COMMONWEALTH OF AUSTRALIA  
THE PATENTS ACT 1952  
CONVENTION APPLICATION FOR STANDARD PATENT OR A STANDARD PATENT OF ADDITION

Full name(s) of Applicant(s)  
We CIBA-GEIGY AG

Name(s) of Applicant(s)  
of Klybeckstrasse 141, 4002 Basle, Switzerland

hereby apply for the grant of a standard patent for an invention entitled

Title of Invention  
"NOVEL ORGANIC ANTIMONY-SULFUR COMPOUNDS AND THEIR USE AS STABILISERS FOR CHLORINE-CONTAINING THERMOPLASTS"

which is described in the accompanying complete specification.

DETAILS OF BASIC APPLICATION(S)

Number(s) of Basic Application(s)  
10005/79-5 and 4963/80-8

Name(s) of Convention Country(ies) in which Basic Application(s) were filed  
Switzerland

Date(s) of Basic Application(s)  
8th November, 1979 and 27th June, 1980 (respectively)

My/Our address for service is:  
C/- SPRUSON & FERGUSON PATENT ATTORNEYS  
CBA CENTRE, 60 MARGARET ST.  
SYDNEY, NEW SOUTH WALES.  
AUSTRALIA.

Dated this FIFTH day of OCTOBER 1980.

CIBA-GEIGY AG

By: [Handwritten signature]
Registered Patent Attorney

To: The Commissioner of Patents
In support of the Convention Application made by CIBA-GEIGY AG for a patent for an invention entitled:

"Novel organic antimony-sulfur compounds and their use as stabilisers for chlorine-containing thermoplasts"

We, Arnold Seiler and Ernst Altherr of CIBA-GEIGY AG, Klybeckstrasse 141, 4002 Basle, Switzerland
do solemnly and sincerely declare as follows:

1. We are authorised by the applicant for the patent to make this declaration on its behalf.

2. The basic application(s) as defined by Section 141 of the Act was(were) made in Switzerland on November 8, 1979 and on June 27, 1980 by CIBA-GEIGY AG, 4002 Basle, Switzerland

3. Klaus-Peter Michaelis, Am Hangweg 8, 6145 Lindenfels/Odenwald, Federal Republic of Germany,
Wolfgang Wehner, Wetzbach 34, 6144 Zwingenberg, Federal Republic of Germany,
Holger Andreas, Mierendorffstrasse 10, 6142 Bensheim/Auerbach, Federal Republic of Germany and
Horst Müller, Reichenberger Str. 12, 6149 Fürth/Odenwald, Federal Republic of Germany

are the actual inventor(s) of the invention and the facts upon which the applicant is entitled to make the application are as follows: The said applicant is the assignee of the actual inventor(s).

4. The basic application(s) referred to in paragraph 2 of this Declaration was(were) the first application(s) made in a Convention country in respect of the invention the subject of the application.

DECLARED at Basle, Switzerland on October 22, 1980

CIBA-GEIGY AG

A. Seiler E. Altherr

To: The Commissioner of Patents
1. A compound of the formula I, II, III or IV

\[
\begin{align*}
\text{I:} & \quad \text{RS-SbX}_2 \\
\text{II:} & \quad (\text{RS})_2\text{SbY} \\
\text{III:} & \quad \text{RS-SbO-SbY} \\
\text{IV:} & \quad \text{RS-SbO-SbR'}
\end{align*}
\]

wherein

- \(X\) is Cl, Br, J, OH, -OR, -OOCR, -OOC-R, -COOR or \(-N(R^5)(R^6)\), or the two \(X\) groups together form a group \(-O-R^9-O-\) or \(-O-CO-R^9-CO-\),
- \(Y\) has one of the meanings given for \(X\), or it is \(-NH\), \(-NHR\), \(-NHNH_2\) or \(-NHNH-phenyl\),
- \(Z\) has one of the meanings given for \(X\), or it is \(SR\),
- \(R\) is \(C_1-C_6\)-alkyl substituted by one or two of the groups \(-OH\), \(-OCOR\), \(-OR\), \(-SR\) or \(-COOR\),
- \(R'\) is \(-CH_2\) or \(-CH_2CH_2\), and
- \(R^1\) is \(C_1-C_8\)-alkyl, \(C_1-C_6\)-alkyl substituted by \(-OR\), \(-SR\), \(-OCOR\), or \(R^1\) is \(C_6-C_{10}\)-aryl, \(C_7-C_9\)-phenylalkyl or \(C_5-C_8\)-cycloalkyl, \(R^2\) is \(C_1-C_8\)-alkyl, \(C_2-C_{18}\)-alkenyl, \(C_5-C_8\)-cycloalkyl, \(C_6-C_{10}\)-aryl, or phenyl or \(C_7-C_9\)-phenylalkyl each substituted by \(C_1-C_4\)-alkyl, hydroxyl and/or...
(11) AU-A1-64 204/80

halogen, R³ is C₁⁻C₁₂-alkyl, allyl, cyclohexyl or phenyl,
R⁴ is C₂⁻C₁₂-alkylene, C₂⁻C₆-alkenylene, C₅⁻C₁₂-cyclo-
alkylene or cycloalkenylene, phenylene or halophenylene,
R⁵ and R⁶ can be identical or different and are each
C₁⁻C₁₂-alkyl, benzyl or cyclohexyl, or R⁵ and R⁶ together
with the N atom form a pyrrolidine, piperidine or
morpholine group, R⁷ is C₁⁻C₁₈-alkyl, CH₃COCH₂⁻, cyclo-
hexyl, benzyl, C₆⁻C₁₀-aryl, or phenyl or C₇⁻C₉-phenylalkyl
each substituted by C₁⁻C₄-alkyl, hydroxyl and/or halogen,
R⁸ is C₁⁻C₁₈-alkyl, allyl, cyclohexyl or phenyl, and R⁹ is
C₂⁻C₆-alkylene, C₃⁻C₆-alkylene interrupted by O, S or
(R⁵)N, or it is propylene interrupted by -OR⁸ or -OCOR⁷.
9. A chlorine-containing thermoplastic stabilised by
an antimony mercaptide, which thermoplastic contains 0.1
to 5 per cent by weight of a compound of Claim 1 as
stabiliser.
Complete Specification

Name of Applicant: CIBA-GEIGY AG

Address of Applicant: Klybeckstrasse 141, 4002 Basle, Switzerland

Actual Inventors: KLAUS-PETER MICHAELIS, WOLFGANG WEHNER, HOLGER ANDREAS and HORST MÜLLER

Address for Service: Spruson & Ferguson, Patent Attorneys, CBA Centre 60 Margaret Street, Sydney, New South Wales, 2000 Australia

Complete Specification for the invention entitled:

"NOVEL ORGANIC ANTIMONY-SULFUR COMPOUNDS AND THEIR USE AS STABILISERS FOR CHLORINE-CONTAINING THERMOPLASTS"

The following statement is a full description of this invention, including the best method of performing it known to me/us:
The invention relates to novel organic antimony-sulfur compounds which can be used as thermal stabilisers for chlorine-containing thermoplasts, particularly for PVC.

The thermal decomposition of chlorine-containing thermoplasts, such as polyvinyl chloride (PVC) constitutes a technically serious problem in the moulding of plastics of this type. A rational processing is virtually possible only by the addition of stabilisers. Additives used for this purpose are especially metal carboxylates, organotin compounds and aminocrotonates. There have been occasionally suggested also antimony mercaptides, for example simple mercaptides of the formula $\text{Sb(SR)}_3$ wherein $R$ is alkyl, aryl or aralkyl (U.S. 2,684,956), or ester mercaptides $\text{Sb(SR'COOR'')}_3$ wherein $R'$ is alkenylene, arylenylene or aralkylene and $R''$ is substituted or unsubstituted alkyl, aryl or arylalkyl (U.S. 2,680,726). A representative of the latter type is the compound $\text{Sb(SR'H}_2C\text{OO-isoC}_8\text{H}_{17})_3$, known under the tradename "Irgastab 511". The disadvantage of antimony mercaptides of this kind is that their stability to storage and to light is lower than that or organotin compounds. There existed therefore a commercial interest in antimony stabilisers having a higher stability to storage and to the action of light.
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It has now been found that, compared with the known tris-mercaptides, specific antimony mercaptides of which the Sb atom is bound only to 1 or 2 mercapto groups have an increased storage stability and an improved light stability, and in their action as PVC stabilisers they are equal or superior to the known tris-mercaptides. Furthermore, compared with these tris-mercaptides they are distinguished also by the fact that when added to chlorine-containing polymers, the thermoplastic processing of these polymers is facilitated. The said specific antimony mercaptides are novel compounds.

The present invention relates therefore to the compounds of the formula I, II, III or IV

\[ RS_{\text{Sb}} X_{2} \quad (RS)_{2} \text{SbY} \quad RS_{\text{Sb}} \text{O-Sb}_{Z} \text{SR} \]  

I \quad II \quad III

\[ RS_{\text{Sb}} \text{O} \text{R} \quad \text{O-CO} \]  

IV

wherein

- X is Cl, Br, J, OH, -OR\(^1\), -OOCR\(^2\), -OOC-R\(^4\)-COOR\(^3\) or \(-N(R^{5})(R^{6})\), or the two X groups together form a group -O-R\(^9\)-O- or -OOC-R\(^9\)-COO-,  
- Y has one of the meanings given for X, or it is -NHR\(^5\), -NHNH\(_2\) or -NHNH-phenyl,  
- Z has one of the meanings given for X, or it is SR,  
- R is C\(_1\)-C\(_6\)-alkyl substituted by one or two of the groups -OH, -OCOR\(^7\), -OR\(^8\), -SR\(^8\) or -COOR\(^8\),  
- R\(^1\) is -CH\(_2\)- or -CH\(_2\)CH\(_2\)-, and  
- R\(^1\) is C\(_1\)-C\(_8\)-alkyl, C\(_1\)-C\(_6\)-alkyl substituted by -OR\(_8\), -SR\(_8\) or -OCOR\(^7\), or R\(^1\) is C\(_6\)-C\(_{10}\)-aryl, C\(_7\)-C\(_9\)-phenyl-alkyl or C\(_5\)-C\(_8\)-cycloalkyl, R\(^2\) is C\(_1\)-C\(_8\)-alkyl, C\(_2\)-C\(_8\)-alkenyl,
C₅-C₈-cycloalkyl, C₆-C₁₀-aryl, or phenyl or C₇-C₉-phenylalkyl each substituted by C₁-C₄-alkyl, hydroxyl and/or halogen, R³ is C₁-C₁₂-alkyl, allyl, cyclohexyl or phenyl, R⁴ is C₂-C₁₂-alkylene, C₂-C₆-alkenylene, C₅-C₁₂-cycloalkylene or cycloalkenylene, phenylene or halophenylene, R⁵ and R⁶ can be identical or different and are each C₁-C₁₂-alkyl, benzyl or cyclohexyl, or R⁵ and R⁶ together with the N atom form a pyrrolidine, piperidine or morpholine group, R⁷ is C₁-C₁₈-alkyl, CH₃COCH₂-, cyclohexyl, benzyl, C₆-C₁₀-aryl, or phenyl or C₇-C₉-phenylalkyl each substituted by C₁-C₄-alkyl, hydroxyl and/or halogen, R⁸ is C₁-C₁₈-alkyl, allyl, cyclohexyl or phenyl, and R⁹ is C₂-C₆-alkylene, C₃-C₆-alkylene interrupted by O, S or (R⁵)N, or it is propylene interrupted by -OR⁸ or -OCOR⁷; and to the use of these compounds as stabilisers for chlorine-containing thermoplasts.

The group R is a mono- or disubstituted alkyl group. In the case of a disubstituted alkyl group, the substituents can be identical or different. The alkyl group itself can be straight-chain or branched-chain. Examples of the group R are: 2-hydroxyethyl, 2-hydroxypropyl, 2,3-dihydroxypropyl, 2-hydroxybutyl, 2-hydroxy-3-butoxypropyl, 2-octyloxyethyl, 2-phenoxypropyl, 2-acetoxybutyl, 2-(dodecylmercapto)-ethyl, 2-hydroxy-3-isopropoxypropyl, 2-hydroxy-3-caproyloxypropyl, 2-lauroyloxyethyl, 2,3-dibutyroylpropyl, 2,3-bis-[4-hydroxy-3,5-di-t-butyl-benzoyloxy]-propyl, 2,3-bis-[2-(4-hydroxy-3,5-di-t-butyl-phenyl)-propionyloxy]-propyl, 2-benzoyloxybutyl, 2,3-bis-(acetoacetoxy)-propyl or 2-acetoxy-3-phenoxypropyl. R is preferably a lower alkyl group substituted by one or two of the groups -COOR⁸, for example octyloxycarbonylmethyl, dodecyloxycarbonylmethyl, 2-(dodecycloxyacetylmethyl), 2-[(butyloxyacetyl)ethyl, 2-(butyloxyacetylmethyl)propyl, 1,3-bis-(octadecyloxyacetyl)-2-propyl or 2,3-bis-(2-ethylhexyloxyacetyl)-propyl. Particularly preferably, R is a group -CH₂COOR⁸, wherein R⁸ is a C₈-C₁₄-alkyl group.
When R¹, R², R³, R⁵, R⁶, R⁷ or R⁸ is alkyl, this can be a straight-chain or branched-chain alkyl group, for example methyl, ethyl, isopropyl, tert-butyl, sec-amyl, n-hexyl, 2-ethylhexyl, n-decyl or n-dodecyl. As alkyl, R¹, R², R⁷ and R⁸ can in addition be longer-chain alkyl, such as tetradecyl, hexadecyl or octadecyl, and are preferably C₈-C₁₄ alkyl.

As alkyl substituted by -OR⁸, -SR⁸ or -OCOR⁷, R¹ can be for example: 2-butoxyethyl, 3-octyloxypropyl, 2-isopropoxypropyl, 2-(dodecylmercapto)-ethyl, 2-(tert-butylmercapto)-propyl, 2-acetoxyethyl, 2-lauroxypropyl or 3-stearoxyethyl.

R¹ or R² as cycloalkyl can be for example: cyclopentyl, cyclohexyl or cyclooctyl. As alkenyl, R² can be for example: vinyl, propenyl, pentadienyl, hexenyl, decenyl or heptadecenyl.

R¹, R² or R⁷ as aryl can be phenyl or naphthyl; R² and R⁷ can also be phenyl substituted by lower-alkyl, hydroxyl and/or halogen, for example: 4-tolyl, 2-tolyl, 4-tert-butylphenyl, 3-chlorophenyl, 2,4-dichlorophenyl, 4-ethyl-2-chlorophenyl, 3-hydroxyphenyl, 4-chloro-2-hydroxyphenyl, 2-methyl-4-hydroxyphenyl or 3,5-di-tert-butyl-4-hydroxyphenyl.

As phenylalkyl, R¹ can be for example: benzyl, 2-phenylethyl, 1-phenylethyl or 2-phenylpropyl, R² and R⁷ as phenylalkyl substituted by lower alkyl, hydroxyl and/or halogen can be for example: 4-butylbenzyl, 3-chlorobenzyl, 2-methyl-4-hydroxybenzyl or 2-(3,5-di-tert-butyl-4-hydroxyphenyl)-ethyl.

R⁴ is a bivalent radical of a dicarboxylic acid, and it can be for example: 1,2-ethylene, 1,2-propylene, 1,3-propylene, 1,4-butylene, 1,2-octylene, 1,2-vinylene, 1-propen-2,3-diy1, cyclopentan-1,2-diy1, cyclohexan-1,2-diy1, cyclooctan-1,2-diy1, 1-cyclohexan-4,5-diy1,
2-norbornen-5,6-diy1,1,2-phenylene or 4-chloro-1,2-phenylene.

R is the bivalent radical of a diol or of a dicarboxylic acid, and can be for example: 1,2-ethylene, 1,2-propylene, 1,3-propylene, 1,2-butylene, 1,4-butylene, 2,2-dimethyl-1,3-propylene, 3-oxa-1,3-propylene, 3-oxa-1,5-pentylene, 3-methylene-aza-1,5-pentylene, 3-phenylaza-1,5-pentylene, 3-octyloxy-1,2-propylene, 3-dodecyloxy-1,2-propylene, 2-stearoyloxy-1,3-propylene, 3-phenyloxy-1,2-propylene, 3-lauroyloxy-1,2-propylene, 3-stearyloxy-1,2-propylene, 3-acetoacetyloxy-1,2-propylene or 2-stearoyloxy-1,3-propylene.

Preferred compounds of the formula I, II or III are those wherein X, Y or Z is chlorine. Also preferred are compounds of the formula I or II wherein X or Y is one of the groups -OR, -OOC-R, -COOR or -00CR .

Examples of compounds of the formula I are the compounds of the following formulae:

\[
\begin{align*}
\text{Cl}_2\text{Sb-SCH}_2\text{COO-iso-C}_8\text{H}_{17} \\
\text{Cl}_2\text{Sb-SCH}_2\text{CH}_2\text{COOC}_4\text{H}_9 \\
\text{Cl}_2\text{Sb-SCH}_2\text{CH}_2\text{OH} \\
\text{Cl}_2\text{Sb-SCH}_2\text{CH}_2\text{OOOC-C}_11\text{H}_{23} \\
\text{Cl}_2\text{Sb-SCH}_2\text{CH(OH)}\text{CH}_2\text{OOOC-C}_17\text{H}_{35} \\
(\text{HO})_2\text{Sb-SCH}_2\text{CH}_2\text{OC}_6\text{H}_5 \\
(\text{C}_4\text{H}_9\text{O})_2\text{Sb-SCH}_2\text{COOC}_12\text{H}_{25} \\
(\text{C}_{12}\text{H}_{25}\text{O})_2\text{Sb-SCH}_2\text{CH}_2\text{COOC}_12\text{H}_{25} \\
(\text{C}_4\text{H}_9\text{OCH}_2\text{CH}_2\text{O})_2\text{Sb-SCH}_2\text{CH}_2\text{OOOC-C}_11\text{H}_{23} \\
(\text{isoC}_8\text{H}_{17}\text{O})_2\text{Sb-SCH}_2\text{CH}_2\text{OOOC-CH}_2\text{CH}_2
\end{align*}
\]
(isoC₈H₁₇O)₂Sb-S-CH₂-CH-CH₂-OisoC₈H₁₇

(C₁₂H₂₅O)₂Sb-S-CH₂-CH-CH₂-OC₆H₅

(C₁₂H₂₅O)₂Sb-S-CH₂-CH-CH₂-OCOCH₂-COCH₃

(C₁₂H₂₅SCH₂COO)₂Sb-SCH₂COOCH₃

(C₈H₁₇CH=CHC₇H₁₄COO)₂Sb-S-CH₂-CH(OH)-CH₂-SC₄H₉
Examples of compounds of the formula II are:

$\text{ErSb(SCH}_2\text{CO}_2\text{C}_8\text{H}_{17})_2$

$\text{ClSb(SCH}_2\text{COOC}_{12}\text{H}_{25})_2$

$\text{ClSb(SCH}_2\text{CH(OH)}\text{CH}_2\text{O-sec-C}_4\text{H}_9)_2$

$\text{ClSb(SCH}_2\text{CHCH}_2\text{O-iso-C}_8\text{H}_{17})_2$

$\text{HO-Sb(SCH}_2\text{COOC}_{18}\text{H}_{37})_2$

$\text{iscC}_8\text{H}_{17}\text{O-Sb(SCH}_2\text{COO-isoC}_8\text{H}_{17})_2$

$\text{C}_1\text{H}_3\text{H}_2\text{O-Sb(SCH}_2\text{COOC}_{4}\text{H}_9)_2$

$\text{C}_1\text{H}_2\text{H}_2\text{O-Sb(SCH}_2\text{CH}_2\text{COOC}_{2}\text{H}_9)_2$

$\text{C}_4\text{H}_9\text{SCH}_2\text{CH}_2\text{O-Sb(SCH}_2\text{CH}_2\text{COOC}_{12}\text{H}_{25})_2$

$\text{C}_6\text{H}_5\text{CH}_2\text{O-Sb(SCH}_2\text{CH}_2\text{COOC}_{17}\text{H}_{35})_2$

$\text{C}_1\text{H}_2\text{COOH}_2\text{CH}_2\text{O-Sb(SCH}_2\text{CH(OH)}\text{CH}_2\text{OC}_4\text{H}_9)_2$

$\text{C}_6\text{H}_5\text{CH}_2\text{COO-Sb(SCH}_2\text{COOisoC}_8\text{H}_{17})_2$

$\text{C}_1\text{H}_3\text{H}_2\text{COO-Sb(SCH}_2\text{COOCH}_3)_2$

$(\text{CH}_3)_3\text{C-}--\text{COO-Sb(SCH}_2\text{CH}_2\text{COOisoC}_8\text{H}_{15})_2$
\[ \text{HO} - \text{COO-Sb(SCH}_2\text{CH}_2\text{OisoC}_8\text{H}_{17})_2 \]

\[ \text{HO} - \text{CH}_2\text{CH}_2\text{COO-Sb(SCH}_2\text{CH}_2\text{SC}_{12}\text{H}_{25})_2 \]

\[ \text{C}_4\text{H}_9\text{OOC-CH}_2\text{CH}_2\text{COO-Sb(SCH}_2\text{CH}_2\text{COOC}_{18}\text{H}_{37})_2 \]

\[ \text{COOisoC}_8\text{H}_{17} \]

\[ \text{COO-Sb(SCH}_2\text{COOisoC}_8\text{H}_{17})_2 \]

\[ \text{COOCH}_3\text{CH=CH}_2 \]

\[ \text{COO-Sb(SCH}_2\text{CH}_2\text{OOCC}_{15}\text{H}_{13})_2 \]

\[ \text{Cl} \]

\[ \text{COOC}_{12}\text{H}_{25} \]

\[ \text{Cl} \]

\[ \text{Cl} \]

\[ \text{COO-Sb(SCH}_2\text{COOC}_{12}\text{H}_{25})_2 \]

\[ (\text{C}_4\text{H}_9)_2\text{N-Sb(SCH}_2\text{CH}_2\text{COOC}_4\text{H}_{9})_2 \]
Examples of compounds of the formula III are:

\[
\text{iso-C}_8\text{H}_{17}\text{OOCCH}_2\text{Sb-O-Sb} \quad \text{CH}_2\text{COOC}_8\text{H}_{17} - \text{iso}
\]

\[
\text{Cl} \quad \text{Cl}
\]

Examples of compounds of the formula IV are:

\[
\text{CH}_3\text{COOCCH}_2\text{CH}_2\text{Sb-O-Sb} \quad \text{SCH}_2\text{CH}_2\text{OOCCH}_3
\]

\[
\text{C}_4\text{H}_9\text{OOCCH=CHCOO} \quad \text{OOCCH=CHCOO}_4\text{H}_9
\]

\[
\text{(C}_12\text{H}_{25}\text{OOCCH}_2\text{S})_2\text{Sb-O-Sb} \quad \text{(C}_12\text{H}_{25}\text{OOCCH}_2\text{S})_2\text{Sb-O-Sb}
\]

\[
\text{(iso-C}_8\text{H}_{17}\text{OCH}_2\text{CHCH}_2\text{S})_2\text{Sb-O-Sb} \quad \text{(iso-C}_8\text{H}_{17}\text{OCH}_2\text{CHCH}_2\text{S})_2\text{Sb-O-Sb}
\]

Examples of compounds of the formula IV are:
Compounds of the formulae I and II can be produced in many cases by comproportionation of antimony tris-mercaptides with compound $\text{SbX}_3$ or $\text{SbY}_3$:

\[
\text{Sb(SR)}_3 + 2 \text{SbX}_3 \rightarrow 3 \text{RS-SbX}_2 \quad (I)
\]
\[
2\text{Sb(SR)}_3 + \text{SbX}_3 \rightarrow 3(\text{RS})_2\text{SbY} \quad (II)
\]

Compounds $\text{SbX}_3$ and $\text{SbY}_3$ suitable for this purpose are in particular the antimony halides $\text{SbCl}_3$, $\text{SbBr}_3$, $\text{SbJ}_3$, antimony alcolholates, for example $\text{Sb(OCH}_2\text{H}_5)_3$, or $\text{Sb(OCH}_3\text{H}_13)_3$, and antimony carboxylates, for example $\text{Sb(OOCCH}_3)_3$.

These comproportionation reactions can be performed without or in an inert solvent. The necessary temperatures are between 100 and 200°C. Suitable solvents are for example toluene, xylene or tetrahydrofuran. The tris-mercaptides $\text{Sb(SR)}_3$ are known compounds, as are described for example in the U.S. Patent Specifications 2,684,956 and 2,680,726 mentioned hereinbefore.

The compounds of the formulae I and II in which X and Y are halogen are usable as intermediates for the other compounds of the formulae I and II. Particularly suitable for this purpose are the corresponding chlorine compounds V and VI:

\[
\text{RS-SbCl}_2 \quad (V) \quad (\text{RS})_2\text{SbCl} \quad (VI).
\]

There are thus formed from V and VI by reaction with $\text{R}^1\text{OH}$ — in the presence or absence of HCl acceptors — compounds of the formulae I and II wherein X or Y is $\text{R}^1\text{O}^-$.

Compounds of the formula I or II wherein X or Y
is R\textsuperscript{2}COO- or R\textsuperscript{3}OOC-R\textsuperscript{4}-COO- are formed from the chlorine compounds V or VI by reaction with monocarboxylic acids or with dicarboxylic acid half-esters, either in the presence of equivalent amounts of a base (preferably of a tertiary amine), or by reaction with the alkali metal salts of such acids.

By hydrolysis of compounds of the formula V are obtained compounds of the formula I wherein X is OH, and compounds of the formula III wherein Z is OH. By hydrolysis of compounds of the formula VI are obtained compounds of the formula II wherein Y is OH, and compounds of the formula III wherein Z is SR.

The compounds of the formula I or II wherein X and Y are each a group \((R\textsuperscript{5})(R\textsuperscript{6})N-) can be produced from the chlorine compounds V or VI by reaction with secondary amines, whereby the HCl acceptor used can be either this amine in excess or another base in an equivalent amount.

There are obtained in an analogous manner from compounds of the formula VI, by reaction with primary amines, hydrazine or phenylhydrazine, the compounds of the formula II wherein Y is \(-\text{NHR}\textsuperscript{5}, -\text{NHNH}_2\) or \(-\text{NHNH-phenyl.}\)

The compounds of the formula I wherein both X groups together form \(-\text{O-}R\textsuperscript{9}-\text{O-}\) can be produced from the compounds V by reaction with one equivalent of a compound HO-R\textsuperscript{9}-OH in the presence of 2 equivalents of an HCl acceptor. Compounds of the formula I wherein both X groups together form \(-\text{O-CO-}R\textsuperscript{9}-\text{CO-}\text{-O-}\) can be produced from the compounds V by reaction with an alkali metal salt of a dicarboxylic acid of the formula HOOC-R\textsuperscript{9}-COOH.

The compounds of the formula IV can be produced from compounds of the formula VII
by alkaline hydrolysis, the meaning of $R^8$ being as defined hereinbefore.

The compounds of the formulae V and VI can be produced also by reaction of antimony trichloride with the corresponding mercapto compounds $RSH$:

$$\text{SbCl}_3 + RSH \xrightarrow{- \text{HCl}} \text{RS-SbCl}_2 \quad (V)$$
$$\text{SbCl}_3 + 2 \text{RSH} \xrightarrow{- 2 \text{HCl}} (\text{RS})_2\text{SbCl} \quad (VI).$$

These reactions are preferably performed in an organic solvent, for example in methylene chloride. Suitable as HCl acceptors are organic or inorganic bases, particularly alkali carbonates, such as NaHCO$_3$ or K$_2$CO$_3$, in solid form.

Also mixtures of compounds can be formed with the methods of synthesis described herein. For example in the production of a compound of the formula V by means of comproportionation, a certain amount of VI can occur as a by-product. Or in the case of hydrolysis of compounds of the formula V, there can be formed besides products of the formula I also products of the formula III. For most purposes, mixtures of this kind can be used in the same manner as the pure compounds. When however the pure compounds are desired, they can be obtained by the customary purification methods, such as fractional distillation, crystallisation or chromatography.

The antimony mercaptides of the formulae I, II, III and IV can be used as stabilisers for chlorine-containing thermoplasts, for example for polymers and copolymers of vinyl chloride or vinylidene chloride, chlorinated polyolefins, post-chlorinated polyvinyl chloride, or chlorinated
rubber. The stabilisation of polyvinyl chloride (PVC) is of particular importance. The materials concerned can be suspension PVC, emulsion PVC, or polymers produced by bulk polymerisation.

The compounds of the formulae I, II, III and IV are added to the chlorine-containing thermoplasts in an amount of 0.1 to 5 per cent by weight, relative to the thermoplasts. The amount preferably used is 0.5 to 3 per cent by weight. It is also possible to use mixtures of two or more compounds of the formulae I, II, III and IV.

Also precursors of the stabilisers according to the invention can be added to the thermoplasts. It is possible to add, for example, instead of a compound of the formula I, a mixture of Sb (SR)₃ and Sb X₃ (preferably in the molar ratio of 1:2), from which, under the conditions of thermoplastic moulding, the compound of the formula I can form in the thermoplast. The direct addition of the compounds of the formulae I, II, III and IV is however preferred.

The incorporation of the stabilisers into the polymeric substrates can be effected by the customary processes for incorporating additives into thermoplasts, for example by a mixing together of the constituents in powder form and subsequent moulding, or by addition of the stabilisers on a roll mill or in a kneading machine. There can be incorporated simultaneously other additives commonly known in the technology of chlorine-containing thermoplasts, for example lubricants, plasticisers, fillers, additives for increasing impact strength, pigments, light stabilisers and antioxidants, or further thermostabilisers, for example metal carboxylates or organic phosphites.

Of particular importance is the addition of co-stabilisers, especially co-stabilisers from the series of pyrocatechol derivatives. It is known, for example
from the U.S. Patent Specifications Nos. 4,029,618 and 4,158,640, that pyrocatechol and derivatives thereof have a synergistic effect together with organic antimony compounds as stabilisers for chlorine-containing thermo-plasts. Co-stabilisers of this type which synergistically intensify the action of the basic stabiliser are also called boosters. This type of booster effect of pyrocatechol and of derivatives of pyrocatechol is to be observed also when they are used in combination with the compounds of the formulae I, II, III and IV. Examples of synergistically acting pyrocatechols of this kind are the compounds of the following formulae:

\[
\begin{align*}
R & \quad \text{R} = \text{H, alkyl, alkenyl, alkoxy carbonyl} \\
R''^{\text{CO}} & \quad \text{R}'' = \text{alkyl, haloalkyl, aryl, aralkyl}
\end{align*}
\]

as well as antimony phenolates and tin phenolates of such pyrocatechols, for example the following compounds:
\[ R \rightarrow \begin{array}{c} \text{Sb-X} \\ X = \text{Cl, OH, OR', SR'} \end{array} \]

\[ R \rightarrow \begin{array}{c} \text{Sb-O-X'-O-Sb} \\ X' = \text{alkylene, oxaalkylene, thioalkylene, phenylene} \end{array} \]

\[ \text{R}' = \text{alkyl, aryl, aralkyl} \]

\[ R \rightarrow \begin{array}{c} \text{Sn} \\ \text{SnR', SnX}_2, \text{SnCl}_4 \end{array} \]

\[ Y = \text{R}_4\text{N}, \text{R}_4\text{P}, \text{R}_3\text{O}, \text{R}_3\text{S} \]

\[ \text{R}' \rightarrow \begin{array}{c} \text{Sb-SCH}_2\text{COOR'} \end{array} \]

\[ \text{OSn(OR')}_3 \]
Further synergistic pyrocatechol derivatives are the cyclic borates or phosphites of pyrocatechols, such as the compounds of the type:

\[
\begin{align*}
R & \equiv \text{borate} - X \\
R & \equiv \text{phosphite} - X
\end{align*}
\]

wherein R and X have the meanings defined in the foregoing.

Other synergistic pyrocatechol derivatives are the halogenated pyrocatechols, for example: 3-chloro-, 3,4-dibromo-, 3-bromo-4-tert-butyl- or 3,4,5,6-tetrabromo-pyrocatechol.

These co-stabilisers are used in an amount of 2-50 per cent by weight, relative to the amount of employed compound I, II, III or IV, so that the weight ratio of stabiliser:co-stabiliser is 2:1 to 98:2. The optimum quantity ratio has to be experimentally ascertained for each stabiliser/co-stabiliser combination.

The stabilised chlorine-containing thermoplasts according to the invention can be moulded into shape by the methods customarily used therefor, for example by means of extrusion, injection moulding or calendering, or by being processed as plastisols.

The following Examples further illustrate production and use of the compounds of the formulae I, II, III and IV. Parts are by weight and temperatures are degrees Centigrade.
Example 1: Comproportionation of SbCl₃ in solution

114.2 g (0.5 mol) of antimony trichloride with 731 g (1 mol) of antimony tris-thioglycolic acid iso-octyl ester in 200 ml of toluene are refluxed for 20 hours. After cooling, the slight amount of impurities is separated by filtration, and the solvent is removed in vacuo. There is obtained in practically quantitative yield a colourless viscous oil having the elements in the ratio Sb:S:Cl = 1:1.924:0.996, with an H-NMR signal for the thiomethylene protons at δ = 3.90 ppm.

That corresponds to the compound of the formula

\[ \text{ClSb(SCH}_2\text{COO-isoC}_8\text{H}_{17})_2 \] (compound No. 1).

The same result is obtained by carrying out the test in ethylene chloride instead of in toluene.

In an analogous manner are obtained, from 228.2 g (1 mol) of SbCl₃ and 365.4 g (0.5 mol) of Sb(SCH₂COO-isoC₈H₁₇)₃, the compound No. 2

\[ \text{Cl}_2\text{SbSCH}_2\text{COO-isoC}_8\text{H}_{17} \]

in the form of a crystalline solid, which melts at 48-49°. The element ratio according to analysis is 1:0.92:2.1; and the H-NMR spectrum shows a singlet for the thiomethylene protons at δ = 4.17.

Example 2: Comproportionation of SbCl₃ without solvent

45.6 g of antimony trichloride and 78 g of Sb[SCH₂CH(OH)CH₂O-iso-C₈H₁₇]₃ are shaken for 12 hours at room temperature. The initially undissolved SbCl₃ disappears during this time. The resulting slightly yellowish oil is crude monomercaptide

\[ \text{Cl}_2\text{SbSCH}_2\text{CH(OH)CH}_2\text{O-isoC}_8\text{H}_{17} \]

(compound No. 3).
There is obtained in an analogous manner, from 11.4 g of SbCl₃ and 78 g of the above tris-mercaptide, the compound No. 4:

\[ \text{ClSb[SCH}_2\text{CH(OH)CH}_2\text{O-isoC}_8\text{H}_{17}]_2 \]

as a light-yellow liquid.

**Example 3: Alcoholysis of antimony chloromercaptides**

113 g of \text{ClSb(SCH}_2\text{COO-isoC}_8\text{H}_{17})_2\) (compound No. 1) are dissolved in 200 ml of diethyl ether. A solution of 26 g of 2-ethylhexanol and 20 g of triethylamine in 100 ml of diethyl ether is slowly added dropwise with stirring, and the mixture is subsequently refluxed for 1 hour. After cooling, the amine hydrochloride which has precipitated is filtered off, and the solution is concentrated by evaporation. The yield is 121 g of a product of the formula

\[ \text{isoC}_8\text{H}_{17}0\text{Sb(SCH}_2\text{COO-isoC}_8\text{H}_{17})_2 \]

(compound No. 5)
as a transparent oily liquid, of which the H-NMR spectrum is in agreement with the above formula.

**Elementary analysis:** found: Sb 18.3% S 9.6%

  calculated: Sb 18.5% S 9.9%

There are obtained in an analogous manner, from 113 g of \text{ClSb(SCH}_2\text{COO-isoC}_8\text{H}_{17})_2\), 54 g of octadecanol (stearyl alcohol) and 20 g of triethylamine, 133 g of the compound No. 6:

\[ \text{C}_{18}\text{H}_{37}0\text{Sb(SCH}_2\text{COO-isoC}_8\text{H}_{17})_2 \]
as a colourless wax, which melts at 48-49°.

**Analysis:** found: Sb 15.5% S 8.3%

  calculated: Sb 15.9% S 8.4%

There are obtained in an analogous manner, from 99 g of \text{Cl}_2\text{Sb SCH}_2\text{COO-isoC}_8\text{H}_{17}\) (compound No. 2), 135 g of
octadecanol and 51 g of triethylamine, 215 g of the compound No. 7:
\[(\text{C}_{18}\text{H}_{37}\text{O})_2\text{SbSCH}_2\text{COO-isoC}_8\text{H}_{17}\]
as colourless wax, which melts at 53-54°.

**Analysis:** found : Sb 12.6%  S 6.6%  
calculated: Sb 13.0%  S 6.9% .

**Example 4: Reaction of antimony chloromercaptides with carboxylic acids**

11.2 g of ClSb(SCH₂COO-isoC₈H₁₇)₂ are dissolved in 20 ml of diethyl ether. There is simultaneously added dropwise, with stirring, a solution of 2 g of triethylamine in 10 ml of ether, and 4.8 g of endomethylene-tetrahydrophthalic acid monobutyl ester in 20 ml of ether, and the whole is refluxed for 1 hour. The amine hydrochloride which has precipitated is filtered off, and the filtrate is concentrated by evaporation. The yield is 13.6 g of a product of the formula

\[
\text{COOSb(SCH}_2\text{COO-isoC}_8\text{H}_{17})\text{_2}
\]
(compound No. 8)
in the form of colourless wax.

**Elementary analysis:** found : Sb 15.8%  S 8.2%  
calculated: Sb 16.1%  S 8.5%.

In an analogous manner are obtained:

\[
\text{COOSb(SCH}_2\text{COO-isoC}_8\text{H}_{17})\text{_2}
\]
(compound No. 9)
yellowish oil ;
COO-isoC₈H₁₇

(compound No. 10)
yellowish oil;

SbSCH₂COO-isoC₈H₁₇

(compound No. 11)
yellowish oil;

C₁₇H₃₅COOSb(SCH₂COO-isoC₈H₁₇)₂

(compound No. 12)
wax, m.p. 47-48°;

(C₁₇H₃₅COO)₂SbSCH₂COO-isoC₈H₁₇

(compound No. 13)
wax, m.p. 61-63°;

C₉H₁₉COOSb(SCH₂COO-isoC₈H₁₇)₂

(compound No. 14)
viscous oil

from "Versatic acid 10",
a commercial mixture of branched-chain C₁₀-monocarboxylic acids.
Example 5: Reaction of SbCl₃ with thioglycolic esters

4.56 g of SbCl₃, 4.08 g of HSCH₂COO-isoC₈H₁₇ and 1.85 g of NaHCO₃ in 50 ml of methylene chloride are reacted at reflux temperature. After the evolution of gas has finished, the reaction mixture is filtered, and the filtrate is concentrated in vacuo. There remains a colourless oil consisting mainly of the compound No. 2. The NMR spectrum of the crude product shows the presence of the compound C₈H₁₇OOCC₂H₂S-Sb(Cl)-O-Sb(Cl)-SCH₂COOC₈H₁₇ as by-product in an amount of about 10 mol %.

There is obtained in an analogous manner, from 4.56 g of SbCl₃, 8.16 g of thioglycolic acid iso-octyl ester and 3.69 g of NaHCO₃, a crude product in the form of a colourless oil consisting mainly of the compound No. 1, and as by-product about 10 mol % of the compound (C₈H₁₇OOCC₂H₂S)₂ Sb-O-Sb(SCH₂COOC₈H₂₇)₂.

Example 6: Stabilisation of PVC

The following recipe suitable for producing drinking-water tubes was used:

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspension PVC of K value 68</td>
<td>100 parts</td>
</tr>
<tr>
<td>Chalk</td>
<td>1.0 part</td>
</tr>
<tr>
<td>TiO₂ (Rutil)</td>
<td>1.0 part</td>
</tr>
<tr>
<td>Paraffin wax</td>
<td>0.8 part</td>
</tr>
<tr>
<td>Calcium stearate</td>
<td>0.8 part</td>
</tr>
<tr>
<td>Stabiliser</td>
<td>0.4 part</td>
</tr>
</tbody>
</table>

The constituents were mixed dry, and the mixture was subjected on a laboratory roll mill at 200° to a long-duration roll test. The discoloration occurring was ascertained, after 3, 6 and 12 minutes respectively, by determination of the Yellowness Index on specimens taken from the 0.3 mm thick rolled sheet. To provide a comparison with the prior art, there was used "Irgastab 511", an
antimony tris-mercapto ester of the formula $\text{Sb}(\text{CH}_2\text{COO-isoC}_8\text{H}_{17})_3$. The results are summarised in the following Table.

<table>
<thead>
<tr>
<th>Employed stabiliser</th>
<th>Yellowness-Index after</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3 min.</td>
</tr>
<tr>
<td>Irgastab 511 (comparison)</td>
<td>20.8</td>
</tr>
<tr>
<td>compound No. 1</td>
<td>12.1</td>
</tr>
<tr>
<td>compound No. 2</td>
<td>11.8</td>
</tr>
<tr>
<td>compound No. 1 + 4-tert-butyl-pyrocatechol in the ratio of 19:1</td>
<td>7.9</td>
</tr>
</tbody>
</table>

Example 7: Stabilisation of PVC with the addition of a co-stabiliser

A mixture was prepared as in Example 6 except that there was used, instead of 0.4 part of stabiliser, 0.35 part of stabiliser and 0.05 part of tetrabromopyrocatechol as the co-stabiliser.

<table>
<thead>
<tr>
<th>Stabiliser</th>
<th>Yellowness Index after</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3 min.</td>
</tr>
<tr>
<td>compound No. 6</td>
<td>7.8</td>
</tr>
<tr>
<td>No. 7</td>
<td>8.5</td>
</tr>
<tr>
<td>No. 12</td>
<td>7.4</td>
</tr>
<tr>
<td>No. 13</td>
<td>7.7</td>
</tr>
<tr>
<td>No. 14</td>
<td>6.6</td>
</tr>
</tbody>
</table>
WHAT IS CLAIMED IS:
The claims defining the invention are as follows:

1. A compound of the formula I, II, III or IV

wherein:

X is Cl, Br, J, OH, -OR, -OOCR, -OOC-R-COOR or 
-N(R')(R'), or the two X groups together form a 
group -O-R or -OCO-R-COO-

Y has one of the meanings given for X, or it is -NHR,
-NHNH₂ or -NHNH-phenyl,

Z has one of the meanings given for X, or it is SR,

R is C₁-C₆-alkyl substituted by one or two of the 
groups -OH, -OOCR, -OR, -SR or -COOR,

R' is -CH₂- or -CH₂CH₂-, and

R₁ is C₁-C₁₈-alkyl, C₆-C₉-alkyl substituted by -OR, 
-SR or -OOCR, or R₁ is C₅-C₁₀-aryl, C₇-C₉-phenylalkyl 
or C₅-C₈-cycloalkyl, R₂ is C₁-C₁₈-alkyl, C₂-C₁₈-alkenyl, 
C₅-C₈-cycloalkyl, C₆-C₁₀-aryl, or phenyl or C₇-C₉-phenyl-
alkyl each substituted by C₁-C₄-alkyl, hydroxyl and/or 
halogen, R₃ is C₁-C₁₂-alkyl, allyl, cyclohexyl or phenyl,
R₄ is C₂-C₁₂-alkylene, C₂-C₆-alkenylene, C₅-C₁₂-cyclo-
alkylene or cycloalkenylene, phenylene or halophenylene,
R₅ and R₆ can be identical or different and are each 
C₁-C₁₂-alkyl, benzyl or cyclohexyl, or R₅ and R₆ together 
with the N atom form a pyrrolidine, piperidine or 
morpholine group, R₇ is C₁-C₁₈-alkyl, CH₃COCH₂-, cyclo-
hexyl, benzyl, C₆-C₁₀-aryl, or phenyl or C₇-C₉-phenylalkyl 
each substituted by C₁-C₄-alkyl, hydroxyl and/or halogen, 
R₈ is C₁-C₁₈-alkyl, allyl, cyclohexyl or phenyl, and R₉ is 
C₂-C₆-alkylene, C₃-C₆-alkylene interrupted by 0, S or
(R^5)_N, or it is propylene interrupted by -OR^8 or -OCOR^7.

2. A compound of the formula I, II or III according to Claim 1, wherein X, Y or Z is chlorine.

3. A compound of the formula I or II according to Claim 1, wherein X or Y is any one of the groups -OR^1, -OOC-R^4-COOR^3 or -OOOCR^2.

4. A compound according to Claim 1, wherein R is a C_1-C_6-alkyl group substituted by one or two groups -COOR^8, and R^8 has the meaning defined in Claim 1.

5. A compound according to Claim 4, wherein R is a group -CH_2-COOR^8, and R^8 is a C_8-C_14-alkyl group.

6. Use of a compound defined in Claim 1, as stabiliser for chlorine-containing thermoplasts.

7. Use according to Claim 6 as stabiliser for polyvinyl chloride.

8. Use according to Claim 6 in combination with a co-stabiliser from the pyrocatechol derivative class.

9. A chlorine-containing thermoplastic stabilised by an antimony mercaptide, which thermoplastic contains 0.1 to 5 per cent by weight of a compound of Claim 1 as stabiliser.

10. A stabilised thermoplastic according to Claim 9, which thermoplastic is polyvinyl chloride.

11. A stabilised thermoplastic according to Claim 9, which thermoplastic contains in addition other additives such as those commonly known in the technology of chlorine-containing thermoplasts.
12. A stabilised thermoplastic according to Claim 11, which thermoplastic contains pyrocatechol or a pyrocatechol derivative as a co-stabiliser.

13. A stabilised thermoplastic according to Claim 12, wherein the weight ratio of stabiliser to co-stabiliser is 2:1 to 98:2.

14. A stabilised thermoplastic according to Claim 11, which thermoplastic contains a calcium or zinc carboxylate as a co-stabiliser.

DATED this FOURTH day of NOVEMBER, 1980.

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