Convention Application for a Patent

We, CIBA-GEIGY AG of Klybeckstrasse 141, 4002 Basle, Switzerland hereby apply for the grant of a Patent for an invention entitled

"SALTS FORMED FROM FORMAMIDINES WITH POLYMERS CONTAINING SULFONIC ACID GROUPS"

which is described in the accompanying complete specification.

This application is a Convention Application and is based on the applications numbered 6095/79-1 and 4053/80-2 for a patent or similar protection made in Switzerland on 29th June, 1979 and 23rd May, 1980 respectively.

Our address for service is:

Care: SPRUSON & FERGUSON PATENT ATTORNEYS ESSEX HOUSE, 51 KENT STREET 60 Margaret Street, SYDNEY, NEW SOUTH WALES, AUSTRALIA.

Dated this NINETEENTH day of JUNE, 1980

CIBA-GEIGY AG

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

"Salts formed from formamidines with polymers containing sulfonic acid groups"

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 June 29, 1979 and on May 23, 1980

both by CIBA-GEIGY AG, 4002 Basle, Switzerland

3. Christian d'Hondt, Unterm Schellenberg 162, 4125 Pfehen, Switzerland, Dieter Lohmann, Unterwartweg 49, 4132 Muttenz, Switzerland and Ernst Neuenschwander, Moosweg 20, 4125 Riehen, Switzerland

is(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 June 11, 1980

To: The Commissioner of Patents

Arnold Seiler  Ernst Altherr
1. A salt having groups bound to side chains, which salt is formed from formamidines with polymers containing sulfoinic acid groups, and corresponds to the formula

\[
\begin{align*}
\text{SO}_3^\ominus & \quad \left[ \begin{array}{c}
\text{N} \\
\begin{array}{c}
Q_1 \\
Q_2 \\
Q_3
\end{array}
\end{array} \right]
\end{align*}
\]

wherein \(Q_1\) and \(Q_2\) are each hydrogen, \(C_1-C_4\)-alkyl, or phenyl which is unsubstituted or substituted by \(C_1-C_4\)-alkyl or halogen, and \(Q_3\) is

\[
\begin{align*}
\text{R}_o & \quad \text{R}_p
\end{align*}
\]

in which \(R_o\) and \(R_p\) are each hydrogen, halogen or \(C_1-C_4\)-alkyl, and wherein the groups of the formula I are bound either
directly or by way of a bridge member, other than \(-\text{COOC}_2\text{H}_4^-,\)
to the polymer main structure, and wherein the proportion
of recurring structural elements in the polymer having
groupings of the formula I is at least 5\% relative to the
number of recurring structural elements of the polymer.
6. A pesticidal composition containing as active
ingredient a salt according to Claim 1, together with
suitable carriers and/or other additives.
Application Number : Lodged :

Complete Specification Lodged :
Accepted :
Published :

Priority :

Related Art :

Name of Applicant : CIBA-GEIGY AG

Address of Applicant : Klybeckstrasse 141, 4002 Basle, Switzerland

Actual Inventors : CHRISTIA. D'HOND'T, DIETER LOHMANN and ERNST NEUENSCHWANDER


Complete Specification for the invention entitled :

"SALTS FORMED FROM FORMAMIDINES WITH POLYMERS CONTAINING SULFONIC ACID GROUPS"

The following statement is a full description of this invention, including the best method of performing it known to me/us :
Salts formed from formamidines with polymers containing sulfonic acid groups

The present invention relates to salts formed from formamidines with polymers containing sulfonic acid groups, to processes for producing the salts, and to their use in combating pests.

The subject matter of the invention is thus salts having groups bound to side chains, which salts are formed from formamidines with polymers containing sulfonic acid groups, and correspond to the formula

\[
\text{SO}_3^+ \Theta^+ \left[ \begin{array}{c} Q_1 \\ Q_2 \end{array} \right]
\]

wherein \( Q_1 \) and \( Q_2 \) are each hydrogen, \( C_1-C_4 \)-alkyl, or phenyl which is unsubstituted or substituted by \( C_1-C_4 \)-alkyl or halogen, and \( Q_3 \) is

\[
\begin{array}{c}
\text{R}_0 \\
\text{R}_p
\end{array}
\]

in which \( \text{R}_0 \) and \( \text{R}_p \) are each hydrogen, halogen or \( C_1-C_4 \)-alkyl, and wherein the groups of the formula I are bound either directly or by way of a bridge member, other than \(-\text{COOC}_2\text{H}_4^-\), to the polymer main structure, and wherein the proportion
of recurring structural elements in the polymer having groupings in the formula I is at least 5% relative to the number of recurring structural elements of the polymer.

By halogen in the case of \( Q_1, Q_2, R_0 \) and \( R_p \) are meant fluorine, chlorine, bromine or iodine, particularly however chlorine and bromine.

Examples of \( C_1-C_4 \)-alkyl groups denoted by \( Q_1, Q_2, R_0 \) and \( R_p \) are methyl, ethyl, propyl, isopropyl, n-, sec-, i- and t-butyl.

The polymers, which can be straight-chain, branched-chain or crosslinked, are for example: polyesters, polyester amides, polyamides, polyimides, polyamide imides, polyester imides, polyethers, polyurethanes, polyureas, polycondensation products of phenol, naphthalene, melamine and/or urea with aldehydes or ketones, such as formaldehyde, polysaccharides, gelatin, organopolysiloxanes, polyphosphacenes, polymers obtained by homo- or copolymerisation of monomers containing multiple compounds, for example \( \text{C} = \text{C} \) double bonds; or by ring-opening polymerisation of saturated or unsaturated aliphatic rings optionally containing hetero atoms. It is also possible to use tanning substances or polymers containing sulphonic acid groups, which are obtained by decomposition or transformation reactions from natural substances, such as cellulose, lignin or chitin, and the like.

The polymers can be straight-chain, branched-chain or crosslinked. If they are straight-chain polymers, they advantageously have a mean molecular weight of at least 500.

Preferred classes of straight-chain polymers are: straight-chain polymerisation products having a mean molecular weight of about 500 to about 2,000,000, especially
of about 1000 to about 200,000; straight-chain polycondensation products having a mean molecular weight of about 500 to 60,000, particularly of about 1000 to about 30,000; straight-chain polyaddition products having a mean molecular weight of about 1000 to about 40,000, especially of about 2000 to about 20,000; straight-chain products which are obtained by ring-opening polymerisation and which have a mean molecular weight of about 500 to about 40,000, particularly about 1000 to about 20,000; decomposition and transformation products from natural substances having a mean molecular weight of about 500 to about 2,000,000, especially of about 1000 to about 100,000.

The mean molecular weights are determined by known methods, generally by means of vapour pressure osmometry, light scattering or viscosity measurement.

$Q_1$ is preferably hydrogen, methyl or n-butyl, $Q_2$ is methyl, and $Q_3$ is

\[
\begin{align*}
&\text{existent molecules:} \quad \text{CH}_3, \quad \text{NH}_2, \\
&\text{aliphatic or aromatic:} \quad \text{C}_2\text{H}_5, \quad \text{C}_6\text{H}_{11}, \quad \text{Ph}
\end{align*}
\]

Of particular importance are polymers having the recurring structural elements of the formula II

\[
\begin{align*}
&\text{wherein } Q_1, Q_2 \text{ and } Q_3 \text{ have the meanings defined under the}
\end{align*}
\]
formula I, R is hydrogen, chlorine, -CN or C\(_1\)-C\(_4\)-alkyl, Z is the direct bond, -O- or straight-chain or branched-chain alkylene having 1-4 C atoms, phenylene or naphthylene each of which is unsubstituted or substituted by halogen atoms, alkyl or alkoxy groups having 1-4 C atoms, or by a group -SO\(_3\)M\(^+\), or Z is -CH\(_2\)O-CH\(_2\)CH\(_2\)-, -CH\(_2\)OCH\(_2\)CH\(_2\)-, -CH\(_2\)SCH\(_2\)CH\(_2\)-, -CH\(_2\)-S-CH\(_2\)CH\(_2\)-, a ring-substituted group , in which the ring is unsubstituted or is substituted by halogen atoms, or by alkyl or alkoxy groups having 1-4 C atoms, or Z is a group  

\[
\begin{align*}
\text{or} \quad & \quad \begin{array}{c}
\text{-O-} \\
\text{CH}_2\text{O-CH}_2\text{CH}_2\text{-} \\
\text{-CH}_2\text{SCH}_2\text{CH}_2\text{-} \\
\text{-CH}_2\text{-S-CH}_2\text{CH}_2\text{-}
\end{array}
\end{align*}
\]

each of which is unsubstituted or substituted by -SO\(_3\)M\(^+\), or Z is -CO\(_2\)R\(_1\) or -CON(R\(_2\))(R\(_3\))-, in which R\(_1\) is straight-chain or branched-chain C\(_3\)-C\(_8\)-alkylene which is unsubstituted or substituted by chlorine or bromine atoms, or interrupted by an oxygen atom, or R\(_1\) is cyclohexylene, naphthylene, naphthylene substituted by a -SO\(_3\)M\(^+\), or it is C\(_2\)-C\(_4\)-alkylene-0-phenylene  

\[
\begin{align*}
\text{or} \quad & \quad \begin{array}{c}
\text{-O-} \\
\text{CH}_2\text{O-CH}_2\text{CH}_2\text{-} \\
\text{-S-CH}_2\text{CH}_2\text{-}
\end{array}
\end{align*}
\]

R\(_2\) is the direct bond, straight-chain or branched-chain C\(_1\)-C\(_6\)-alkylene optionally interrupted by an oxygen atom, straight-chain or branched-chain oxyalkylene having 1-6 C atoms, phenylene, naphthylene, naphthylene substituted by a group -SO\(_3\)M\(^+\), C\(_1\)-C\(_4\)-alkylene-0-phenylene,  

\[
\begin{align*}
\text{or} \quad & \quad \begin{array}{c}
\text{-O-} \\
\text{CH}_2\text{O-CH}_2\text{CH}_2\text{-} \\
\text{-CH}_2\text{SCH}_2\text{CH}_2\text{-} \\
\text{-CH}_2\text{-S-CH}_2\text{CH}_2\text{-}
\end{array}
\end{align*}
\]

and R\(_3\) is hydrogen or C\(_1\)-C\(_6\)-alkyl, and
Me is hydrogen or \( \oplus [N(Q_1)(Q_2)(Q_3)] \), the proportion of structural elements of the formula II being at least 5%, preferably 30-100%, relative to the number of recurring structural elements of the polymer.

Preferred polymers of this type are: linear polymers having a mean molecular weight of about 500 to 2,000,000, which consist of recurring structural elements of the formula II and recurring structural elements of the formula III

\[
\begin{array}{c}
\text{CH}_2 \text{C} \\
\text{Z-SO}_3 \text{H}
\end{array}
\]  

wherein R and Z have the above-given meanings, and the proportion of recurring structural elements of the formula III is 0.5 to 95% relative to the number of recurring structural elements of the polymer; polymers having recurring structural elements of the formula II, recurring structural elements of the formula IV

\[
\begin{array}{c}
\text{CH}_2 \text{C} \\
\text{R}_4
\end{array}
\]  

wherein R is hydrogen, chlorine, -CN or \(-C_1-C_4\)-alkyl, \(R_4\) is hydrogen, halogen, -CON(R_5)(R_6), -COOH, -COO \(\oplus \text{Me} \), phenyl which is unsubstituted or substituted by chlorine, or \(R_4\) is alkyl, alkoxy or alkenyl each having up to 4 C atoms, cyclohexyl, -COO-alkyl having 1-12 C atoms in the alkyl moiety, -COO(CH_2)_x-OH, -COO-phenyl, -OCO-alkyl having 1-4 C atoms in the alkyl moiety, -OCO-phenyl, -CO-alkyl having 1-4 C atoms in the alkyl moiety, phenoxy or a group

\[
\begin{array}{c}
\text{Me}
\end{array}
\]  

\(\text{Me}\) is a monovalent metal, \(x\) is an integer
from 2-6 inclusive, \( A' \) is \(-\text{(CH}_2\text{)}_3^-\), \(-\text{(CH}_2\text{)}_5^-\), \(-\text{CO-(CH}_2\text{)}_2^-\), \(-\text{CO-CH=CH}^-\) or \(-\text{CO-CH}_3^-\), \( R_5 \) is hydrogen, \( \text{C}_1-\text{C}_4\)-alkyl, \( \text{C}_1-\text{C}_6\)-hydroxyalkyl or phenyl, and \( R_6 \) is hydrogen or \( \text{C}_1-\text{C}_4\)-alkyl, and optionally structural elements of the formula III, and the proportion of recurring structural elements of the formulae III and IV together is 0.5 to 95%, relative to the number of recurring structural elements of the polymer; crosslinked polymers having recurring structural elements of the formula II, recurring structural elements of the formula V, 

\[
\begin{array}{cccc}
\text{R} & \text{R} \\
\text{CH} - \text{C} - \text{A} - \text{C} - \text{CH}_2 \\
\end{array}
\]

wherein \( R \) is hydrogen, chlorine, \(-\text{CN} \) or \( \text{C}_1-\text{C}_4\)-alkyl, \( A \) is the direct bond, \(-\text{O}^-\), \(-\text{SO}_2^-\), \(-\text{CON}^-\), \(-\text{CONHC}H_2^-\), \( \text{Me}^{2+}(-\text{OOC})_2 \), \( \text{Me}^{3+}(-\text{OOC})_2 \), \(-\text{OOC-CH}-\), \(-\text{CONH}(\text{CH}_2)_y\text{NHC}O^-\), \(-\text{COO(} \text{CH}_2\text{)}_x\text{OCO}^-\) or \(-\text{COO(} \text{CH}_2\text{)}_y(0-(\text{CH}_2)_x\text{OCO}^-\), \( R_7 \) is hydrogen, ethyl, \(-\text{SO}_3H \) or \(-\text{SO}_3^-\) with \( N \) \( \frac{Q_1}{Q_2} \) \( \frac{Q_3}{Q_4} \), \( \text{Me} \) is a bi- or trivalent metal, \( y \) is an integer from 1-6 inclusive, and \( x \) is an integer from 2-6 inclusive, and \( Q_1, Q_2 \) and \( Q_3 \) have the above-given meanings, and optionally recurring structural elements of the formula III and/or IV, and the proportion of recurring structural elements of the formula V is 0.2 - 20%, and the proportion of recurring structural elements of the formula III and/or IV together is at most 94.5%, relative to the number of recurring structural
elements of the polymer.

In the above formulae, alkyl and hydroxyalkyl groups denoted by R_1, R_3, R_4 and R_5, alkenyl groups denoted by R_4 as well as alkyl and alkoxy substituents in groups Z and R_4 can be straight-chain or branched-chain, but are preferably straight-chain. Alkyl groups R_2, R_5 and R_6 and alkyl or alkoxy substituents in groups Z preferably contain 1 or 2 C atoms. When Z groups are substituted by halogen atoms, they are in particular chlorine or bromine atoms. Alkylene groups R_1 and R_2 are preferably unsubstituted and contain 3-5 C atoms and 1-5 C atoms, respectively. Oxyalkylene groups R_4 and hydroxyalkyl groups R_5 advantageously contain 1-4 C atoms.

Examples of mono- to trivalent metals Me which may be mentioned are: Na, K, Ba, Mg, Ca and Al.

Particularly preferred polymers are those having recurring structural elements of the formulae II to V wherein R is hydrogen or methyl, Z is the direct bond, -COO-alkylene having 3-4 C atoms and especially phenylene, R_1 is alkylene having 2-4 C atoms, R_2 is -(CH_2)_2-4-, -C(CH_3)(CH_3)CH_2-, naphthylene and particularly phenylene each substituted by a group -SO_3\{N\leftarrow O_1O_2\}\rightarrow O_3, R_3 is hydrogen, R_4 is hydrogen, chlorine, unsubstituted phenyl, -CON(R_5)(R_6), -COO-alkyl having 1-8 C atoms in the alkyl moiety, -OCO-alkyl having 1 or 2 C atoms in the alkyl moiety, or alkoxy having 1-4 C atoms, R_5 and R_6 independently of one another are each hydrogen or methyl, A is the direct bond, -O- or -COC-CH_2-, -CO-NH-CH_2-, -CONH(CH_2)_y NHCO- or -COO(CH_2)_xOOC-, y is an integer from 1-6 inclusive, x is an integer from 2-6, R_7 is hydrogen, -SO_3H or
\(-\text{SO}_3\) \(\Theta\) \(\Theta\) \(\left[ N \left( Q_1 \right) \left( Q_2 \right) \left( Q_3 \right) \right]\),

\(Q_1\) is hydrogen, methyl or n-butyl, \(Q_2\) is methyl and

\(Q_3\) is

\[
\begin{array}{c}
\text{CH}_3 \\
\text{Cl}
\end{array}
\]

or

\[
\begin{array}{c}
\text{CH}_3 \\
\text{Br}
\end{array}
\]

Very particularly preferred are salts of cations of the formulae

\[
\begin{array}{c}
\text{CH}_3 \\
\text{Cl}
\end{array}
\]

or

\[
\begin{array}{c}
\text{CH}_3 \\
\text{Br}
\end{array}
\]

\[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3
\end{array}
\]

or

\[
\begin{array}{c}
\text{CH}_3 \\
\text{C}_2\text{H}_5
\end{array}
\]

or

\[
\begin{array}{c}
\text{CH}_3 \\
\text{Cl}
\end{array}
\]
with anions of polyvinylsulfonic acids, polystyrenesulfonic acids, poly[\(N\)-(sulfoalkyl)-acrylamide] and sulfonated cation exchangers formed from styrene and about 8-12 per cent by weight of divinyl benzene (crosslinking agent), or sulfonated cation exchangers having macroporous structures.

A further class of preferred polymers are those consisting of recurring structural elements of the formulae VIa to VIe

or mixtures thereof, wherein \(R_8\) is hydrogen or methyl

\[ M^+ \text{CH}_3 \]

\(R'_8\) is hydrogen or \(-\text{CH}_3\), and \(M^+\) is hydrogen or a group
[N(Q₁)(Q₂)(Q₃)], and Q₁, Q₂ and Q₃ have the above-given meanings, and the proportion of structural elements of the formulae VIa, VIb, VIc and VIe, where M⁺ is other than hydrogen, is at least 5%, preferably 30 - 100%, relative to the number of recurring structural elements of the polymer.

Among the polymers having structural elements of the formulae II to VIe, those which have ion-exchanging properties have a particular importance. Polymer resins having a macroporous structure prove to be particularly suitable by virtue of their large internal surface and their high capacity for salt formation with the active substance, and by virtue of the adequate release of active substance under biological conditions.

Also preferred are straight-chain polycondensation products which have a mean molecular weight of about 500 to about 60,000 and which consist of recurring structural elements of the formula VII

\[
\left[ \frac{\gamma_1 - L - \gamma_2 - Q}{\gamma_1 \gamma_2} \right]
\]

wherein \( L \) is a group

\[
\begin{align*}
-\left(\text{CH}_2\right)_z - & \left(\text{CH}_2\right)_{z'}
\end{align*}
\]

\( \text{SO}_3 \) or \( \text{SO}_3 \)

\( \gamma_1 \) is the number 1 or 2, \( \gamma_2 \) is naught, 1 or 2, \( M^+ \) is hydrogen or a group \( [N(Q_1)(Q_2)(Q_3)] \), \( \gamma_1 \) and \( \gamma_2 \) independently of one another are each -OCO-, -COO-, -CONH-, -NHCO-, -OCONH-, -NHCO or -NHCONH-, optionally branched-chain alkylene having 2-10 C atoms, or alkylene having 2-10 C atoms which is optionally interrupted by -O- or
-NR₈-, or they are phenylene or naphthylene each of which is unsubstituted or is substituted by halogen atoms, methyl, methoxy or -SO₃M⁺ groups, or they are cyclohexylene, \( \text{or} \quad -\text{CH}_2-\text{C}_2-\text{CH}_2- \), and \( G \) is the direct bond, -O-, -CH₂-, -C(CH₃)₂ or -SO₂-, and \( Q_1 \), \( Q_2 \) and \( Q_3 \) have the above-given meanings, and the proportion of structural elements of the formula VII, where \( M^+ \) is not hydrogen, is at least 5%, preferably 30-100%, relative to the number of recurring structural elements of the polymer.

The polymers according to the invention can be produced essentially by three methods known per se, namely:

a) by reacting an optionally crosslinked or branched-chain polymer, which contains laterally bound -SO₃H groups, which are bound directly or by way of a bridge member different from -COOC₂H₄⁻ to the polymer main structure, the proportion of these groups being at least 5% relative to the number of recurring structural elements of the polymer, with a compound of the formula VIII

\[
\text{Q}_1 \text{Q}_2 \text{Q}_3
\]

wherein \( Q_1 \), \( Q_2 \) and \( Q_3 \) have the meanings given under the formula I;

b) by firstly reacting a monomer, which contains -SO₃H groups bound directly or by way of a bridge member different from -COOC₂H₄⁻, with a compound of the formula VIII, and subsequently converting the resulting monomer salt, optionally in the presence of comonomers and/or crosslinking agents, into a polymer, the molar ratio of monomer salt to comonomer and/or crosslinking agent being 1:19 to 1:0; or
c) by reacting a polymer, which contains reactive groups, for example the anhydride, acid chloride, ester, isocyanate or epoxide groups, with at least 5\%, relative to the number of recurring structural elements of the polymer, of a compound of the formula IXa or IXb

\[
\begin{align*}
&\text{H}_2\text{N}-Z_1\text{-SO}_3\left[\begin{array}{c}
\text{O}_1 \\
\text{O}_2 \\
\text{O}_3
\end{array}\right]
\end{align*}
\] (IXa)

\[
\begin{align*}
&\text{HO}-Z_2\text{-SO}_3\left[\begin{array}{c}
\text{O}_1 \\
\text{O}_2 \\
\text{O}_3
\end{array}\right]
\end{align*}
\] (IXb)

wherein \( Q_1 \), \( Q_2 \) and \( Q_3 \) have the meanings given in Claim 1, \( Z_1 \) is the direct bond, straight-chain or branched-chain \( C_1\text{-}C_8 \)-alkylene which is unsubstituted or substituted by chlorine or bromine or is optionally interrupted by an oxygen atom, or \( Z_1 \) is cyclohexylene, or phenylene or naphthylene each of which is unsubstituted or substituted by a group \(-\text{SO}_3\text{M}^+\), \( Z_2 \) is the direct bond, straight-chain or branched-chain \( C_3\text{-}C_8 \)-alkylene which is unsubstituted or substituted by chlorine or bromine, or \( Z_2 \) is cyclohexylene, phenylene or naphthylene each unsubstituted or substituted by a group \(-\text{SO}_3\text{M}^+\), or \( Z_2 \) is \( (\text{CH}_2)_2\text{SO}_3\text{M}^+ \), and \( \text{M}^+ \) is hydrogen or

\[
\begin{align*}
&\text{N}\left[\begin{array}{c}
\text{O}_1 \\
\text{O}_2 \\
\text{O}_3
\end{array}\right]
\end{align*}
\]

The above reactions are performed advantageously in the presence of a suitable solvent, such as dioxane, chloroform, \( \text{CH}_2\text{Cl}_2 \), tetrahydrofuran, ethanol, methanol, and so forth. The reaction can be carried out in a
homogeneous solution, in a dispersion or in a suspension. Salt formation is effected generally at a temperature between about 25 and 80°C. The fixation yield can be determined by customary analytical methods, such as by elementary analysis, thin-layer chromatography and gas-chromatography. The conversion of the monomer salts into the corresponding polymers and also the reaction of the salts of the formula IXa or IXb with the defined polymers according to process variant c) are performed, depending on the type of monomer or polymer, for example by polymerisation, polycondensation or polyaddition, in a manner known per se and with the use of customary solvents, catalysts and/or polymerisation initiators.

Polymers having structural elements of the formula II are produced, using a process analogous to those described in the foregoing,

a) by reacting a polymer, which contains recurring structural elements of the formula III

\[
\begin{align*}
\text{CH}_2 & \quad \text{C-R} \\
\text{2-SO}_3 & \quad \text{H} 
\end{align*}
\]  

in a ratio of 20:1 to 1:1 relative to the number of recurring structural elements of the polymer, with a compound of the formula VIII, or

b) by firstly reacting a monomer of the formula IIa

\[
\begin{align*}
\text{CH}_2 & \quad \text{C-R} \\
\text{2-SO}_3 & \quad \text{H} 
\end{align*}
\]  

with a compound of the formula VIII, and then polymerising the resulting monomer salt of the formula IIb

\[
\begin{align*}
\text{CH}_2 & \quad \text{C-R} \\
\text{2-SO}_3 & \quad \text{H} 
\end{align*}
\]

optionally in the presence of comonomers and/or crosslinking
agents, the molar ratio of compounds of the formula IIb to comonomers and/or crosslinking agents being 1:19 to 1:0, and R, Z, Q₁, Q₂ and Q₃ having the meanings defined in the foregoing.

Polymers having a mean molecular weight of about 500 to about 2,000,000, which consist of recurring structural elements of the formula II and 0.5 - 95% of recurring structural elements of the formula III, can be produced by reacting a polymer consisting of recurring structural elements of the formula III, in a ratio of 20:1 to 100:99.5 relative to the number of recurring structural elements of the polymer, with a compound of the formula VIII; or by polymerising a monomer salt of the formula IIb, in a molar ratio of 1:19 to 199:1, with a comonomer of the formula IIa.

Polymers having a mean molecular weight of about 500 to 2,000,000, which consist of recurring structural elements of the formula II and all together 0.5 to 95% of recurring structural elements of the formula IV and optionally of recurring structural elements of the formula III, can be obtained by reacting a polymer consisting of recurring structural elements of the formula III and 0.5 to 95% of recurring structural elements of the formula IV, in a ratio of 20:1 to 100:99.5 relative to the number of recurring structural elements of the polymer, with a compound of the formula VIII; or by polymerising a monomer salt of the formula IIb, in a molar ratio of 1:19 to 199:1, with a comonomer of the formula IVa

\[
\text{CH}_2\text{-C-R} \\
\text{R}_4
\]

and optionally a comonomer of the formula IIa.

Finally, polymers consisting of recurring structural elements of the formula II, 0.5 - 20% of recurring
structural elements of the formula \( V \) and optionally 75 - 94.5\% of recurring structural elements of the formula III and/or IV can be produced either by reacting a polymer consisting of recurring structural elements of the formula III, 0.5 - 20\% of recurring structural elements of the formula V and optionally 75 - 94.5\% of recurring structural elements of the formula IV, in a ratio of 20:1 to 100:99.5 relative to the number of recurring structural elements of the polymer, with a compound of the formula VIII, or by polymerising a monomer salt of the formula IIb, in a molar ratio of 1:19 to 199:1, with a crosslinking agent of the formula Va

\[
\text{CH}_2\text{--A--C--CH}_2^n
\]

(Va)

and optionally a comonomer of the formula IVa and/or a comonomer of the formula IIa.

Polymers formed from recurring structural elements of the formulae VIa to VIe can be produced

a) by reacting a polymer consisting of recurring structural elements of the formulae VIa' to VIe'

\[
\text{(VIa')}
\]

\[
\text{(VIb')}
\]

\[
\text{(VIc')}
\]
or of mixtures thereof, in a ratio of 20:1 to 1:1 relative to the number of recurring structural elements of the formulae VIa, VIb, VIC and VIe, with a compound of the formula VIII; or

b) by firstly reacting a compound of the formula VIa”, VIb”, VIC” or VIe”

or a mixture of such compounds, with a compound of the formula VIII, and subsequently polycondensing the resulting monomer salt of the formula VIa””, VIb”’ , VIC’” or VIe”’
or the resulting mixture of such monomer salts, optionally in the presence of phenol and/or of a compound of the formula VIa"", VIb"", VIC"" or VIe"", with a compound of the formula X

(X),

in which formulae the symbols Q_1, Q_2, Q_3, R_8 and (W) have the meanings defined in the foregoing, and the molar ratio of monomer salt of the formulae VIa"", VIb"", VIC"" and/or VIe"" to compound of the formulae VIa"", VIb"", VIC"", VIe"" and/or phenol is 1:19 to 1:0.

Polymers consisting of structural elements of the formula VII are advantageously produced
a) by reacting a polymer consisting of recurring structural elements of the formula VIIa

\[
\left[ Y_1 - L_1 - Y_2 - Q \right]
\]  

(VIIa),

in a ratio of 20:1 to 1:1 relative to the number of recurring structural elements of the polymer, with a compound of the formula VIII; or

b) by firstly reacting a compound of the formula VIIb

\[
Y_3 - L_1 - Y_4
\]  

(VIIb)

with a compound of the formula VIII, and subsequently polycondensing or polyadding the resulting monomer salt of the formula VIIc

\[
Y_3 - L_2 - Y_4
\]  

(VIIc),

optionally in the presence of a compound of the formula VIIb, with a compound of the formula VIIId

\[
Y_5 - Q - Y_6
\]  

(VIIId),

in which formulae the symbols have the following meanings:

\[ L_1 \] is a group

or

\[ L_2 \] is a group
Y₃ and Y₄ independently of one another are each -OH, -NH₂, -COCl, -COOH, -COO-phenyl or -COO-alkyl having 1-3 C atoms in the alkyl moiety, and when Y₃ and/or Y₄ are -OH or NH₂, Y₅ and Y₆ independently of one another are each -COCl, -COOH, -COOP-phenyl, -COO-alkyl having 1-3 C atoms in the alkyl moiety or they are each -NCO, and, when Y₃ and/or Y₄ are -COCl, -COOH, -COO-alkyl having 1-3 C atoms in the alkyl moiety or -COOP-phenyl, Y₅ and Y₆ independently of one another are each -OH or -NH₂, and Y₁, Y₂, Q, Q₁, Q₂ and Q₃ are as defined in the foregoing, and the molar ratio of compound of the formula VIIc to compound of the formula VIIb is 1:19 to 1:0.

The reactants to be used for the above reactions are known or can be produced by methods known per se. Polymers having laterally-bound -SO₃H groups bound as defined can be produced for example as follows:

1) By introduction of the -SO₃H groups into an existing linear, branch-chain or crosslinked polymer chain by substitution, condensation or addition reactions, for example by sulfonation with SO₃, H₂SO₄, and the like, sulfochlorination, sulfomethylation, sulfoethylation with vinylsulfonic acids, sulfoalkylation with sulfones or sodium bisulfite addition reaction with double bonds, for example with polyethylene fumarate or butadiene-polymers; or by reaction of polymers having reactive groups, such as anhydride, acid chloride, ester, isocanate or epoxide groups, for example polyacrylic acid chloride, -methyl ester or -glycidyl ester, with functional sulfonic acids or functional polysulfonic acids which carry hydroxyl or
amino groups, or by reaction of HO- or HN-containing polymers with cyclic sulfones.

2) By synthesis of the polymer chain formed from monomers which contain the -SO$_3$H group in the free or masked form, for example as salt, whereby the polymer chain can be formed by polymerisation, polyaddition, polycondensation or ring-opening polymerisation, optionally in the presence of suitable comonomers and/or crosslinking agents.

Examples for the formation of the polymer chain from suitable monomers are in particular the homo- and copolymerisation of polymerisable sulfonic acids, optionally in the presence of crosslinking agents, as described for example in the U.S. Patent Specifications Nos. 2,983,712 and 2,914,499, and in the German Auslegeschriften (publication after examination) Nos. 1,224,506 and 1,292,129; polycondensation of diols, diamines, amino alcohols, dicarboxylic acids and derivatives thereof or diisocyanates, all containing sulfonic acid groups, with suitable Co-condensation components; and polycondensation of sulfonic acids of aromatic hydroxyl compounds, for example phenolsulfonic acids, with aldehydes or ketones, such as formaldehyde.

It is also possible to use as starting polymers sulfated or sulfoalkylated polysaccarides, such as cellulose, amylose, and so forth, ligninsulfonic acids or sulfoalkylated proteins, which can be produced in a manner known per se.

Examples of monomers to be used in process variant b), as well as of comonomers and crosslinking agents to be if need be concomitantly used, are to be found in the above-mentioned U.S. Patent Specifications and German Auslegeschriften. Salts of the formulae IXa and IXb can be produced, using customary methods, by reaction of the appropriate amino- or hydroxysulfonic acids with compounds.
of the formula VII.

The polymers having groups of the formula I are suitable for combating various pests on animals and plants.

The polymers containing groups of the formula I are particularly suitable for controlling all development stages, such as eggs, larvae, pupae and adults of insects, phytopathogenic and zooparasitic lice, mites and also ticks, for example of the orders: Lepidoptera, Coleoptera, Homoptera, Heteroptera, Diptera, Acarina, Thysanoptera, Orthoptera, Anoplura, Siphonaptera, Mallophaga, Thysanura, Isoptera, Psocoptera and Hymenoptera.

The polymers having groups of the formula I are especially suitable for combating insects which damage plants, in particular insects which damage plants by eating, in crops of ornamental plants and useful plants, especially in cotton crops (for example against Spodoptera littoralis and Heliothis virescens) and in crops of vegetables (for example against Leptinotarsa decemlineata and Myzus persicae), as well as for combating parasitic bee mites (Varroa jacobsonii and Acarapis woodi).

The polymers containing groups of the formula I surprisingly have a stability and long-term effect that are better than those of analogous salts known from the British Patent Specification No. 1,394,990. The compounds of the formula I are also safer in application than the free bases.

The polymers having groups of the formula I can be used on their own or together with suitable carriers and/or additives. Suitable additives can be solid or liquid and correspond to the substances common in formulation practice, such as natural or regenerated substances, solvents, dispersing agents, wetting agents, adhesives, thickeners, binders and/or fertilisers.

The compositions according to the invention are produced
in a manner known per se by the intimate mixing and/or grinding of the polymers containing groups of the formula I with the appropriate formulation auxiliaries, optionally with the addition of dispersing agents or solvents which are inert to the active substances.

**Example 1**: Production of polyvinylsulfonic acid and reaction thereof with N*-N'-dimethyl-N*- (4-chloro-o-tolyl)-formamidine (chlorodimeform) to form the salt.

By the method described by W. Kern and R.C. Schulz (Houben-Weyl, Methoden der organischen Chemie, Vol. 14/1, p. 1100), 291 g of sodium vinyl sulfonate, dissolved in 700 ml of water, are polymerised at about 5°C with 2.4 g of potassium persulfate and 1 g of sodium hydrogen sulfite. The polymer is isolated by precipitation from the aqueous solution by the addition of 2.1 litres of methanol, and purified by reprecipitation from water/methanol.

To produce the free polyvinylsulfonic acid, 45 g of the sodium polyvinyl sulfonate obtained are dissolved in 115 ml of distilled water, and the solution is saturated at 0-5°C with gaseous hydrogen chloride. After removal of the sodium chloride which has precipitated, the solution is concentrated in a rotary evaporator, and is then freed from excess hydrogen chloride by repeated distillation with freshly added water. The polyvinylsulfonic acid obtained is isolated by freeze drying, and subsequently dried over phosphorus pentoxide under high vacuum.

27.2 g of the polyvinylsulfonic acid obtained are suspended in 300 ml of anhydrous chloroform, and the suspension is stirred with a solution of 49.4 g (0.264 mol) of chlorodimeform firstly for 10 hours at room temperature and then for 10 hours at 50°C. After cooling, the supernatant solution is decanted, and the product is freed by repeated digestion with chloroform from unreacted
chlorodimeform. After pulverisation and drying, the yield is 61 g of beige-coloured product, which softens at about 110°C, contains 10.6 per cent by weight of sulfur and 7.8 per cent by weight of nitrogen, and has a mean molecular weight $\bar{M}$, calculated from a viscosity of $[\bar{\eta}] = 0.0075$ dl/g in chloroform at 20°C, of about 75,000. The content of chlorodimeform is about 54 per cent by weight.

Example 2: Production of polystyrenesulfonic acid and reaction thereof with chlorodimeform to give the salt.

By use of a method described by P. Schneider (Houben-Weyl, Methoden der organischen Chemie, Vol. 14/1, p. 683), 107 g of polystyrene ($\bar{M}_w$ = about 200,000) are dissolved in 650 ml of dichloromethane, and a solution of 100 g of solid sulfur trioxide in 1350 ml of dichloromethane is slowly added at 0°C with vigorous stirring and with cooling with dry ice/ethanol. The resulting suspension of sulfonated polystyrene is subsequently stirred at 0°C for 43 hours, filtered, and then carefully washed with anhydrous diethyl ether. The white pulverulent, hygroscopic product is dried under high vacuum, and it contains 16.5 per cent by weight of sulfur.

100 g of the polystyrenesulfonic acid obtained are slowly introduced into a solution of 90 g of chlorodimeform in 1000 ml of chloroform. After the exothermic reaction has subsided, stirring is maintained for 24 hours at room temperature. The product is filtered and subsequently washed with anhydrous diethyl ether until no further unreacted chlorodimeform can be detected. Drying under high vacuum yields a pulverulent white product having a softening point of about 194°C and containing 5.8 per cent by weight of nitrogen and 7.9 per cent by weight of sulfur. The content of chlorodimeform is about 41 per cent by weight.
**Example 3:** In order to obtain a system free from water, a cation exchanger, which is produced by polymerisation of styrene with simultaneous crosslinking with 8 per cent by weight of divinyl benzene and subsequent sulfonation ["Dowex HCR-S", Dow Chemical], is ground, and then dried at 90°C in vacuo. The exchange capacity of the ion-exchanger is 4.7 m equiv. of $-\text{SO}_3\text{H}/g$.

150 g of chlorodimeform are dissolved in 561 g of Diesel oil, and 165 g of the dried and ground cation-exchanger are introduced portionwise into this solution. To the suspension obtained are added dropwise 24 g of methanol in the course of 15 minutes. An exothermic reaction commences, and the reaction mixture is held for 3 hours at 50°C with continuous stirring. The liquid phase after this period of time contains no further chlorodimeform. To stabilise the suspension, 100 g of oleyl polyglycol ether and 10 g of bentone are stirred in. The stable suspension obtained contains per litre 150 g of chlorodimeform.

**Example 4:** A cation exchanger, produced by polymerisation of styrene in the presence of 8 per cent by weight of divinyl benzene and subsequent sulfonation ("Amberlyst 15", Röhm + Haas), and having an exchange capacity of 2.9 val./l, a particle size of 0.3 - 1.2 mm and a macro-reticular structure, is largely freed, before charging, from residual water by repeated mixing with dioxane and filtration (moisture content < 1 per cent by weight). 5 g (0.025 mol) of chlorodimeform, dissolved in 4.14 g of dioxane, are subsequently added to 5 g of the cation-exchanger resin and 5.86 g of dioxane. The reaction mixture is heated with stirring to 60°C, and after one hour, a small amount of the supernatant solution is taken for the purpose of analysis of the active substance by gas-chromatography. The heating
is turned off after 8 hours, and 24 hours after commencement of the charging process, a second analysis specimen is taken. The total reaction time is 31 hours. The reaction mixture is filtered by means of a Büchner funnel, and washed four times with 50 ml of acetone each time. The ion-exchanger resin charged with chlorodimeform is subsequently dried at room temperature until the weight is constant. The content of chlorodimeform in the ion-exchanger resin is calculated from the drop in concentration in the supernatant solution. The initial concentration of the solution is 33.3 per cent by weight (5 g of chlorodimeform in 10 g of dioxane). After a reaction time of one hour, the concentration is 23.8 per cent by weight, and after one day it is 18.7 per cent by weight. From that is obtained a calculated content of chlorodimeform in the charged ion-exchanger of 35 per cent by weight. In order to confirm this value, a chlorine and nitrogen elementary analysis is performed:

- calculated Cl 6.3 % N 4.9 %
- found Cl 6.4 % N 5.2 %
  (average of 6.2 and 6.8)  (average of 5.3 and 5.1)

From the nitrogen content there is given a calculated value of 36.5 per cent by weight of chlorodimeform, and from the chlorine content a calculated value of 35.5 per cent by weight of chlorodimeform, values which agree very well with the expected (theoretical) value of 35 per cent by weight.

The ion-exchanger pellets charged with chlorodimeform are subsequently ground to a fine powder. The chlorodimeform content in the charged ion-exchanger is checked by another method:

10 ml of chloroform, which contains 0.25 per cent by weight of eicosane as international standard for gas-
chromatographical analysis and 0.5 ml of diethylamine, 
are added to 150 mg of the ion-exchanger charged with 
chlorodimeform. In this way the chlorodimeform on the 
ion-exchanger is to be exchanged by the stronger 
base, diethylamine, and the content of released chloro-
dimeform to be then measured according to the gas-
chromatogram. After a reaction time of one day, a 
specimen of the chloroform solution is examined with 
respect to the chlorodimeform content in comparison with 
that of a standard solution of 50 ml of chlorodimeform in 
10 ml of chloroform containing 0.25 wt.% of eicosane as 
international standard for gas-chromatographical analysis. 
From this analysis is obtained a calculated content of 
chlorodimeform in the ion-exchanger of 34 per cent by weight. 
This value is in good agreement both with the value 
obtained by elementary analysis and with the value given 
from the drop in concentration during the charging of the 
resin (35%).

In an analogous manner, a cation-exchanger resin, 
produced by polymerisation of styrene in the presence of 
8% of divinyl benzene and subsequent sulfonation 
(wt.% of S), was charged with the following active 
substances:

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>N(^1)-methyl-N(^2)-(4-chloro-o-tolyl)-formamidine,</td>
</tr>
<tr>
<td>II</td>
<td>N(^1)-N(^1)-dimethyl-N(^2)-(4-bromo-o-tolyl)-formamidine,</td>
</tr>
<tr>
<td>III</td>
<td>N(^1)-methyl-N(^1)-n-butyl-N(^2)-(4-chloro-o-tolyl)-formamidine,</td>
</tr>
<tr>
<td>IV</td>
<td>N(^1)-methyl-N(^1)-n-butyl-N(^2)-(2,6-diethylphenyl)-formamidine,</td>
</tr>
<tr>
<td>V</td>
<td>N(^1)-N(^1)-dimethyl-N(^2)-(2,4-diethylphenyl)-formamidine.</td>
</tr>
</tbody>
</table>

The results are summarised in the following Table I.
<table>
<thead>
<tr>
<th>Compound No. No.</th>
<th>Initial concentration of the solution wt.%</th>
<th>Concentration of the solution after 1 h, wt.%</th>
<th>Concentration of the solution after 1 day, wt.%</th>
<th>Calculated charge wt.%</th>
<th>Charge according to elementary analysis wt.%</th>
<th>Charge after exchange with diethylamine wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>31.5</td>
<td>20.6</td>
<td>19</td>
<td>31</td>
<td>29.5</td>
<td>32</td>
</tr>
<tr>
<td>II</td>
<td>37.9</td>
<td>25.2</td>
<td>23</td>
<td>38.3</td>
<td>35.1</td>
<td>37</td>
</tr>
<tr>
<td>III</td>
<td>37.5</td>
<td>26.6</td>
<td>26.6</td>
<td>32.5</td>
<td>34.1</td>
<td>33</td>
</tr>
<tr>
<td>IV</td>
<td>38.3</td>
<td>31</td>
<td>27.5</td>
<td>32.5</td>
<td>33.9</td>
<td>32.5</td>
</tr>
<tr>
<td>V</td>
<td>30.5</td>
<td>16.8</td>
<td>15.7</td>
<td>33.7</td>
<td>32.4</td>
<td>33</td>
</tr>
</tbody>
</table>
Table 1

<table>
<thead>
<tr>
<th>Compound No. No.</th>
<th>Initial concentration of the solution wt.%</th>
<th>Concentration of the solution after 1 h, wt.%</th>
<th>Concentration of the solution after 1 day, wt.%</th>
<th>Calculated charge wt.%</th>
<th>Charge according to elementary analysis wt.%</th>
<th>Charge after exchange with diethylamine wt.%</th>
</tr>
</thead>
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<td>20.6</td>
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<td>31</td>
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<td>II</td>
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<td>25.2</td>
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</tr>
<tr>
<td>V</td>
<td>30.5</td>
<td>16.8</td>
<td>15.7</td>
<td>33.7</td>
<td>32.4</td>
<td>33</td>
</tr>
</tbody>
</table>
Example 5:

\[
\begin{array}{c}
\text{CH}_2 = \text{CH} - \begin{array}{c}
\text{NH} - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{SO}_3\text{H} \\
\text{CH}_3
\end{array} + \begin{array}{c}
\text{CH}_3 \\
\text{N} - \text{CH} = \text{N} - \begin{array}{c}
\text{CH}_3
\end{array}
\end{array} \rightarrow \begin{array}{c}
\text{CH}_2 = \text{CH} - \begin{array}{c}
\text{NH} - \text{C} - \text{CH}_2 - \text{SO}_3\text{H} \\
\text{CH}_3
\end{array} + \begin{array}{c}
\text{CH}_3 \\
\text{N} - \text{CH} = \text{N} - \begin{array}{c}
\text{CH}_3
\end{array}
\end{array}
\end{array}
\]

Monomeric salt from chlorodimeform and 2-acrylamido-2-methylpropanesulfonic acid:

A solution of 19.6 g (0.1 mol) of chlorodimeform in 250 ml of methanol is slowly added dropwise at room temperature, in the course of 45 minutes, to a suspension of 20.7 g (0.1 mol) of 2-acrylamido-2-methylpropanesulfonic acid in 400 ml of methanol. After the slightly exothermic reaction has subsided, stirring is continued for 6 hours at room temperature. The resulting clear solution of the chlorodimeform salt is concentrated by evaporation in a rotary evaporator, and the residue is stirred up with 500 ml of anhydrous ether. The white suspension obtained is filtered, and the residue is again treated with 200 ml of anhydrous ether. Filtration and subsequent drying under high vacuum yield the salt in the form of a white crystalline solid product, which slowly decomposes on melting in the range of 110-114°C.

Yield: 39.4 g = 97.7% of theory

Analytical composition: \( \text{C}_{17}\text{H}_{26}\text{N}_3\text{O}_4\text{S Cl} \)

Calculated: C = 50.55  H = 6.49  N = 10.40  S = 7.94  Cl = 8.78 %

Found:  C = 50.18  H = 6.24  N = 10.45  S = 7.93  Cl = 8.86.
Example 6:

Polymerisation of the monomer salt formed from chlorodimeform and 2-acrylamido-2-methylpropanesulfonic acid:

\[
\begin{align*}
\text{CH}_2 = \text{CH} & \quad \text{NH} - \text{C} - \text{CH}_2 - \text{SO}_3 \text{H} \cdot (\text{CH}_3)_2 \text{N} - \text{CH} = \text{N} - \text{C} \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

with azo-isobutyronitrile (AIBN) in N,N-dimethylacetamide (DMA).

a) 2 g (0.01 mol) of chlorodimeform are dissolved in 10 ml of anhydrous DMA, and a solution of 2.07 g (0.01 mol) of 2-acrylamido-2-methylpropanesulfonic acid in 10 ml of anhydrous DMA is added. The formed solution of the chlorodimeform salt is stirred for 6 hours at room temperature with the passing through of dry nitrogen, and is subsequently polymerised, with the addition of 40 mg of AIBN, at 55-60°C for 15 hours. The formed polymer is isolated by precipitation in the reaction solution by the addition of 300 ml of anhydrous diethyl ether. After filtration, washing 3 times with 50 ml of anhydrous ether each time, and drying under high vacuum, the yield is 3.8 g of white pulverulent material, which on melting slowly decomposes above 100°C; yield: 94% of theory.
molecular weight:
elementary analysis:

calculated: C 50.5 H 6.5 N 10.4 S 7.9 Cl 8.8 %
found : C 49.8 H 6.7 N 10.4 S 7.5 Cl 8.3 %.

The H-NMR spectrum of the product in DMSO-d₆ no longer shows the multiplets in the region of 5.3 - 6.1 ppm which are characteristic for the monomer salt.

b) In an analogous manner, 4.03 g (0.01 mol) of the monomer salt produced according to Example 5 are dissolved in 20 ml of anhydrous DMA, and then polymerised under N₂ at 55-60°C with AIBN. The product obtained corresponds in structure and composition to the polymer produced under a).

Example 7

Insecticidal stomach-poison action

Cotton plants were sprayed with an 0.02% (relative to the active substance) aqueous suspension (obtained from a 25% wettable powder, or from a 20% suspension). After the drying of the coating, the cotton plants were each infested with Spodoptera littoralis larvae in the L₁ stage. The test was carried out at 30-35°C with 60% relative humidity.

Compounds according to Examples 1-6 exhibited in the above test a good insecticidal stomach-poison action against Spodoptera littoralis larvae.

Example 8

Acaricidal action

Phaseolus vulgaris plants were infested, 12 hours before the test for acaricidal action, with an infested piece of leaf from a mass culture of Tetranychus urticae.
The transferred mobile stages were sprayed with the suspended test preparations from a chromatography-sprayer in a manner ensuring no overflow of the spray liquid. An assessment was made after two and seven days, by examination under a binocular microscope, of the living larvae and dead larvae, adults and eggs, and the results were expressed as percentages. The treated plants were kept during the "holding time" in greenhouse compartments at 25°C.

Compounds according to Examples 1-6 inclusive were effective in the above test against adults, larvae and eggs of Tetranychus urticae.
The claims defining the invention are as follows:

1. A salt having groups bound to side chains, which salt is formed from formamidinates with polymers containing sulfonic acid groups, and corresponds to the formula

\[ \text{I} \]

wherein \( Q_1 \) and \( Q_2 \) are each hydrogen, \( C_1 - C_4 \)-alkyl, or phenyl which is unsubstituted or substituted by \( C_1 - C_4 \)-alkyl or halogen, and \( Q_3 \) is

\[ \text{II} \]

in which \( R_0 \) and \( R_p \) are each hydrogen, halogen or \( C_1 - C_4 \)-alkyl, and wherein the groups of the formula I are bound either directly or by way of a bridge member, other than \(-\text{COOC}_2\text{H}_4-\), to the polymer main structure, and wherein the proportion of recurring structural elements in the polymer having groupings of the formula I is at least 5% relative to the number of recurring structural elements of the polymer.

2. A salt according to Claim 1, wherein \( Q_1 \) is hydrogen, methyl or \( n \)-butyl, \( Q_2 \) is methyl, and \( Q_3 \) is
3. A salt according to Claim 1 of the formula

wherein $Q_1$, $Q_2$ and $Q_3$ have the meanings given in Claim 1, $R$ is hydrogen, chlorine, $-CN$ or $C_1-C_4$-alkyl, $Z$ is the direct bond, $-O-$, straight-chain or branched-chain alkylene having 1-4 C atoms, phenylene or naphthylene each of which is unsubstituted or substituted by halogen atoms, alkyl or alkoxy groups having 1-4 C atoms or by a group $-SO_3 M^+$, or $Z$ is $-CH_2O-CH_2-CH_2-$, $-CH_2OCH_2CH_2O-$, $-CH_2-S-CH_2CH_2-$, $-CH_2-S-CH_2CH_20-$, a ring-substituted group $\begin{array}{c}
\text{CH}_2
\end{array}^{X(CH_2)}_{0-3}$, in which the ring is unsubstituted or is substituted by halogen atoms, or by alkyl or alkoxy groups having 1-4 C atoms, or $Z$ is a group $\begin{array}{c}
\text{CH}_2
\end{array}^{X(CH_2)}_{0-3}$ or $\begin{array}{c}
\text{CH}_2
\end{array}^{X(CH_2)}_{0-3}$, each of which is unsubstituted or substituted by $-SO_3 M^+$, or $Z$ is $-COOR_1$ or $-CON(R_2)(R_3)$, in which $R_1$ is straight-chain or branched-chain $C_3-C_8$-alkylene which is unsubstituted or substituted by chlorine or bromine atoms, or optionally interrupted by an oxygen atom, or $R_1$ is cyclohexylene, phenylene, naphthylene, naphthylene substituted by a group $-SO_3 M^+$, or it is $C_2-C_4$-alkylene-$O$-phenylene $\begin{array}{c}
\text{CH}_2
\end{array}^{X(CH_2)}_{1-2}$, $R_2$ is the direct bond, straight-chain or branched-chain $C_1-C_6$-alkylene optionally
interrupted by an oxygen atom, or it is straight-chain or branched-chain oxyalkylene having 1-6 C atoms, phenylene, naphthylene, naphthylene substituted by a group -SO_3 \ M^+ , or it is C_1-C_4-alkylene-O-phenylene,

\[ \text{(-CH}_2\text{)}_{1-2} \text{ or (-O(CH}_2\text{)}_{1-3}, \text{ and R}_3 \text{ is} \]

hydrogen or C_1-C_6-alkyl, and M^+ is hydrogen or [HN(Q_1)(O_2)(Q_3)]^+, the proportion of structural elements of the formula II being at least 5%, preferably 30-100%, relative to the number of recurring structural elements of the polymer.

4. A salt according to Claim 3 of the formula

\[ -\text{SO}_3 \oplus \oplus \left[ \frac{Q_1}{Q_3} \right] \]

wherein R is hydrogen or methyl, Z is the direct bond, -COO-alkylene having 3-4 C atoms and particularly phenylene, R_1 is alkylene having 2-4 C atoms, R_2 is -(CH_2)_{2-4} , -C(CH_3)(CH_3)CH_2 - , naphthylene and in particular phenylene each substituted by a group

\[ -\text{SO}_3 \oplus \oplus \left[ \frac{Q_1}{Q_3} \right] \text{; R}_3 \text{ is hydrogen, R}_4 \text{ is hydrogen, chlorine, unsubstituted phenyl, -CON(R}_5\text{)(R}_6\text{), -COO-alkyl having 1-8 C atoms in the alkyl moiety, -OCO-alkyl having 1 or 2 C atoms in the alkyl moiety, or alkoxy having 1-4 C atoms, R}_5 \text{ and R}_6 \text{ independently of one another are each hydrogen or methyl, A is the direct bond, -O-}, \\
\text{or -COO(CH}_2\text{)}_x -\text{OOC, } y \text{ is an integer from 1-6 inclusive,} \]
x is an integer from 2-5 inclusive, $R_7$ is hydrogen, $\text{-SO}_3\text{H or -SO}_3\text{O}^{\oplus}$ $[\text{N}(Q_1)(Q_2)(Q_3)]$, in which $Q_1$ is hydrogen, methyl or n-butyl, $Q_2$ is methyl, and $Q_3$ is

\[
\begin{align*}
\text{H} & \quad \text{N} \quad \text{C} \quad \text{Cl} \\
\text{CH}_3 & \quad \text{H} \quad \text{N} \quad \text{C} \\
\text{H} & \quad \text{N} \quad \text{C} \quad \text{Cl} \\
\text{CH}_3 & \quad \text{H} \quad \text{N} \quad \text{C} \\
\end{align*}
\]

or

\[
\begin{align*}
\text{H} & \quad \text{N} \quad \text{C} \quad \text{Br} \\
\text{CH}_3 & \quad \text{H} \quad \text{N} \quad \text{C} \\
\text{C}_2\text{H}_5 & \quad \text{H} \quad \text{N} \quad \text{C} \\
\end{align*}
\]

5. A salt according to Claim 1 of the cations of the formulae

\[
\begin{align*}
\left[ \begin{array}{c}
\text{CH}_3 \\
\text{H} \\
\end{array} \right] & \quad \text{H} \\
\left[ \begin{array}{c}
\text{CH}_3 \\
\text{H} \\
\end{array} \right] & \quad \text{N} \\
\left[ \begin{array}{c}
\text{CH}_3 \\
\text{H} \\
\end{array} \right] & \quad \text{C} \\
\left[ \begin{array}{c}
\text{CH}_3 \\
\text{C}_2\text{H}_5 \\
\end{array} \right] & \quad \text{H} \\
\left[ \begin{array}{c}
\text{C}_4\text{H}_9 \\
\text{CH}_3 \\
\end{array} \right] & \quad \text{H} \\
\left[ \begin{array}{c}
n\text{C}_4\text{H}_9 \\
\text{CH}_3 \\
\end{array} \right] & \quad \text{H} \\
\end{align*}
\]

or
with the anions of polyvinylsulfonic acids, polystyrene-sulfonic acids or poly[N-(sulfoalkyl)-acrylamide] and sulfonated cation-exchangers formed from styrene and about 0.5 - 12 per cent by weight of divinyl benzene (crosslinking agent), or sulfonated cation-exchangers having macroporous structures.

6. A pesticid composition containing as active ingredient a salt according to Claim 1, together with suitable carriers and/or other additives.

7. A method of combating pests of the class Insecta or of the order Acarina at a locus, which method comprises applying to the locus a compound as claimed in Claim 1.

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