

[54] AMINE FRUIT ABSCISSION AGENTS

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[51] Int. Cl..... **A01n 9/20**

[58] Field of Search 71/121, 78, 70, 76

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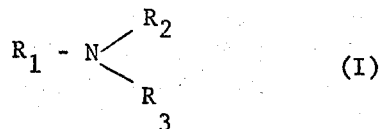
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[57]

ABSTRACT

The present invention describes a composition and a method for the promotion of the abscission of fruits of all kinds particularly of citrus fruit. The active principle therefore is an amine of formula I



wherein:

R₁ is an alkyl or alkenyl radical of 8 to 22 carbon atoms

R₂ and R₃ are independently of each other hydrogen alkyl radicals of 1 to 12 carbon atoms, unsubstituted or substituted by amino, alkyl- or dialkylamino,

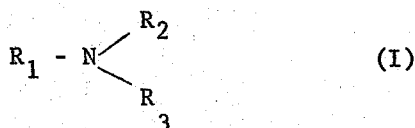
as well as an acid addition or quaternary ammonium salt of such an amine.

2 Claims, No Drawings

AMINE FRUIT ABSCISSION AGENTS

The present invention relates to new agents for the promotion of the abscission of fruit of all kinds, particularly of citrus fruits, by the application, as active substances, of amines, their addition salts with inorganic or organic acids, as well as quaternary salts of such amines.

The active substances contained in the agents according to the invention are amines of formula I

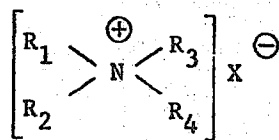


or their addition salts with inorganic or organic acids. The symbols in this formula have the following meanings:

R_1 represents an alkyl or alkenyl radical having 8 to 22 carbon atoms,

R_2 and R_3 each independently represent hydrogen, or an alkyl radical having 1 to 12 carbon atoms, which can be substituted by amino, alkyl- or dialkyl-amino.

The quaternary salts of such amines, which likewise come into consideration as active substances in the new agents, correspond to the formula



wherein R_1 , R_2 and R_3 have the meanings given under formula I, R_4 stands for a lower alkyl radical having 1 to 4 carbon atoms, and X for the anion of an inorganic or organic acid.

Alkyl radicals in these formulae are straight-chain or branched radicals. The symbols R_2 and R_3 denote, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl or tert-butyl, as well as n-pentyl, n-hexyl, n-octyl, n-decyl or n-dodecyl radicals, and their

isomers. The symbol R_1 represents, for example, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-hexadecyl or n-octadecyl radicals, n-nonadecylamine, n-eicosylamine, and their branched isomers containing up to 22 carbon atoms. Alkenyl radicals R_1 can be straight-chain or branched; those preferred are the oleyl radical and the undecenyl radical. Alkylaminoalkyl radicals and dialkylaminoalkyl radicals contain in all preferably 4 to 12 carbon atoms. The symbol R_4 represents the methyl, ethyl, n-propyl or isopropyl radical or one of the butyl radicals.

Suitable addition salts are preferably salts of strong mineral acids such as hydrohalic acids: for example, hydrochloric acid, fluoboric acid (HBF_4), nitric acid, phosphoric acid, thio- or dithiophosphoric acids or sulphuric acid; or organic acids such as benzoic acid, halo-benzoic acids, cinnamic acid and substituted cinnamic acids, naphthoic acid, acetic acid, haloacetic acids, propionic acid, halopropionic acids, butyric acid, lactic acid, stearic acid, oxalic acid, tartaric acid, maleic acid, etc.

The anion X of the quaternary salts can be an anion of the given acids.

The amines and their salts (by which are meant in the following both the addition salts and the quaternary salts) contained in the agents according to the invention are known, and have been suggested for use as, among other things, herbicides and defoliants.

The herbicidal and plant-growth-regulating applications of amines for the purpose of increasing resistance to frost and improving fruit setting have been mentioned in the U.S. Pat. No. 3,460,936, in the French Patent Specification No. 1,375,967, as well as in the German Patent Specification No. 1,032,023. The inhibition of lateral shoots on plants, e.g. on tobacco, soya bean and cotton plants, is described in the U.S. Pat. Nos. 3,223,517 and 3,506,433, and also in the German 'Offenlegungsschrift' No. 2,121,009. The defoliating action of amines in cotton crops is described in the U.S. Pat. Specification No. 3,056,066 and in the French Patent Specification No. 1,032,967.

The agents according to the invention can contain as active substances, for example, the following amines of formula I and their salts:

Active substance	Number	Physical data
$\text{CH}_3-(\text{CH}_2)_7-\text{NH}_2 \cdot \text{HCl}$	1	M.P. 200°-202°
$\text{CH}_3-(\text{CH}_2)_{11}-\text{NH}_2 \cdot \text{HCl}$	2	M.P. 182°-185°
$\text{CH}_3-(\text{CH}_2)_{13}-\text{NH}_2 \cdot \text{HCl}$	3	M.P. 174°-177°
$\text{CH}_3-(\text{CH}_2)_8-\text{NH}_2 \cdot \text{HCl}$	4	
$\text{CH}_3-(\text{CH}_2)_{10}-\text{NH}_2 \cdot \text{HCl}$	5	M.P. 195°-199°
$\text{CH}_3-(\text{CH}_2)_{12}-\text{NH}_2 \cdot \text{HCl}$	6	M.P. 165°-166°
$\text{CH}_3-(\text{CH}_2)_{11}-\text{N} \begin{matrix} \nearrow \text{CH}_3 \\ \searrow \text{CH}_3 \end{matrix} \cdot \text{HCl}$	7	M.P. 170°-172°
$\text{CH}_3-(\text{CH}_2)_{15}-\text{NH}_2 \cdot \text{HCl}$	8	M.P. 125°-130°
$\text{CH}_3-(\text{CH}_2)_{13}-\text{N} \begin{matrix} \nearrow \text{CH}_3 \\ \searrow \text{CH}_3 \end{matrix} \cdot \text{HCl}$	9	M.P. 150°-155°

Active substance	Number	Physical data
$\text{CH}_3-(\text{CH}_2)_7-\text{NH}_2$	10	<u>B.P.</u> 75°-77°/11 mm
$\text{CH}_3-(\text{CH}_2)_8-\text{NH}_2$	11	<u>B.P.</u> 80°-82°/10 mm
$\text{CH}_3-(\text{CH}_2)_9-\text{NH}_2$	12	<u>M.P.</u> 11°-15°
$\text{CH}_3-(\text{CH}_2)_{10}-\text{NH}_2$	13	<u>B.P.</u> 125°-126°/11 mm
$\text{CH}_3-(\text{CH}_2)_{11}-\text{NH}_2$	14	<u>M.P.</u> 25°-28°
$\text{CH}_3-(\text{CH}_2)_{12}-\text{NH}_2$	15	<u>M.P.</u> 26°-29°
$\text{CH}_3-(\text{CH}_2)_{13}-\text{NH}_2$	16	<u>M.P.</u> 36°-38°
$\text{CH}_3-(\text{CH}_2)_{11}-\text{N} \begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \end{array}$	17	techn. 95%
$\text{CH}_3-(\text{CH}_2)_{15}-\text{NH}_2$	18	<u>B.P.</u> 130°-132°/0.1 mm
$\text{CH}_3-(\text{CH}_2)_{13}-\text{N} \begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \end{array}$	19	techn. 95%
$[\text{CH}_3-(\text{CH}_2)_{13}-\text{N} \begin{array}{l} \text{CH}_3 \\ \\ \text{CH}_3 \end{array} \text{CH}_3]^\oplus \text{J}^\ominus$	20	<u>M.P.</u> 228°-230°
$[\text{CH}_3-(\text{CH}_2)_{14}-\text{N} \begin{array}{l} \text{CH}_3 \\ \\ \text{CH}_3 \end{array} \text{CH}_3]^\oplus \text{J}^\ominus$	21	<u>M.P.</u> 212°-214°
$\text{CH}_3-(\text{CH}_2)_{11}-\text{N} \begin{array}{l} \text{CH}_2-\text{CH}_2-\text{NH}_2 \\ \text{CH}_2-\text{CH}_2-\text{NH}_2 \end{array}$	22	
$(\text{CH}_3)_3\text{C}-\text{CH}_2-\text{C}(\text{CH}_3)_2-\text{NH}_2$	23	
$\text{CH}_3-(\text{CH}_2)_{17}-\text{NH}_2$	24	
$\text{CH}_3-(\text{CH}_2)_7-\text{NH}-(\text{CH}_2)_7-\text{CH}_3$	25	
$\text{CH}_3-(\text{CH}_2)_9-\text{NH}-(\text{CH}_2)_9-\text{CH}_3$	26	
$\text{CH}_3-(\text{CH}_2)_{10}-\text{CH}-\text{NH}_2$	27	<u>B.P.</u> 124°/20 Torr
$[\text{CH}_3-(\text{CH}_2)_7-1_3\text{N}^\oplus \text{CH}_3]^\oplus$	28	<u>B.P.</u> 167-169°/0.1 Torr
$\text{CH}_3-(\text{CH}_2)_{11}-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_3$	29	
$\text{CH}_3-(\text{CH}_2)_{11}-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}_2 \cdot \text{HCl}$	30	
$\text{CH}_3-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{CH}_2-\text{NH}_2$	31	
$\text{CH}_3-(\text{CH}_2)_9\text{CH}(\text{CH}_3)\text{NH}_2$	32	<u>B.P.</u> 124°-/20 Torr
$[\text{CH}_3-(\text{CH}_2)_n-1_2\text{N}^\oplus (\text{CH}_3)_2]^\oplus \text{Cl}^\ominus$	33	
$n=19-21$		
$\text{CH}_3-(\text{CH}_2)_n-\text{NH}_2$	34	
$n=19-21$		
$[\text{CH}_3-(\text{CH}_2)_n]_2-\text{NH}_2$	35	

As was shown by tests, particularly valuable for the promotion of fruit abscission in the case of citrus crops are agents according to the invention which contain as active substances amines of formula I wherein R₁ represents an alkyl radical having 8 to 18 carbon atoms, R₂ and R₃ each represent hydrogen, a lower alkyl radical, preferably a methyl or ethyl radical, or a β -amino-ethyl radical. Of the addition salts, those to be emphasized are addition salts of inorganic acids, especially of hydrohalic acids. Outstanding among the quaternary salts are, in particular, the trimethylammonium salts of inorganic acids, e.g. of hydrohalic acids.

With regard to the practical application, the active substances applicable are those which effect the promotion of fruit abscission but which do not produce defoliation.

The following have proved particularly satisfactory: dimethyldodecylamine-hydrochloride, decylamine, dodecylamine (laurylamine), tridecylamine, nonylamine, hexadecylamine (palmitylamine, cetylamine).

The promotion of fruit abscission on citrus fruits is illustrated by the following test:

The active substances are sprayed, as solutions in the given concentrations, onto branches well hung with fruit on various orange trees of the varieties "Hamlin" and "Pineapple". The results of the tests are evaluated after 7 days by the method developed by W. C. Wilson and C. H. Hendershott [Proc. Am. Soc. Hort. Sci. 90, 123-129 (1967)]. The force to be applied to effect abscission of the fruit is measured; the results are expressed in the following table as percentages of the respective force measured in the case of the untreated control fruit.

Active-substance number*	Concentration in ppm**	Force required to effect abscission, as % of that measured in control test	Defoliation %
2	4000	0	
3	2000	35	
4	2000	0	
5	2000	0	
6	2000	0	
7	2000	0	
8	2000	30	
9	2000	0	
10	2000	<5	5-10
11	2000	0	0
12	2000	0	0
13	2000	0	
14	2000	0	
15	2000	0	
16	2000	0	20
17	2000	0	
18	2000	<5	5
19	2000	0	
20	2000	<6	
21	2000	<6	
22	2500	27	
23	4000	84	
24	4000	100	
25	4000	50	
27	4000	77	
28	4000	80	
29	4000	50	
31	4000	82	
32	4000	10	
control	4000	100	

The active substances are used in the form of aqueous suspensions, emulsions and solutions, which are obtained from active-substance concentrates in the form of

- a. wettable powders and
- b. emulsion concentrates.

The agents according to the invention are produced in a manner known per se by the intimate mixing and/or grinding of active substances of the general formula I with suitable carriers, optionally with the addition of dispersing agents or solvents which are inert to the active substances. The active substances can be obtained and used in the following forms:

- 10 water-dispersible active-substance concentrates: wettable powders and emulsifiable concentrates; liquid preparations: solutions.

Water-dispersible concentrates of active substances, i.e. wettable powders and emulsifiable concentrates, are agents which can be diluted with water to obtain any desired concentration. They consist of active substance, carrier, optionally additives which stabilise the active substance, surface-active substances, antifoam agents and, optionally, solvents. The concentration of active substance in these agents is between 5 and 80%.

The wettable powders and pastes are obtained by the mixing and grinding of the active substances with dispersing agents and pulverulent carriers, in suitable devices, until homogeneity is obtained. Suitable carriers are, e.g. kaolin, talcum, bole, loess, chalk, limestone, ground limestone, attapulgite, dolomite, diatomaceous earth, precipitated silicic acid, alkaline-earth silicates, sodium and potassium aluminium silicates (feldspars and mica), calcium and magnesium sulphates, magnesium oxide, ground synthetic materials, fertilisers such as ammonium sulphate, ammonium phosphate, ammonium nitrate, urea, ground vegetable products such as bran, bark dust, sawdust, ground nutshells, cellulose powder, residues of plant extractions, active charcoal, etc., singly or in admixture with each other.

As dispersing agents it is possible to use, e.g. condensation products of sulphonated naphthalene and sulphonated naphthalene derivatives with formaldehyde, condensation products of naphthalene or of naphthalene-sulphonic acids with phenol and formaldehyde, as well as alkali, ammonium and alkaline-earth metal salts of ligninsulphonic acid, also alkylarylsulphonates, alkali metal salts and alkaline-earth metal salts of dibutyl naphthalenesulphonic acid, fatty alcohol sulphates such as salts of sulphated hexadecanols, heptadecanols, octadecanols, and salts of sulphated fatty alcohol glycol ethers, the sodium salt of oleyl methyl tauride, ditertiary ethylene glycols, dialkyl dilauryl ammonium chloride, and fatty acid alkali-metal and alkaline-earth metal salts.

Suitable antifoam agents are, for example, silicones.

The active substances are so mixed, ground, sieved and strained with the above mentioned additives that the solid constituent in the case of wettable powders has a particle size not exceeding 0.02 to 0.04 mm. For the preparation of emulsion concentrates, dispersing agents are used such as those mentioned in the preceding paragraphs, organic solvents and water. Suitable solvents are, e.g. alcohols, benzene, xylenes, toluene, dimethylsulphoxide, N,N-dialkylated amides, N-oxides of amines, particularly trialkylamines, and mineral oil fractions boiling in the range of 120° to 350°C. The solvents must be practically odourless, non-phytotoxic, inert to the active substances and not readily combustible.

Furthermore, the agents according to the invention can be used in the form of solutions. For this purpose, the active substance (or several active substances) of the general formula I is (or are) dissolved in water, or in suitable organic solvents, solvent mixtures, or mixtures of organic solvents with water. As organic solvents it is possible to use aliphatic and aromatic hydrocarbons, their chlorinated derivatives, alkylnaphthalenes, mineral oils on their own or in admixture with each other. The solutions should contain the active substances in concentrations of from 1 to 20%.

For preservation purposes, it is possible to add to the described agents according to the invention other biocidal active substances or agents; for example: fungicides, bactericides, fungistatics or bacteriostatics. The agents according to the invention may also contain trace elements, and so forth.

The procedure for the producing of preparations of active substances of the general formula I is described in the following. The term 'parts' denotes parts by weight. The numbers of the active substances relate to the tables.

Wettable Powders

The following substances are used for the preparation of 25% wettable powders:

- | | | |
|----|------|--|
| a) | 25 | parts of active substance No. 2, |
| | 8 | parts of a mixture of nonylphenolpolyoxyethylene and calcium dodecylbenzenesulphonate, |
| | 2 | parts of octylphenoxyethylene glycol with 9 to 10 moles of ethylene oxide per mole of octylphenol, |
| | 5 | parts of silicic acid, |
| | 60 | parts of kaolin; |
| b) | 25 | parts of active substance No. 3, |
| | 8 | parts of a mixture of nonylphenolpolyoxyethylene and calcium dodecylbenzenesulphonate, |
| | 2 | parts of octylphenoxyethylene glycol with 9 to 10 moles of ethylene oxide per mole of octylphenol, |
| | 10 | parts of silicic acid, |
| | 55 | parts of kaolin; |
| c) | 25 | parts of active substance No. 6, |
| | 25 | parts of silicic acid, |
| | 5 | parts of naphthalenesulphonic acid/phenol-sulphonic acid/formaldehyde condensate 3:2:1, |
| | 5 | parts of sodium dibutyl-naphthylsulphonate, |
| | 40 | parts of kaolin; |
| d) | 25 | parts of active substance No. 8, |
| | 7.5 | parts of silicic acid, |
| | 5.3 | parts of octylphenol-octaglycol ether, |
| | 2.2 | parts of 1-benzyl-2-stearyl-benzimidazole-6,3'-disulphonic acid sodium, |
| | 0.5 | part of oleic acid, |
| | 59.5 | parts of bolus alba. |

The given active substance is absorbed onto the appropriate carriers (kaolin and bolus), and the whole subsequently mixed and ground. Wettable powders are obtained which possess excellent wettability and suspension properties. It is possible to prepare from such wettable powders, by dilution with water, suspensions of any desired concentration of active substance.

Emulsifiable Concentrate

The following constituents are mixed together in the preparation of 25% emulsifiable concentrates:

- | | | |
|----|------------|--|
| a) | 250 g | of active substance No. 9, |
| | 10 g | of octylphenoxyethylene glycol with 9 to 10 moles of ethylene oxide per mole of octylphenol, |
| | 250 g | of methanol, |
| | ad 1000 ml | of water; |
| b) | 250 g | of active substance No. 10, |
| | 100 g | of a mixture of alkylarylsulphonate and alkylaryl-polyglycol ether, |
| | ad 1000 ml | of xylene; |
| c) | 250 g | of active substance No. 11, |
| | 100 g | of a mixture of alkylarylsulphonate and alkylaryl-polyglycol ether, |
| | ad 1000 ml | of xylene; |
| d) | 250 g | of active substance No. 17, |
| | 100 g | of emulsifier (G-3634 A), |
| | ad 1000 ml | of benzyl alcohol; |
| e) | 250 g | of active substance No. 19, |
| | 100 g | of emulsifier (G-3634 A), |
| | ad 1000 ml | of benzyl alcohol. |

This concentrate can be mixed with water to form emulsions of suitable concentrations.

Solutions:

- | | | |
|----|------------|----------------------------|
| a) | 250 g | of active substance No. 4, |
| | ad 1000 ml | of water; |
| b) | 250 | of active substance No. 5, |
| | ad 1000 ml | of water; |
| c) | 250 g | of active substance No. 7, |
| | ad 1000 ml | of water. |

I claim:

1. A method for the promotion of citrus fruit abscission which comprises applying to the citrus fruit-bearing plants an effective amount of nonylamine.

2. A method for the promotion of citrus fruit abscission which comprises applying to the citrus fruit-bearing plants an effective amount of decylamine.

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