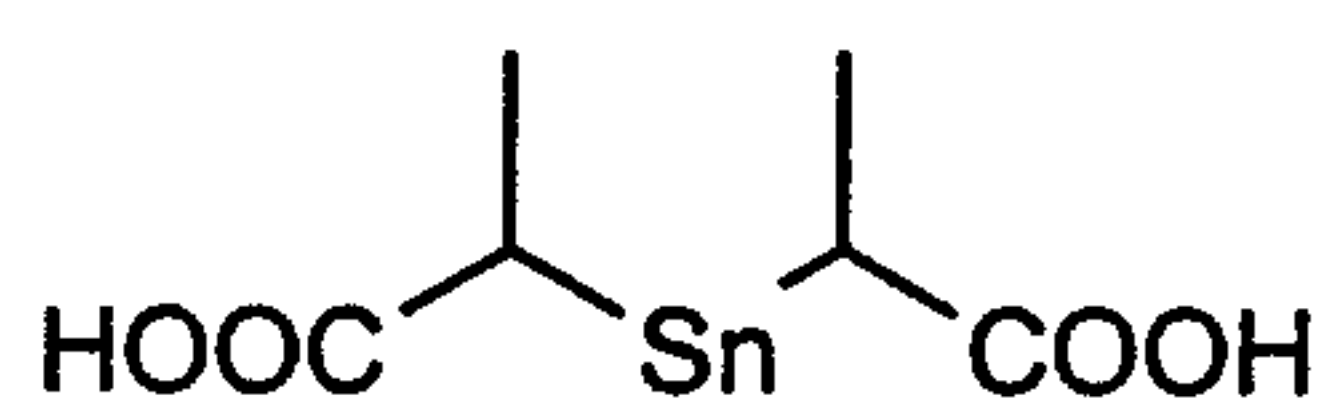
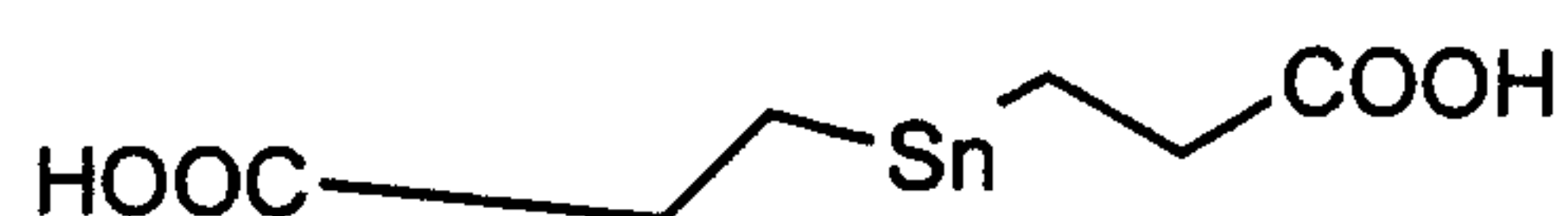
25 Examples which may be mentioned of ammonium groups serving as cations are:
ammonium, N-butylammonium, N-cyclohexylammonium, N-octadecylammonium,
trimethylammonium, triethylammonium and tributylammonium.

Possible 1- to 4-valent metal ions are e.g.:

30 Li, Na, K, Mg, Ca, Zn, Al and Ti.

Possible mercaptoalkylcarboxylic acids of the above formulae (IIa) and (IIb) are e.g. thioglycollic acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid, 4-mercaptobutyric acid, ω -mercaptoundecanoic acid and 2-mercaptosuccinic acid, more preferably 2-mercaptopropionic acid, 3-mercaptopropionic acid and 2-mercaptosuccinic acid.

Polythiocarboxylic acids which are preferably prepared by the process according to the present invention are of the following formulae:



The preferred compounds, of course, also include their corresponding ammonium or metal salts. In the formulae, the number n has the above-mentioned meaning with the preferred range described.

5 Because of the incorporation of varying amounts of sulfur during the process according to the present invention, the compounds (I) are as a rule mixtures of polysulfide compounds, so that n in the empirical composition of the compound (I) can also assume non-integral arithmetic mean values, so that the mean value n is preferably in the range from 2.5 to 7, more preferably 2.5 to 5.

10

To carry out the process according to the present invention, the mercaptocarboxylic acids in question, either individually or as a mixture with one another, are mixed with sulfur in the above-mentioned molar ratio and the mixture is heated to the temperatures also stated. Hydrogen sulfide escapes during the reaction. The reaction
15 times for the reaction are in the range from a few minutes up to several hours, depending on the reaction conditions and the mercaptocarboxylic acid employed.

The reaction according to the present invention can be accelerated by catalysts. Suitable catalysts are e.g. water and basic compounds, such as amines, e.g. water
20 and cyclohexylamine or primary C_{12} - or C_{24} -alkylamines, such as dodecylamine, oleylamine or stearylamine, or acid compounds, such as disulfur dichloride.

The catalysts are preferably employed in amounts of 0.01 to 1 wt.%, in particular 0.05 to 0.5 wt.%, based on the total amount of the reaction mixture.

25

The reaction according to the present invention can optionally be carried out in a suitable inert solvent, such as an ether, e.g. tetrahydrofuran and dioxane, or an aliphatic hydrocarbon, such as cyclohexane. However, the process according to the present invention is preferably carried out without a solvent.

30

After the reaction, the reaction mixture can be after-treated by known measures for further purification and removal of the dissolved hydrogen sulfide, e.g. by degassing in vacuo or blowing out with nitrogen or air, washing with water or extraction with organic solvents, or by treatment with appropriate oxidizing agents, e.g. hydrogen peroxide or organic peroxides. In the normal case, the purity of the resulting polythiopolycarboxylic acid after the degassing is already sufficient, so that further washing with water or extraction with organic solvents can be omitted.

Both natural and synthetic rubbers are suitable for the production of the rubber mixtures according to the invention containing the polythiocarboxylic acids prepared according to the invention.

Preferred synthetic rubbers are described for example in W. Hofmann, Kautschuk-technologie, Gentner Verlag, Stuttgart 1980, and I. Franta, Elastomers and Rubber Compounding Materials, Elsevier, Amsterdam 1989. They include, inter alia:

	BR	polybutadiene
	ABR	butadiene/acrylic acid C1-4 alkyl ester copolymers
	CR	polychloroprene
20	IR	polyisoprene
	SBR	styrene/butadiene copolymers having styrene contents of 1-60, preferably 20-50 wt. %
	IIR	isobutylene/isoprene copolymers having isoprene contents of 0.01 to 5 wt. % (butyl rubber)
25	BR-IIR	brominated isobutylene copolymers having bromine contents of between 0.01 and 4 wt. % (bromobutyl rubber)
	Cl-IIR	chlorinated isobutylene copolymers having chlorine contents of between 0.01 and 4 wt. % (chlorobutyl rubber)
30	BIMS	brominated copolymers containing 0.05 to 3 mol% of benzyl- bound bromine

	NBR	butadiene/acrylonitrile copolymers having acrylonitrile contents of 5-60, preferably 10-40 wt. %
	HNBR	partially or completely hydrogenated NBR rubber
5	EPDM	ethylene/propylene/diene copolymers having diene contents of between 0.1 and 20 wt. %, preferably 0.5 to 10 wt. %
	CO	polyepichlorohydrin
	ECO	copolymers of epichlorohydrin and ethylene oxide
	EAM	ethylene/vinyl acetate copolymers having vinyl acetate contents of 20 to 90 wt. %, preferably 40 to 80 wt. %

10

and mixtures of these rubbers. Of interest for the production of motor vehicle tyres are in particular natural rubber, polyisoprene, emulsion SBR and solution SBR rubbers having a glass transition temperature of higher than -50°C , which can optionally be modified with silyl ethers or other functional groups, in accordance with EP-A 447,066, polybutadiene rubber having a high 1,4-cis content ($>90\%$) which has been produced with catalysts based on Ni, Co, Ti or Nd, as well as polybutadiene rubber having a vinyl content of up to 75%, butyl rubber, bromobutyl rubber, chlorobutyl rubber and mixtures thereof.

Suitable fillers for the rubber mixtures according to the invention are all known fillers used in the rubber industry, including both active and inactive fillers.

15

The following fillers may be mentioned:

20

- highly dispersed silicas produced for example by the precipitation of solutions of silicates or by the flame hydrolysis of silicon halides having specific surface areas of 5 - 1000, preferably 20-400 m^2/g (BET surface area) and primary particle sizes of 10-400 nm. The silicas can optionally also be present in the form of mixed oxides with other metal oxides, such as for example Al, Mg, Ca, Ba, Zn, Zr or Ti oxides;

- synthetic silicates, such as for example aluminium silicate, alkaline earth silicate, such as magnesium silicate or calcium silicate, having BET surface areas of 20-400 m²/g and primary particle diameters of 10-400 nm;
- 5 - natural silicates, such as kaolin and other naturally occurring silicas; glass fibres and glass fibre products (mats, strands) or microglass beads;
- metal oxides, such as zinc oxide, calcium oxide, magnesium oxide and aluminium oxide;
- 10 - metal carbonates, such as magnesium carbonate, calcium carbonate and zinc carbonate;
- metal hydroxides, such as for example aluminium hydroxide and magnesium
15 hydroxide; and
- carbon blacks. The carbon blacks to be used are produced by the flame black, furnace or gas black processes and have BET surface areas of 20 - 200 m²/g, e.g. SAF, ISAF, HAF, FEF or GBF blacks.

20

Highly dispersed silicas and/or carbon blacks are preferably used as the fillers, the mixing ratio of carbon black to silica being 0.05 to 30, more preferably 0.1 to 10.

25

The rubber mixtures according to the invention can also contain other rubber auxiliaries which serve, for example, to further crosslink the rubber mixtures, or which improve the physical properties of the vulcanizates produced from the rubber mixtures according to the invention for their specific type of application.

30

The cross-linking agents used are sulphur or sulphur-donating compounds or peroxides. Sulphur or sulphur-donating compounds are particularly preferably used in quantities of 0.01 to 3 parts by weight, based on the rubber. In addition, as

mentioned, the rubber mixtures according to the invention can contain other auxiliaries, such as the known reaction accelerators, antioxidants, heat stabilizers, light-stability agents, antiozonants, processing aids, reinforcing resins, such as for example phenolic resins, steel cord bonding agents, such as for example silica/resorcinol/hexamethylene tetramine or cobalt naphthenate, plasticizers, tackifiers, blowing agents, dyestuffs, pigments, waxes, extenders, organic acids, retardants, metal oxides and filler activators, and in particular polysulphidic silanes, such as bis-(triethoxysilylpropyl)-tetrasulphide.

10 The rubber auxiliaries according to the invention are used in the customary, known quantities, the quantity used depending on the subsequent type of application of the rubber mixtures. Quantities of rubber auxiliaries in the range from 2 to 70 parts by weight, based on 100 parts by weight of rubber, are for example customary.

15 The rubber mixtures according to the invention can for example be produced by mixing the rubbers with the polythiocarboxylic acids prepared according to the invention, fillers, rubber auxiliaries and crosslinking agents, in suitable mixing apparatuses, such as kneaders, rollers or extruders.

EXAMPLEPreparation of $\text{HOOC-CH}_2\text{CH}_2\text{-S}_n\text{-CH}_2\text{CH}_2\text{-COOH}$

- 5 A mixture of 53 g (0.5 mol) 3-mercaptopropionic acid, 24 g (0.75 mol) sulfur and 0.3 g oleylamine was heated to 130°C, during which evolution of hydrogen sulfide started. The mixture was subsequently stirred at 130°C for 2.5 hours and a vacuum was then applied for 5 minutes in order to remove residual hydrogen sulfide. After cooling, 69.1 g polythiodipropionic acid were obtained as pale yellow crystals.
- 10 Melting range: 95 to 130°C. The HPLC chromatogram shows that it is a mixture of homologous polysulfides where $n = 3-11$. (Mean value: 4).

TABLE 1

Elemental Analysis:

	C	H	S
Calculated for $-\text{S}_4-$	26.3	3.7	46.7%
Found	26.3	3.6	47.5%

15

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

WHAT IS CLAIMED IS:

1. A process for the preparation of polythiopolycarboxylic acids of the formula



wherein

10 R^1 and R^2 are identical or different and represent a linear or branched C_1 - C_{36} -alkyl radical or a C_5 - C_{18} -cycloalkyl radical, wherein the alkyl radical and the cycloalkyl radical are substituted by 1 to 4 carboxyl or carboxylate groups and wherein, in the case of a carboxylate group, an ammonium group, a C_1 - C_{18} -mono-, -di- or -trialkylammonium group, a C_6 - C_{18} -mono-, -di- or -triarylammmonium group, a C_7 - C_{21} -mono-, -di-
15 or -trialkylarylammonium group or a 1- to 4-valent metal ion is present as the cation, and

n represents an integer from 2 to 14,

20 wherein mercaptoalkylcarboxylic acids of the formulae



25

wherein

R^1 and R^2 have the above meaning,

30 or mixtures of corresponding mercaptoalkylcarboxylic acids are reacted with sulfur in a molar ratio of 1:0.25 to 1:5 at temperatures of 70 to 220°C,

optionally in the presence of catalysts and optionally in the presence of an inert solvent.

2. A process according to claim 1, wherein R^1 and R^2 is independently of one another $-\text{CH}_2\text{COOH}$, $-\text{CH}_2\text{CH}_2\text{COOH}$, $-\text{CH}(\text{CH}_3)\text{COOH}$,
5 $-\text{CH}(\text{COOH})\text{CH}_2\text{COOH}$, $-\text{cyclohexyl}-\text{COOH}$.
3. A process according to claim 1, wherein said mercaptoalkylcarboxylic acid is selected from the group consisting of thioglycollic acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid, 4-mercaptoputyric acid,
10 ω -mercaptoundecanoic acid and 2-mercaptosuccinic acid.
4. A process according to claim 3, wherein said mercaptoalkylcarboxylic acid is selected from the group consisting of 2-mercaptopropionic acid, 3-mercaptopropionic acid and 2-mercaptosuccinic acid.
- 15 5. A process for the preparation of rubber mixtures comprising admixing polythiopolycarboxylic acids of formula (I) prepared according to the process of any one of claims 1 to 4 with a rubber.
6. A process for the preparation of rubber vulcanization products comprising vulcanization of rubber mixtures prepared according to the process of claim 5.

FETHERSTONHAUGH & CO.

OTTAWA, CANADA

PATENT AGENTS