

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
3 March 2005 (03.03.2005)

PCT

(10) International Publication Number
WO 2005/018326 A1

(51) International Patent Classification⁷: **A01N 41/04**,
37/20, 37/12

(21) International Application Number:
PCT/GB2004/003458

(22) International Filing Date: 10 August 2004 (10.08.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0319506.2 19 August 2003 (19.08.2003) GB

(71) Applicant (for all designated States except US): **SYNGENTA LIMITED** [GB/GB]; European Regional Centre, Priestley Road, Surrey Research Park, Guildford, Surrey, GU2 7YH (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **MAY, Leslie, Francis** [GB/GB]; Syngenta Limited, Jealott's International Research Centre, Bracknell, Berkshire RG42 6EY (GB). **MULQUEEN, Patrick, Joseph** [GB/GB]; Syngenta Limited, Jealott's International Research Centre, Bracknell, Berkshire RG42 6EY (GB).

(74) Agents: **SWIFT, Jane, Elizabeth** et al.; Intellectual Property Department, Syngenta Limited, P.O. Box 3538, Jealott's Hill International Research Centre, Bracknell RG42 6YA (GB).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

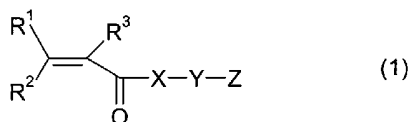
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: FUNGICIDAL METHOD COMPRISING THE APPLICATION OF AN ACRYLIC POLYMER



(57) Abstract: A method of combating phytopathogenic diseases on plants and harvested food crops which comprises applying to a plant, to the seed of a plant, to the locus of the plant or seed or to a harvested food crop a fungicidally effective amount of a fungicidal polymer obtained by the polymerization of a monomer of the general formula (1): wherein X is O or NR⁴, Y is a C₁₋₅₀ substituted or unsubstituted aliphatic hydrocarbyl group, Z is H, NR⁵R⁶, N⁺R⁵R⁶R⁷ A⁻ or SO₃R⁸, R¹ and R² are independently H or C₁₋₅ aliphatic hydrocarbyl groups, R³ is H or CH₃, R⁴, R⁵, R⁶ and R⁷ are independently H or substituted or unsubstituted C₁₋₅₀ aliphatic hydrocarbyl groups, R⁸ is H, an alkali metal atom, an alkaline earth metal atom, an ammonium or alkylammonium group or a C₁₋₅₀ substituted or unsubstituted aliphatic hydrocarbyl group and A⁻ is an anion is disclosed.

WO 2005/018326 A1

FUNGICIDAL METHOD COMPRISING THE APPLICATION OF AN ACRYLIC POLYMER

This invention relates to a method of combating phytopathogenic diseases on plants and harvested food crops. More particularly, it relates to the use of certain
5 polymers as plant and food crop fungicides and to fungicidal compositions containing these polymers.

The biocidal use of certain polymers known as sustainable active microbicidal (SAM)-Polymers is described in an article in GIT Labor-Fachzeitschrift (2002), 46(4), 452, 454-456. These polymers are said to be suitable for incorporation into paints,
10 coatings and plastic products. Examples of such polymers are described in WO 01/18077 and WO 01/85813 and are commercially available under the trade names AMINA T 100 and LIMAGO T 100. (SAM-polymers, AMINA and LIMAGO are registered trade marks of CREAVIS Gesellschaft für Technologie und Innovation mbH).

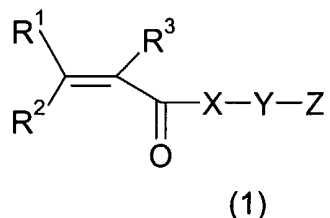
Biocides are substances that kill or inhibit the growth of microorganisms such as
15 bacteria, moulds, slimes, fungi, etc. They are normally used in situations where they are not a danger to plants or animals, for example, on ships' hulls, building facades and plastics surfaces and in paints and varnishes. It is, therefore, unnecessary for them to act specifically against their target organisms and they are often phytotoxic, toxic to humans, skin sensitisers or irritants. Consequently, most biocides are not suitable for use as plant
20 fungicides. In any case, they are targeted at different organisms and would not be expected to be suitable for use as plant fungicides or have an acceptable toxicological profile.

Most commercial synthetic fungicides are monomeric organic compounds or organometallic compounds. It has not been known before to use polymers as plant
25 fungicides.

As plants build resistance to constantly used fungicides, there is a continuing need for alternative fungicides and preferably ones that have a new mode of action. The present invention is concerned with the provision of alternative plant fungicides and alternative methods of combating phytopathogenic fungi.

30 According to the present invention, there is provided a method of combating phytopathogenic diseases on plants and harvested food crops which comprises applying to a plant, to the seed of a plant, to the locus of the plant or seed or to a harvested food

crop a fungicidally effective amount of a fungicidal polymer obtained by the polymerization of a monomer of the general formula (1):



wherein X is O or NR⁴, Y is a C₁₋₅₀ substituted or unsubstituted aliphatic hydrocarbyl group, Z is H, NR⁵R⁶, N⁺R⁵R⁶R⁷A⁻ or SO₃R⁸, R¹ and R² are independently H or C₁₋₅ aliphatic hydrocarbyl groups, R³ is H or CH₃, R⁴, R⁵, R⁶ and R⁷ are independently H or substituted or unsubstituted C₁₋₅₀ aliphatic hydrocarbyl groups, R⁸ is H, an alkali metal atom, an alkaline earth metal atom, an ammonium or alkylammonium group or a C₁₋₅₀ substituted or unsubstituted aliphatic hydrocarbyl group and A⁻ is an anion. The hydrocarbyl groups may be branched or straight chain and substituted or unsubstituted. Generally they will be unsubstituted. Examples of hydrocarbyl groups are alkyl groups, for instance alkyl groups containing from 1 to 7 carbon atoms. In the case of Y, examples of hydrocarbyl groups are alkylene groups, for instance alkylene groups containing from 1 to 5 carbon atoms.

15 X in the monomer of formula (1) may be oxygen or NR⁴. R⁴ is preferably hydrogen but may be a substituted or usually unsubstituted C₁₋₅₀ aliphatic hydrocarbonyl group. Suitably, it is a C₁₋₅₀ alkyl group, for example a C₁₋₅ alkyl group.

Y in the monomer of formula (1) may be a substituted or usually unsubstituted C₁₋₅₀ aliphatic hydrocarbonyl group. Suitably, it is a C₁₋₅₀ alkylene group, for example a C₁₋₅ alkylene group such as ethylene or n-propylene.

Z in the monomer of formula (1) may be hydrogen, NR^5R^6 , $\text{N}^+\text{R}^5\text{R}^6\text{R}^7\text{A}^-$ or SO_3R^8 .

When Z is NR⁵R⁶, R⁵ and R⁶ are independently hydrogen or substituted or usually unsubstituted C₁₋₅₀ aliphatic hydrocarbyl groups. Suitably, the hydrocarbyl groups are C₁₋₅₀ alkyl groups, for example C₁₋₇ alkyl groups. Examples are methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *sec*-butyl, *iso*-butyl and *tert*-butyl.

When Z is $N^+R^5R^6R^7A^-$, R^5 , R^6 and R^7 are independently hydrogen or substituted or usually unsubstituted C_{1-50} aliphatic hydrocarbyl groups. Suitably, the hydrocarbyl groups are C_{1-50} alkyl groups, for example C_{1-5} alkyl groups. Examples are methyl, ethyl,

n-propyl, *iso*-propyl, *n*-butyl, *sec*-butyl, *iso*-butyl and *tert*-butyl. The anion A⁻ may be any suitable anion such as CH₃SO₄⁻, NO₃⁻, F⁻, Cl⁻, Br⁻, CH₃CO₂⁻, NO₂⁻, NO⁻, CN⁻, SCN⁻, CNO⁻, ClO⁻, ClO₂⁻, ClO₃⁻ or ClO₄⁻. Typically it is a halide, for example chloride, or the methosulphate anion. Thus, the group N⁺R⁵R⁶R⁷A⁻ is conveniently a trialkylammonium salt, particularly a tri(C₁₋₄)alkylammonium salt, for example, a trimethylammonium salt
5 such as trimethylammonium chloride or trimethylammonium methosulphate.

When Z is SO₃R⁸, R⁸ is H, an alkali metal atom, an alkaline earth metal atom, an ammonium or alkylammonium group, for example a tri(C₁₋₄)alkylammonium group, or a C₁₋₅₀ substituted or usually unsubstituted aliphatic hydrocarbyl group. Alkali metal atoms
10 include lithium, sodium and potassium. Alkaline earth metals include magnesium, calcium, strontium and barium. When R⁸ is a hydrocarbyl group it is typically C₁₋₅ alkyl, for example, methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *sec*-butyl, *iso*-butyl or *tert*-butyl. An example of the group Y-SO₃R⁸ is 2-linked 2-methylpropane sulphonic acid.

R¹ and R² are independently H or C₁₋₅ aliphatic hydrocarbyl groups. Usually they
15 will both be hydrogen, but one may be hydrogen and the other a C₁₋₅ aliphatic hydrocarbyl group or both may be the same or different C₁₋₅ aliphatic hydrocarbyl groups. C₁₋₅ aliphatic hydrocarbyl groups are typically C₁₋₅ alkyl groups, for example, methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *sec*-butyl, *iso*-butyl or *tert*-butyl.

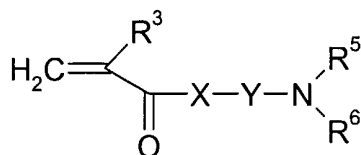
The fungicidal polymers used in the invention may be obtained by the
20 polymerization of the monomer of the formula (1) using any conventional chemical, thermal, irradiation-induced or other polymerization technique documented in the literature. Either one particular monomer of the formula (1) may be polymerized to form a homopolymer or two or more different monomers of the formula (1) may be used in any proportions to form a copolymer. In addition, other suitable monomers not of the formula
25 (1), for example other unsaturated aliphatic monomers, may be used to form copolymers. These other monomers are discussed in more detail later. Further, cross-linking agents may be employed to modify the properties of the fungicidal polymer as described in WO 02/092650. Examples of suitable cross-linking agents are ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, diethylene glycol diacrylate, ethylene glycol vinylether, diethylene glycol vinylether, polyethylene glycol dimethacrylate, 1,4-butanediol
30 vinylether, 1,1,1-tris(hydroxymethyl)propanebenzoate diacrylate, 1,1,1-

tris(hydroxymethyl)propane trivinylether and 1,1,1-tris(hydroxymethyl)propane-propoxylate triacrylate.

The fungicidal polymer used in the invention may be prepared as a solution in a suitable solvent, as a solid in powdered granular form or as an aqueous dispersion and formulated for use as a fungicide using formulation techniques well established in the art and described in more detail later. Alternatively it may be prepared by emulsion polymerization as described in WO 02/069709. The emulsion polymerization is carried out by polymerizing one or more monomers of the formula 1 and optionally one or more other monomers in water with an emulsifier using a thermal or photochemical radical starter. Ionic or nonionic compounds, such as polyethylene glycol derivatives, polyethylene glycol ether, especially 4-octylphenol polyethoxylate (sold under the trade name 'Triton'), alkylbenzyl sulphonates, alkylsulphates, alkyl sulphonates, ethoxylated fatty alcohols, alkyl phenols and fatty acids may be used as emulsifiers. The fungicidal polymers prepared in this way tend to have higher molecular weights than polymers prepared by solution or substance polymerization.

The fungicidal polymers may be formulated for plant fungicidal use either alone or in admixture with other polymers, for example, polyurethanes, PVCs, polyolefins such as polyethylenes or polypropylenes, polysiloxanes, polystyrenes, other polyacrylates or polymethacrylates or other synthetic materials such as polyamides or polyterephthalates. When mixed with other polymers the amount of the fungicidal polymer obtained from the monomer of formula (1) will normally be present in amounts of from 0.2 to 90 % by weight, preferably from 40 to 90% by weight, of the total polymer content.

In one aspect of the invention the fungicidal polymer is obtained by the polymerization of a monomer of the general formula (2):



(2)

wherein X is O or NR⁴, Y is a C₁₋₅ aliphatic hydrocarbyl group, R³ is H or CH₃, and R⁴, R⁵ and R⁶ are independently H or C₁₋₇ aliphatic hydrocarbyl groups. The hydrocarbyl groups may be branched or unbranched. Typically they are alkyl groups or, in the case of Y, an alkylene group. For instance, R⁵ and R⁶ are independently H or C₁₋₄ alkyl and Y is

C₁₋₃ alkylene. Examples of Y are ethylene and *n*-propylene and examples of the alkyl value of R⁵ and R⁶ are methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *sec*-butyl, *iso*-butyl and *tert*-butyl. Thus, in one embodiment of the monomer of formula (2), X is O, Y is C₁₋₃ alkylene (typically ethylene or propylene), R³ is H or CH₃ and R⁵ and R⁶ are
5 independently H or C₁₋₄ alkyl. Typically R⁵ is H and R⁶ is *tert*-butyl or R⁵ and R⁶ are both methyl or both ethyl.

In another embodiment of the monomer of formula (2), X is NH, Y is C₁₋₃ alkylene (typically ethylene or propylene), R³ is H or CH₃ and R⁵ and R⁶ are independently H or C₁₋₄ alkyl. Typically R⁵ is H and R⁶ is *tert*-butyl or R⁵ and R⁶ are both
10 methyl or both ethyl.

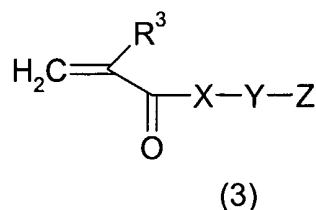
Examples of the monomer of the formula (2) are 2-(*tert*-butylamino)ethyl methacrylate, 2-(diethylamino)ethyl methacrylate, 2-(dimethylamino)methyl methacrylate, 2-(*tert*-butylamino)ethyl acrylate, 3-(dimethylamino)propyl acrylate, 2-(diethylamino)ethyl acrylate, 2-(dimethylamino)ethyl acrylate, *N*-(3-dimethylaminopropyl)-
15 methacrylamide, *N*-(3-diethylaminopropyl)methacrylamide, *N*-(3-dimethylaminopropyl)-acrylamide and *N*-(3-diethylaminopropyl)acrylamide.

The fungicidal polymers of this aspect of the invention are prepared as described in WO 01/18077 by the homopolymerization of the monomer of formula (2) using conventional free radical- or irradiation-initiated polymerization chemistry. The weight-
20 average molecular weight of these polymers is from 10,000 to 7,000,000, for example from 20,000 to 5,000,000 and typically from 30,000 to 500,000.

Specific examples of polymers used in the invention, which are commercially available, are Amina® T100, in the form of a white powder, and Limago® T100, in the form of an aqueous dispersion. Both are polymers formed from the monomer 2-(*tert*-
25 butylamino)ethyl methacrylate and both are obtainable from Creavis Technologies & Innovation, Paul-Baumann-Strasse 1, 45764 Marl, Germany.

In another aspect of the invention the fungicidal polymer may be obtained by the copolymerization of a monomer of the formula (2) as defined above with a monomer of the formula (3):

- 6 -



wherein X, Y and R³ have the meanings defined above and Z is H.

In the monomer of formula (3), it is preferred that X is oxygen and that Y-Z is a C₁₋₅ alkyl group, for instance, methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *sec*-butyl, *iso*-butyl or *tert*-butyl.

Examples of the monomer of formula (3) are methyl methacrylate, methyl acrylate, *tert*-butyl methacrylate, *tert*-butyl acrylate, *iso*-butyl methacrylate, *iso*-butyl acrylate, butyl methacrylate, butyl acrylate, ethyl methacrylate, ethyl acrylate, propyl methacrylate, *iso*-propyl methacrylate, propyl acrylate and *iso*-propyl acrylate.

Of particular interest are the copolymers where the monomer of formula (2) is an acryloyloxyalkylamine (X is O) or an alkylaminoacrylamide (X is NH) and where all aliphatic hydrocarbon groups are C₁₋₄ alkyl groups.

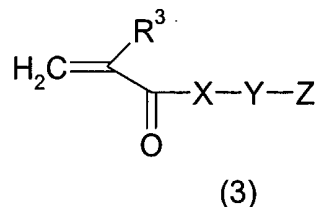
The copolymers can be produced as described in WO 01/85813 by copolymerization of the monomers of formulae (2) and (3), optionally with a further aliphatic unsaturated monomer, such as another acrylate or methacrylate, using well established chemical, thermal or irradiation-induced polymerization techniques.

Further, the copolymers of this aspect of the invention may be blended with other polymers such as polyurethanes, polyamides, polyesters and polyethers, polyether block amides, polystyrenes, polyvinyl chlorides, polycarbonates, polyorganosilanes, polyolefins, polysulfones, polyisoprenes, poly-chloroprenes, polytetrafluoroethylenes (PTFE) or polyterephthalate or copolymers thereof. When mixed with other polymers the amount of the copolymer of this aspect of the invention will normally be present in amounts of from 0.2 to 70 % by weight, preferably from 0.2 to 30% by weight, and especially from 1 to 20% by weight.

The weight-average molecular weight of the fungicidal copolymer may vary within wide limits but will usually be from 10,000 to 7,000,000 for example from 20,000 to 5,000,000 and typically from 30,000 to 500,000. However, if oligomers are produced they should be selected so that they are not appreciably water soluble (c.f. WO 02/017724 and WO 02/017725). Alternatively, the oligomers may be copolymerized with another

monomer either in a bulk polymerization or as a dispersion in water to form a latex by techniques well known in the art.

In yet another aspect of the invention the fungicidal polymer may be obtained by the copolymerization of a monomer of the formula (3):



wherein X is O or NH, Y is a C₁₋₅ branched or straight chain aliphatic hydrocarbyl group, Z is NR⁵R⁶ or N⁺R⁵R⁶R⁷A⁻, R³ and A⁻ have the meanings defined above and R⁵, R⁶ and R⁷ are independently H or a C₁₋₅ branched or straight chain aliphatic hydrocarbyl group; with at least one other aliphatic unsaturated monomer.

The C₁₋₅ branched or straight chain aliphatic hydrocarbyl groups are typically alkyl groups or, in the case of Y, an alkylene group. For instance, R⁵, R⁶ and R⁷ are independently H or C₁₋₄ alkyl and Y is C₁₋₃ alkylene. Examples of Y are ethylene and *n*-propylene and examples the alkyl value of R⁵, R⁶ and R⁷ are methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *sec*-butyl, *iso*-butyl and *tert*-butyl.

Of particular interest in this aspect of the invention are those monomers of the formula (3) where

(a) X is O, Y is C₁₋₄ alkylene (for example, ethylene or propylene) and Z is NR⁵R⁶ wherein R⁵ and R⁶ are independently H or C₁₋₄ alkyl (for example, both methyl or ethyl);

(b) X is NH, Y is C₁₋₄ alkylene (for example, ethylene or propylene) and Z is NR⁵R⁶

wherein R⁵ and R⁶ are independently H or C₁₋₄ alkyl (for example, both methyl or ethyl);

(c) X is O, Y is C₁₋₄ alkylene (for example, ethylene or propylene) and Z is N⁺R⁵R⁶R⁷A⁻ wherein R⁵, R⁶ and R⁷ are independently H or C₁₋₄ alkyl (for example, all methyl) and A⁻ is a halide anion (for example, chloride) or methosulphate; and

(d) X is NH, Y is C₁₋₄ alkylene (for example, ethylene or propylene) and Z is

N⁺R⁵R⁶R⁷A⁻ wherein R⁵, R⁶ and R⁷ are independently H or C₁₋₄ alkyl (for example, all methyl) and A⁻ is a halide anion (for example, chloride) or methosulphate.

Examples of (a) are 2-(diethylamino)ethylmethacrylate, 2-(dimethylamino)ethylmethacrylate, 2-(diethylamino)ethylacrylate and 2-(dimethylamino)ethylacrylate.

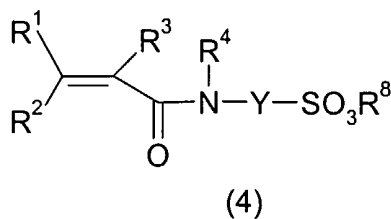
Examples of (b) are *N*-3-(diethylaminopropyl)methacrylamide, *N*-3-(dimethylamino-

propyl)methacrylamide, *N*-3-(diethylaminopropyl)acrylamide and *N*-3-(dimethylamino-propyl)acrylamide. Examples of (c) are 2-(methacryloyloxy)ethyltrimethylammonium chloride and the equivalent methosulphate salt and 2-(acryloyloxy)ethyltrimethyl-ammonium chloride and the equivalent methosulphate salt. Examples of (d) are 3-
 5 (methacryloylamino)propyltrimethylammonium chloride and the equivalent methosulphate salt and 3-(acryloylamino)propyltrimethylammonium chloride and the equivalent methosulphate salt.

The other aliphatic unsaturated monomer or monomers used in this aspect of the invention to form the copolymer with the monomer of the formula (3) may be an acrylate or methacrylate, such as acrylic acid, *tert*-butyl methacrylate or methylmethacrylate,
 10 styrene, vinyl chloride, vinyl ether, acrylamide, acrylonitrile, an olefin, such as ethylene, propylene, butylene or isobutylene, an allyl compound, vinyl ketone, vinyl acetic acid, vinyl acetate or a vinyl ester. Of especial mention are methyl methacrylate, ethyl methacrylate, butyl methacrylate, *tert*-butyl methacrylate, methyl acrylate, ethyl acrylate,
 15 butyl acrylate, *tert*-butyl acrylate or 2-diethylaminoethylvinyl ether. Alternatively the other aliphatic unsaturated monomer may be a different monomer of the formula (3). Examples of monomers of the formula (3) which form at least one component of the copolymer, including where the other component is a different monomer of the formula (3), are 2-(*tert*-butylamino)ethyl methacrylate, 2-(*tert*-butylamino)ethyl acrylate, 2-
 20 (diethylaminoethyl) methacrylate, *N*-3-(dimethylaminopropyl)methacrylamide, *N*-3-(diethylaminopropyl)methacrylamide, 2-(methacryloyloxy)ethyltrimethylammonium methosulphate or halide and 3-(methacryloylamino)propyltrimethylammonium methosulphate or halide.

The preparation of the fungicidal polymers used in this aspect of the invention is
 25 described in more detail in WO 01/16193 and WO 01/19878.

In yet another aspect of the invention the fungicidal polymer may be obtained by the polymerization of a monomer of the general formula (4):



wherein Y, R¹, R², R³ and R⁸ have the meanings defined above and R⁴ is H or a C₁₋₅ branched or straight chain aliphatic hydrocarbonyl group.

Y in the monomer of formula (4) may be a substituted or unsubstituted C₁₋₅₀ aliphatic hydrocarbonyl group, generally unsubstituted. Suitably, it is a C₁₋₅₀ alkylene group, for example a C₁₋₅ alkylene group such as ethylene or n-propylene.

R¹ and R² are independently H or a C₁₋₅ aliphatic hydrocarbonyl group. Usually they will both be hydrogen, but one may be hydrogen and the other a C₁₋₅ aliphatic hydrocarbonyl group or both may be the same or a different C₁₋₅ aliphatic hydrocarbonyl group. C₁₋₅ aliphatic hydrocarbonyl groups are typically C₁₋₅ alkyl groups, for example, methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, iso-butyl or tert-butyl.

R⁴ is preferably hydrogen but may be a substituted or unsubstituted C₁₋₅₀ aliphatic hydrocarbonyl group, generally unsubstituted. Suitably, it is a C₁₋₅₀ alkyl group, for example a C₁₋₅ alkyl group.

R⁸ is H, an alkali metal atom, an alkaline earth metal atom, an ammonium or alkylammonium group, for example a tri(C₁₋₄)alkylammonium group, or a C₁₋₅₀ substituted or unsubstituted aliphatic hydrocarbonyl group, generally unsubstituted. Alkali metal atoms include lithium, sodium and potassium. Alkaline earth metals include magnesium, calcium, strontium and barium. When R⁸ is a hydrocarbonyl group it is typically C₁₋₅ alkyl, for example, methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, iso-butyl or tert-butyl. An example of the group Y-SO₃R⁸ is 2-linked 2-methylpropane sulphonic acid.

Typical examples of the monomer of the formula (4) is 2-acrylamido-2-methylpropane sulphonic acid and its alkali metal and alkaline earth metal salts such as the sodium salt.

The monomer of the formula (4) may be used on its own to form the fungicidal polymer of the invention by a homopolymerization process or it may be copolymerized with at least one other aliphatic unsaturated monomer. For example, the other monomer may be an acrylate or methacrylate, such as acrylic acid, tert-butyl methacrylate or methylmethacrylate, styrene, vinyl chloride, vinyl ether, acrylamide, acrylonitrile, an olefin, such as ethylene, propylene, butylene or isobutylene, an allyl compound, vinyl ketone, vinyl acetic acid, vinyl acetate or a vinyl ester. Of especial mention are methyl methacrylate, ethyl methacrylate, butyl methacrylate, tert-butyl methacrylate, methyl

acrylate, ethyl acrylate, butyl acrylate, *tert*-butyl acrylate, 2-diethylaminoethylvinyl ether, 2-(*tert*-butylamino)ethyl methacrylate, 2-(*tert*-butylamino)ethyl acrylate, 2-(diethylaminoethyl) methacrylate, *N*-3-(dimethylaminopropyl)methacrylamide, *N*-3-(diethylaminopropyl)methacrylamide, 2-(methacryloyloxy)ethyltrimethylammonium
5 methosulphate or halide and 3-(methacryloylamino)propyltrimethylammonium methosulphate or halide.

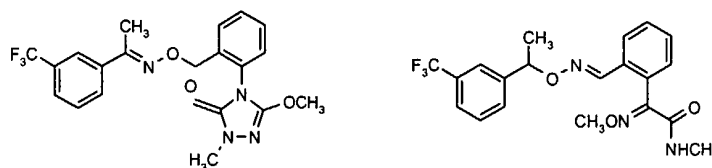
The preparation of the polymers used in this aspect of the invention is more fully described in WO 01/72859. These polymers may optionally be graft polymerized on substrates such as polyurethanes, polyamides, polyesters and polyethers, polyether block
10 amides, polystyrenes, polyvinyl chlorides, polycarbonates, polyorganosilanes, polyolefins, polysulfones, polyisoprenes, poly-chloroprenes, polytetrafluoroethylenes (PTFE) or polyterephthalate or copolymers thereof.

The compositions of this invention may contain other compounds having biological activity, for example micronutrients or compounds having similar or
15 complementary fungicidal activity or which possess plant growth regulating, herbicidal, insecticidal, nematocidal or acaricidal activity.

The addition of another active ingredient may provide a composition having a broader spectrum of activity or increased persistence at a locus, synergise the activity or complement the activity (for example by increasing the speed of effect or overcoming
20 repellency) of the fungicidal polymer, or help to overcome or prevent the development of resistance to individual components. The particular additional active ingredient will depend upon the intended utility of the composition.

Examples of fungicidal compounds which may be included in the composition of the invention are AC 382042 (*N*-(1-cyano-1,2-dimethylpropyl)-2-(2,4-dichlorophenoxy)
25 propionamide), acibenzolar-S-methyl, alanycarb, aldimorph, anilazine, azaconazole, azafenidin, azoxystrobin, benalaxyl, benomyl, benthiavalicarb, biloxazol, bitertanol, blastidicin S, boscalid (new name for nicobifen), bromuconazole, bupirimate, captafol, captan, carbendazim, carbendazim chlorhydrate, carboxin, carpropamid, carvone, CGA 41396, CGA 41397, chinomethionate, chlorbenzthiazole, chlorothalonil, chlorozolate,
30 clozylacon, copper containing compounds such as copper oxychloride, copper oxyquinate, copper sulphate, copper tallate, and Bordeaux mixture, cyamidazosulfamid, cyazofamid (IKF-916), cyflufenamid, cymoxanil, cyproconazole, cyprodinil, debacarb,

di-2-pyridyl disulphide 1,1'-dioxide, dichlofluanid, diclocymet, diclomezine, dicloran, diethofencarb, difenoconazole, difenzoquat, diflumetorim, *O,O*-di-*iso*-propyl-*S*-benzyl thiophosphate, dimefluzole, dimetconazole, dimethirimol, dimethomorph, dimoxystrobin, diniconazole, dinocap, dithianon, dodecyl dimethyl ammonium chloride, dodemorph, dodine, doguadine, edifenphos, epoxiconazole, ethaboxam, ethirimol, ethyl (Z)-*N*-benzyl-*N*[(methyl(methyl-thioethylideneaminooxycarbonyl)amino)thio]- β -alaninate, etridiazole, famoxadone, fenamidone, fenarimol, fenbuconazole, fenfuram, fenhexamid, fenoxanil (AC 382042), fempiclonil, fenpropidin, fenpropimorph, fentin acetate, fentin hydroxide, ferbam, ferimzone, fluazinam, fludioxonil, flumetover, flumorph, fluoroimide, fluoxastrobin, fluquinconazole, flusilazole, flusulfamide, flutolanil, flutriafol, folpet, fosetyl-aluminium, fuberidazole, furalaxyl, furametpyr, guazatine, hexaconazole, hydroxyisoxazole, hymexazole, imazalil, imibenconazole, iminoctadine, iminoctadine triacetate, ipconazole, iprobenfos, iprodione, iprovalicarb, isopropanyl butyl carbamate, isoprothiolane, kasugamycin, kresoxim-methyl, LY186054, LY211795, LY 248908, mancozeb, maneb, mefenoxam, mepanipyrim, mepronil, metalaxyl, metalaxyl M, metconazole, metiram, metiram-zinc, metominostrobin, metrafenone, MON65500 (*N*-allyl-4,5-dimethyl-2-trimethylsilylthiophene-3-carboxamide), myclobutanil, NTN0301, neoasozin, nickel dimethyldithiocarbamate, nitrothale-isopropyl, nuarimol, ofurace, organomercury compounds, orysastrobin, oxadixyl, oxasulfuron, oxolinic acid, oxpoconazole, oxycarboxin, pefurazoate, penconazole, pencycuron, phenazin oxide, phosphorus acids, phthalide, picoxystrobin, polyoxin D, polyram, probenazole, prochloraz, procymidone, propamocarb, propamocarb hydrochloride, propiconazole, propineb, propionic acid, proquinazid, prothioconazole, pyraclostrobin, pyrazophos, pyrifenox, pyrimethanil, pyroquilon, pyroxyfur, pyrrolnitrin, quaternary ammonium compounds, quinomethionate, quinoxifen, quintozone, silthiofam (MON 65500), S-imazalil, simeconazole, sipconazole, sodium pentachlorophenate, spiroxamine, streptomycin, sulphur, tebuconazole, tecloftalam, tecnazene, tetraconazole, thiabendazole, thifluzamide, 2-(thiocyanomethylthio)benzothiazole, thiophanate-methyl, thiram, tiadinil, timibenconazole, tolclofos-methyl, tolylfluanid, triadimefon, triadimenol, triazbutil, triazoxide, tricyclazole, tridemorph, trifloxystrobin, triflumizole, triforine, triticonazole, validamycin A, vapam, vinclozolin, XRD-563, zineb, ziram, zoxamide and compounds of the formulae:



The fungicidal polymers are active fungicides in their own right and may be used to control one or more of the following pathogens: *Pyricularia oryzae* (*Magnaporthe grisea*) on rice and wheat and other *Pyricularia* spp. on other hosts; *Puccinia triticina* (or *recondita*), *Puccinia striiformis* and other rusts on wheat, *Puccinia hordei*, *Puccinia striiformis* and other rusts on barley, and rusts on other hosts (for example turf, rye, coffee, pears, apples, peanuts, sugar beet, vegetables and ornamental plants); *Erysiphe cichoracearum* on cucurbits (for example melon); *Blumeria* (or *Erysiphe*) *graminis* (powdery mildew) on barley, wheat, rye and turf and other powdery mildews on various hosts, such as *Sphaerotheca macularis* on hops, *Sphaerotheca fusca* (*Sphaerotheca fuliginea*) on cucurbits (for example cucumber), *Leveillula taurica* on tomatoes, aubergine and green pepper, *Podosphaera leucotricha* on apples and *Uncinula necator* on vines; *Cochliobolus* spp., *Helminthosporium* spp., *Drechslera* spp. (*Pyrenophora* spp.), *Rhynchosporium* spp., *Mycosphaerella graminicola* (*Septoria tritici*) and *Leptosphaeria nodorum* (*Phaeosphaeria nodorum*, *Stagonospora nodorum* or *Septoria nodorum*), *Pseudocercospora herpotrichoides* and *Gaeumannomyces graminis* on cereals (for example wheat, barley, rye), turf and other hosts; *Cercospora arachidicola* and *Cercosporidium personatum* on peanuts and other *Cercospora* spp. on other hosts, for example sugar beet, bananas, soya beans and rice; *Botrytis cinerea* (grey mould) on tomatoes, strawberries, vegetables, vines and other hosts and other *Botrytis* spp. on other hosts; *Alternaria* spp. on vegetables (for example carrots), oil-seed rape, apples, tomatoes, potatoes, cereals (for example wheat) and other hosts; *Venturia* spp. (including *Venturia inaequalis* (scab)) on apples, pears, stone fruit, tree nuts and other hosts; *Cladosporium* spp. on a range of hosts including cereals (for example wheat) and tomatoes; *Monilinia* spp. on stone fruit, tree nuts and other hosts; *Didymella* spp. on tomatoes, turf, wheat, cucurbits and other hosts; *Phoma* spp. on oil-seed rape, turf, rice, potatoes, wheat and other hosts; *Aspergillus* spp. and *Aureobasidium* spp. on wheat and other hosts; *Ascochyta* spp. on peas, wheat, barley and other hosts; *Stemphylium* spp. (*Pleospora* spp.) on apples, pears, onions and other hosts; summer diseases (for example

bitter rot (*Glomerella cingulata*), black rot or frog-eye leaf spot (*Botryosphaeria obtusa*), Brooks fruit spot (*Mycosphaerella pomii*), Cedar apple rust (*Gymnosporangium juniperi-virginianae*), sooty blotch (*Gloeodes pomigena*), flyspeck (*Schizothyrium pomii*) and white rot (*Botryosphaeria dothidea*) on apples and pears; *Plasmopara viticola* on vines;

5 other downy mildews, such as *Bremia lactucae* on lettuce, *Peronospora* spp. on soybeans, tobacco, onions and other hosts, *Pseudoperonospora humuli* on hops and *Pseudoperonospora cubensis* on cucurbits; *Pythium* spp. (including *Pythium ultimum*) on turf and other hosts; *Phytophthora infestans* on potatoes and tomatoes and other *Phytophthora* spp. on vegetables, strawberries, avocado, pepper, ornamentals, tobacco,

10 cocoa and other hosts; *Thanatephorus cucumeris* on rice and turf and other *Rhizoctonia* spp. on various hosts such as wheat and barley, peanuts, vegetables, cotton and turf; *Sclerotinia* spp. on turf, peanuts, potatoes, oil-seed rape and other hosts; *Sclerotium* spp. on turf, peanuts and other hosts; *Gibberella fujikuroi* on rice; *Colletotrichum* spp. on a range of hosts including turf, coffee and vegetables; *Laetisaria fuciformis* on turf;

15 *Mycosphaerella* spp. on bananas, peanuts, citrus, pecans, papaya and other hosts; *Diaporthe* spp. on citrus, soybean, melon, pears, lupin and other hosts; *Elsinoe* spp. on citrus, vines, olives, pecans, roses and other hosts; *Verticillium* spp. on a range of hosts including hops, potatoes and tomatoes; *Pyrenopeziza* spp. on oil-seed rape and other hosts; *Oncobasidium theobromae* on cocoa causing vascular streak dieback; *Fusarium*

20 spp., *Typhula* spp., *Microdochium nivale*, *Ustilago* spp., *Urocystis* spp., *Tilletia* spp. and *Claviceps purpurea* on a variety of hosts but particularly wheat, barley, turf and maize; *Ramularia* spp. on sugar beet, barley and other hosts; post-harvest diseases particularly of fruit (for example *Penicillium digitatum*, *Penicillium italicum* and *Trichoderma viride* on oranges, *Colletotrichum musae* and *Gloeosporium musarum* on bananas and *Botrytis*

25 *cinerea* on grapes); other pathogens on vines, notably *Eutypa lata*, *Guignardia bidwellii*, *Phellinus igniarius*, *Phomopsis viticola*, *Pseudopeziza tracheiphila* and *Stereum hirsutum*; other pathogens on trees (for example *Lophodermium seeditiosum*), notably *Cephalosporium frugis*, *Ceratocystis* spp., *Ophiostoma piceae*, *Penicillium* spp., *Trichoderma pseudokoningii*, *Trichoderma viride*, *Trichoderma harzianum*, *Aspergillus niger*,

30 *Leptographium lindbergii* and *Aureobasidium pullulans*; and fungal vectors of viral diseases (for example *Polymyxa graminis* on cereals as the vector of barley yellow mosaic virus (BYMV) and *Polymyxa betae* on sugar beet as the vector of rhizomania).

The fungicidal polymers show particularly good activity against *Plasmopara* species, e.g. *Plasmopara viticola*, against *Leptosphaeria nodorum* and against *Fusarium graminearum*.

The invention therefore provides the use of the fungicidal polymers of the
5 invention for combating phytopathogenic diseases on plants and harvested food crops.

The term "plant" as used herein includes seedlings, grasses, bushes and trees. Furthermore, the fungicidal method of the invention includes protectant, curative, systemic, eradicator and antispore treatments. The term "harvested food crops" means the edible product of any plant stored for human or animal consumption, including grain,
10 fruit and seed.

The fungicidal polymers are preferably used for agricultural, horticultural and turfgrass purposes in the form of a composition.

In order to apply a fungicidal polymer of the invention to a plant, to a seed of a plant, to the locus of the plant or seed or to soil or any other growth medium, the polymer
15 is usually formulated into a composition which includes, in addition to the polymer, a suitable inert diluent or carrier and, optionally, a surface active agent (SFA). SFAs are chemicals that are able to modify the properties of an interface (for example, liquid/solid, liquid/air or liquid/liquid interfaces) by lowering the interfacial tension and thereby leading to changes in other properties (for example dispersion, emulsification and
20 wetting). It is preferred that all compositions (both solid and liquid formulations) comprise, by weight, 0.0001 to 95%, more preferably 1 to 85%, for example 5 to 60%, of the fungicidal polymer. The composition is generally used for the control of fungi such that the fungicidal polymer is applied at a rate of from 0.1g to 10kg per hectare, preferably from 1g to 6kg per hectare, more preferably from 1g to 1kg per hectare.

25 When used in a seed dressing, the fungicidal polymer is used at a rate of 0.0001g to 10g (for example 0.001g or 0.05g), preferably 0.005g to 10g, more preferably 0.005g to 4g, per kilogram of seed. When used to treat harvested crops, such as oranges, grapefruit and apples, by dipping or rolling the crop in a liquid medium, typically in an aqueous medium, the concentration of the polymer in the liquid medium will be in the range of
30 0.01g to 5,000g, usually in the range of 0.2g to 2,000g, for example 0.2g to 200g, and typically in the range of from 25g to 50g of polymer in 100 litres of liquid.

In another aspect the present invention provides a fungicidal composition comprising a fungicidally effective amount of a polymer of the invention and an agriculturally acceptable carrier or diluent therefor.

In a still further aspect the invention provides a method of combating and
5 controlling fungi at a locus, which comprises treating the fungi, or the locus of the fungi with a fungicidally effective amount of a composition comprising a fungicidally effective amount of a polymer as defined in claim 1 and an agriculturally acceptable carrier.

The compositions can be chosen from a number of formulation types, including dustable powders (DP), soluble powders (SP), water soluble granules (SG), water
10 dispersible granules (WG), wettable powders (WP), granules (GR) (slow or fast release), soluble concentrates (SL), oil miscible liquids (OL), ultra low volume liquids (UL), emulsifiable concentrates (EC), dispersible concentrates (DC), emulsions (both oil in water (EW) and water in oil (EO)), micro-emulsions (ME), suspension concentrates (SC), aerosols, fogging/smoke formulations and seed treatment formulations. The formulation
15 type chosen in any instance will depend upon the particular purpose envisaged and the physical, chemical and biological properties of the fungicidal polymer.

Dustable powders (DP) may be prepared by mixing the fungicidal polymer with one or more solid diluents (for example natural clays, kaolin, pyrophyllite, bentonite, alumina, montmorillonite, kieselguhr, chalk, diatomaceous earths, calcium phosphates,
20 calcium and magnesium carbonates, sulphur, lime, flours, talc and other organic and inorganic solid carriers) and mechanically grinding the mixture to a fine powder.

Soluble powders (SP) may be prepared by mixing the fungicidal polymer with one or more water-soluble inorganic salts (such as sodium bicarbonate, sodium carbonate or magnesium sulphate) or one or more water-soluble organic solids (such as a
25 polysaccharide) and, optionally, one or more wetting agents, one or more dispersing agents or a mixture of said agents to improve water dispersibility/solubility. The mixture is then ground to a fine powder. Similar compositions may also be granulated to form water soluble granules (SG).

Wettable powders (WP) may be prepared by mixing the fungicidal polymer with
30 one or more solid diluents or carriers, one or more wetting agents and, preferably, one or more dispersing agents and, optionally, one or more suspending agents to facilitate the

dispersion in liquids. The mixture is then ground to a fine powder. Similar compositions may also be granulated to form water dispersible granules (WG).

Granules (GR) may be formed either by granulating a mixture of the fungicidal polymer and one or more powdered solid diluents or carriers, or from pre-formed blank
5 granules by absorbing the fungicidal polymer (or a solution thereof, in a suitable agent) in a porous granular material (such as pumice, attapulgite clays, fuller's earth, kieselguhr, diatomaceous earths or ground corn cobs) or by adsorbing the fungicidal polymer (or a solution thereof, in a suitable agent) on to a hard core material (such as sands, silicates, mineral carbonates, sulphates or phosphates) and drying if necessary. Agents which are
10 commonly used to aid absorption or adsorption include solvents (such as aliphatic and aromatic petroleum solvents, alcohols, ethers, ketones and esters) and sticking agents (such as polyvinyl acetates, polyvinyl alcohols, dextrans, sugars and vegetable oils). One or more other additives may also be included in granules (for example an emulsifying agent, wetting agent or dispersing agent).

15 Dispersible Concentrates (DC) may be prepared by dissolving the fungicidal polymer in water or an organic solvent, such as a ketone, alcohol or glycol ether. These solutions may contain a surface active agent (for example to improve water dilution or prevent crystallisation in a spray tank).

Emulsifiable concentrates (EC) or oil-in-water emulsions (EW) may be prepared
20 by dissolving the fungicidal polymer in an organic solvent (optionally containing one or more wetting agents, one or more emulsifying agents or a mixture of said agents). Suitable organic solvents for use in ECs include aromatic hydrocarbons (such as alkylbenzenes or alkylnaphthalenes, exemplified by SOLVESSO 100, SOLVESSO 150 and SOLVESSO 200; SOLVESSO is a Registered Trade Mark), ketones (such as
25 cyclohexanone or methylcyclohexanone), alcohols (such as benzyl alcohol, furfuryl alcohol or butanol), *N*-alkylpyrrolidones (such as *N*-methylpyrrolidone or *N*-octylpyrrolidone), dimethyl amides of fatty acids (such as C₈-C₁₀ fatty acid dimethylamide) and chlorinated hydrocarbons. An EC product may spontaneously emulsify on addition to water, to produce an emulsion with sufficient stability to allow
30 spray application through appropriate equipment. Preparation of an EW involves obtaining the fungicidal polymer either as a liquid (if it is not a liquid at room temperature, it may be melted at a reasonable temperature, typically below 70°C) or in

solution (by dissolving it in an appropriate solvent) and then emulsifying the resultant liquid or solution into water containing one or more SFAs, under high shear, to produce an emulsion. Suitable solvents for use in EWs include vegetable oils, chlorinated hydrocarbons (such as chlorobenzenes), aromatic solvents (such as alkylbenzenes or
5 alkyl naphthalenes) and other appropriate organic solvents that have a low solubility in water.

Microemulsions (ME) may be prepared by mixing water with a blend of one or more solvents with one or more SFAs, to produce spontaneously a thermodynamically stable isotropic liquid formulation. The fungicidal polymer is present initially in either
10 the water or the solvent/SFA blend. Suitable solvents for use in MEs include those hereinbefore described for use in ECs or in EWs. An ME may be either an oil-in-water or a water-in-oil system (which system is present may be determined by conductivity measurements) and may be suitable for mixing water-soluble and oil-soluble pesticides in the same formulation. An ME is suitable for dilution into water, either remaining as a
15 microemulsion or forming a conventional oil-in-water emulsion.

Suspension concentrates (SC) may comprise aqueous or non-aqueous suspensions of finely divided insoluble solid particles of the fungicidal polymer. SCs may be prepared by ball or bead milling the solid fungicidal polymer in a suitable medium, optionally with one or more dispersing agents, to produce a fine particle suspension of the polymer. One
20 or more wetting agents may be included in the composition and a suspending agent may be included to reduce the rate at which the particles settle. Alternatively, the fungicidal polymer may be dry milled and added to water, containing agents hereinbefore described, to produce the desired end product.

Aerosol formulations comprise the fungicidal polymer and a suitable propellant
25 (for example *n*-butane). The fungicidal polymer may also be dissolved or dispersed in a suitable medium (for example water or a water miscible liquid, such as *n*-propanol) to provide compositions for use in non-pressurised, hand-actuated spray pumps.

The fungicidal polymer may be mixed in the dry state with a pyrotechnic mixture to form a composition suitable for generating, in an enclosed space, a smoke containing
30 the polymer.

The compositions may provide for controlled release of the fungicidal polymer and they may be used for seed treatment. The fungicidal polymer may also be formulated in a biodegradable polymeric matrix to provide a slow, controlled release of the polymer.

A composition may include one or more additives to improve the biological
5 performance of the composition (for example by improving wetting, retention or distribution on surfaces; resistance to rain on treated surfaces; or uptake or mobility of the fungicidal polymer. Such additives include surface active agents, spray additives based on oils, for example certain mineral oils or natural plant oils (such as soy bean and rape seed oil), and blends of these with other bio-enhancing adjuvants (ingredients which may aid
10 or modify the action of the fungicidal polymer).

The fungicidal polymer may also be formulated for use as a seed treatment, for example as a powder composition, including a powder for dry seed treatment (DS), a water soluble powder (SS) or a water dispersible powder for slurry treatment (WS), or as a liquid composition, including a flowable concentrate (FS) or a solution (LS). The
15 preparations of DS, SS, WS, FS and LS compositions are very similar to those of, respectively, DP, SP, WP, SC and DC compositions described above. Compositions for treating seed may include an agent for assisting the adhesion of the composition to the seed (for example a mineral oil or a film-forming barrier).

Wetting agents, dispersing agents and emulsifying agents may be SFAs of the
20 cationic, anionic, amphoteric or non-ionic type.

Suitable SFAs of the cationic type include quaternary ammonium compounds (for example cetyltrimethyl ammonium bromide), imidazolines and amine salts.

Suitable anionic SFAs include alkali metals salts of fatty acids, salts of aliphatic monoesters of sulphuric acid (for example sodium lauryl sulphate), salts of sulphonated
25 aromatic compounds (for example sodium dodecylbenzenesulphonate, calcium dodecylbenzenesulphonate, butylnaphthalene sulphonate and mixtures of sodium di-*isopropyl*- and tri-*isopropyl*-naphthalene sulphonates), ether sulphates, alcohol ether sulphates (for example sodium laureth-3-sulphate), ether carboxylates (for example sodium laureth-3-carboxylate), phosphate esters (products from the reaction between one or more fatty
30 alcohols and phosphoric acid (predominately mono-esters) or phosphorus pentoxide (predominately di-esters), for example the reaction between lauryl alcohol and tetraphos-

phoric acid; additionally these products may be ethoxylated), sulphosuccinamates, paraffin or olefine sulphonates, taurates and lignosulphonates.

Suitable SFAs of the amphoteric type include betaines, propionates and glycines.

- 5 Suitable SFAs of the non-ionic type include condensation products of alkylene oxides, such as ethylene oxide, propylene oxide, butylene oxide or mixtures thereof, with fatty alcohols (such as oleyl alcohol or cetyl alcohol) or with alkylphenols (such as octylphenol, nonylphenol or octylcresol); partial esters derived from long chain fatty acids or hexitol anhydrides; condensation products of said partial esters with ethylene oxide;
- 10 block polymers (comprising ethylene oxide and propylene oxide); alkanolamides; simple esters (for example fatty acid polyethylene glycol esters); amine oxides (for example lauryl dimethyl amine oxide); and lecithins.

- Suitable suspending agents include hydrophilic colloids (such as polysaccharides, polyvinylpyrrolidone or sodium carboxymethylcellulose) and swelling clays (such as
- 15 bentonite or attapulgate).

- The fungicidal polymer may be applied by any of the known means of applying fungicidal compounds. For example, it may be applied, formulated or unformulated, to any part of the plant, including the foliage, stems, ears, seed heads, fruits, branches or roots, to the seed before it is planted or to other media in which plants are growing or are
- 20 to be planted (such as soil surrounding the roots, the soil generally or paddy water), directly or it may be sprayed on, dusted on, applied by dipping, applied as a cream or paste formulation, applied as a vapour or smoke or applied through distribution or incorporation of a composition (such as a granular composition or a composition packed in a water-soluble bag) in soil or an aqueous environment.

- 25 The fungicidal polymer may also be injected into plants or sprayed onto vegetation using electrodynamic spraying techniques or other low volume methods, or applied by land or aerial irrigation systems.

- Compositions for use as aqueous preparations (aqueous solutions or dispersions) are generally supplied in the form of a concentrate containing a high proportion of the
- 30 fungicidal polymer, the concentrate being added to water before use. These concentrates, which may include DCs, SCs, ECs, EWs, MEs SGs, SPs, WPs and WGs, are often required to withstand storage for prolonged periods and, after such storage, to be capable

of addition to water to form aqueous preparations which remain homogeneous for a sufficient time to enable them to be applied by conventional spray equipment. Such aqueous preparations may contain varying amounts the fungicidal polymer (for example 0.0001 to 10%, by weight) depending upon the purpose for which they are to be used.

5 The fungicidal polymer may be used in mixtures with fertilisers (for example nitrogen-, potassium- or phosphorus-containing fertilisers). Suitable formulation types include granules of fertiliser. The mixtures suitably contain up to 25% by weight of the fungicidal polymer.

 The invention therefore also provides a fertiliser composition comprising a
10 fertiliser and a fungicidally effective amount of a fungicidal polymer of the invention.

 The fungicidal polymer may be mixed with soil, peat or other rooting media for the protection of plants against seed-borne, soil-borne or foliar fungal diseases.

 Another active ingredient may be used in admixture with the fungicidal polymer of the invention that has significantly different physical, chemical or biological properties
15 to the polymer such that it does not easily lend itself to the same conventional formulation type. In these circumstances other formulation types may be prepared. For example, where one of the active ingredient and polymer is a water insoluble solid and the other a water insoluble liquid, it may nevertheless be possible to disperse each active ingredient in the same continuous aqueous phase by dispersing the solid ingredient as a
20 suspension (using a preparation analogous to that of an SC) and dispersing the liquid ingredient as an emulsion (using a preparation analogous to that of an EW). The resultant composition is a suspoemulsion (SE) formulation.

EXAMPLE

 This Example illustrates the fungicidal properties of the fungicidal polymers of
25 the invention.

 The polymers Amina® T100 and Limago® T100 (obtained from Creavis Technologies & Innovation) were tested against a variety of fungal foliar, seed, fruit and post harvest diseases of food crops. The techniques employed were as follows.

 Plants were either grown in John Innes Potting Compost No. 2 in 4cm diameter,
30 3.5cm depth minipots or on an artificial, cellulose based growing medium. For tests on fruit the fruit (or fruit pieces) were washed/surface sterilised and placed in sterile multi well plates for the duration of the tests. For tests on wheat ear diseases the plants were

grown in 10cm pots. Liquid culture tests were conducted in 96 well plates using artificial media (Vogel's minimal media) inoculated with spores/mycelial fragments of the pathogens being evaluated. The test polymers were individually formulated as a solution either in acetone or acetone/ethanol (1:1 by volume), which was diluted in reverse osmosis water, to the required concentration immediately before use. When foliar sprays were applied to monocotyledonous crops, TWEEN 20 (0.05% by volume) was added. TWEEN is a registered trade mark.

Individual polymers were applied as a foliar application (where the chemical solution was applied to the foliage/ears of the test plants by spraying the target to maximum droplet retention); as a surface application (where the fruit was dipped or rolled in the chemical solution); or as a liquid culture application (where the chemical was dispensed into a 96 well microtitre plate and diluted to the appropriate rate with a mixture of fungal inoculum and media).

Whole plant tests were carried out against *Plasmopara viticola* (PLASVI) on vines; *Phytophthora infestans lycopersici* (PHYTIN) on tomatoes; *Blumeria graminis f.sp. tritici* (ERYSGT), *Stagonospora nodorum* (LEPTNO) and *Puccinia triticina* (PUCCRT), on wheat. Ear disease tests were carried out against *Fusarium graminearum* (GIBBZE) on ears of wheat that had entered the flowering stage. Chemical applications to whole plants were made 6-24 hours before inoculation. Surface application tests were carried out using "plugs" of oranges or whole pea fruit. Pathogens evaluated were *Penicillium expansum* (PENIEX) and *Botrytis cinerea* (BOTRCI). The plants / fruits were inoculated with a calibrated fungal spore suspension 4-24 hours after chemical application. Each treatment was applied to two or more replicate plants/fruits. Liquid culture tests were carried out against *Septoria tritici* (SEPTTR), *Phytophthora infestans* (PHYTIN) and *Fusarium graminearum* (GIBBZE). Microtitre plates were prepared by adding chemical samples dissolved in acetone at the appropriate rates to sterile media. After 24 hours plates were inoculated by adding a mixture of fungal inoculum (spores/mycelium), dispersed in sterile media, to individual wells.

After chemical application and inoculation, the plants were incubated under high humidity conditions and then put into an appropriate environment to allow infection to proceed, until the disease was ready for assessment. For *Plasmopara viticola*, the plants were reincubated under high humidity conditions for 24hours prior to assessment. The

time period between chemical application and assessment varied from five to fourteen days according to the disease and environment. However, each individual disease was assessed after the same time period for all polymers.

At assessment, liquid culture assays were assessed visually. Wells containing treatments were compared to control wells and scored as either 0, 55 or 100% disease control. Results for individual replicates were meaned to provide mean disease control values. For tests on plant material the disease level present (that is, the percentage leaf area, ear area or fruit surface area covered by actively sporulating disease) or percentage of infected plants, ears or fruit per pot or test unit was assessed visually. For each treatment, the assessed values for all replicates were meaned to provide mean disease values. Untreated control plants were assessed in the same manner. The data were then processed by the method described hereinafter, providing a PRCO (Percentage Reduction from Control) value.

METHOD

This method uses banded assessment values.

The mean disease values are banded in the manner shown below. If the disease level value falls exactly mid-way between two of the points, the result will be the lower of the two points.

0 =	0% disease present	10 =	5.1-10% disease present
1 =	0.1-1% disease present	20 =	10.1-20% disease present
3 =	1.1-3% disease present	30 =	20.1-30% disease present
5 =	3.1-5% disease present	60 =	30.1-60% disease present
		90 =	60.1-100% disease present

An example of a typical banded calculation is as follows:

Mean disease level for treatment A = 25%

Therefore banded mean disease level for treatment A = 30

Mean disease level on untreated controls = 85%

Therefore banded mean disease level on untreated controls = 90

$$\text{PRCO} = 100 - \left\{ \frac{\text{Banded mean disease level for treatment A}}{\text{Banded mean disease level on untreated controls}} \right\} \times 100$$

$$= 100 - \left(\frac{30}{90} \times 100 \right) = 66.7$$

The PRCO is then rounded to the nearest whole number; therefore, in this particular example, the PRCO result is 67.

Example results, derived as described above, are shown below.

TABLE 1: Tests on Whole Plants

COMPOUND	Test rate (ppm)	PLASVI	LEPTNO	PUCCRT
Amina® T100	300*	100	100	72
	100	100	100	95
	50	100	94	0
	25	100	98	0

Key to Table 1:

* 300ppm rate was evaluated in a separate test series

PLASVI = *Plasmopara viticola* PUCCRT = *Puccinia triticina*

LEPTNO = *Leptosphaeria nodorum*

TABLE 2: Tests in Liquid Media

COMPOUND	TEST RATE ppm	GIBBZE
Amina® T100	100	100
	25	100
	2.5	100

Key to Table 2:

GIBBZE = *Fusarium graminearum*

TABLE 3: Tests on Wheat Ears

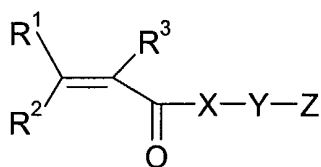
COMPOUND	TEST RATE ppm	GIBBZE
Amina® T100	1000	81
	300	81
	100	63
Limago® T100	1000	100

Key to Table 3:

GIBBZE = *Fusarium graminearum*

CLAIMS

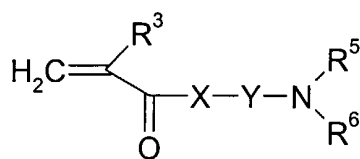
1. A method of combating phytopathogenic diseases on plants and harvested food crops which comprises applying to a plant, to the seed of a plant, to the locus of the plant or seed or to a harvested food crop a fungicidally effective amount of a fungicidal polymer obtained by the polymerization of a monomer of the general formula (1):



(1)

wherein X is O or NR⁴, Y is a C₁₋₅₀ substituted or unsubstituted aliphatic hydrocarbyl group, Z is H, NR⁵R⁶, N⁺R⁵R⁶R⁷A⁻ or SO₃R⁸, R¹ and R² are independently H or C₁₋₅ aliphatic hydrocarbyl groups, R³ is H or CH₃, R⁴, R⁵, R⁶ and R⁷ are independently H or substituted or unsubstituted C₁₋₅₀ aliphatic hydrocarbyl groups, R⁸ is H, an alkali metal atom, an alkaline earth metal atom, an ammonium or alkylammonium group or a C₁₋₅₀ substituted or unsubstituted aliphatic hydrocarbyl group and A⁻ is an anion.

- 15
2. A method according to claim 1 wherein the fungicidal polymer is obtained by the polymerization of a monomer of the general formula (2):

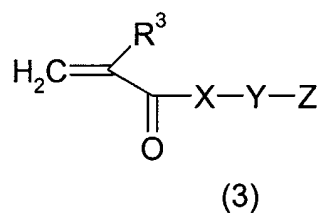


(2)

wherein X is O or NR⁴, Y is a C₁₋₅ aliphatic hydrocarbyl group, R³ is H or CH₃,
and R⁴, R⁵ and R⁶ are independently H or C₁₋₇ aliphatic hydrocarbyl groups.

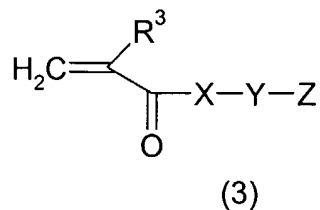
3. A method according to claim 2 wherein X is O, Y is C₁₋₃ alkylene, R³ is H or CH₃ and R⁵ and R⁶ are independently H or C₁₋₄ alkyl.
- 25 4. A method according to claim 2 wherein X is NH, Y is C₁₋₃ alkylene, R³ is H or CH₃ and R⁵ and R⁶ are independently H or C₁₋₄ alkyl.

5. A method according to claim 2 wherein the monomer of the formula (2) is selected from the group consisting of 2-(tert-butylamino)ethyl methacrylate, 2-(diethylamino)ethyl methacrylate, 2-(dimethylamino)methyl methacrylate, 2-(tert-butylamino)ethyl acrylate, 3-(dimethylamino)propyl acrylate, 2-(diethylamino)-ethyl acrylate, 2-(dimethylamino)ethyl acrylate, N-(3-dimethylaminopropyl)-methacrylamide, N-(3-diethylaminopropyl)methacrylamide, N-(3-dimethylaminopropyl)acrylamide are N-(3-diethylaminopropyl)acrylamide.
6. A method according to claim 2 wherein the fungicidal polymer is obtained by the copolymerization of a monomer of the formula (2) as defined in claim 2 with a monomer of the formula (3):



wherein X, Y and R³ have the meanings defined in claim 2 and Z is H.

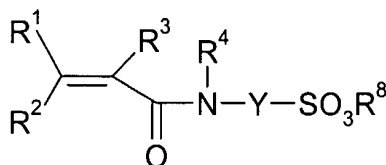
7. A method according to any one of claims 2 to 5 wherein the fungicidal polymer is blended with other polymers selected from the group consisting of polyurethanes, polyamides, polyesters and polyethers, polyether block amides, polystyrenes, polyvinyl chlorides, polycarbonates, polyorganosilanes, polyolefins, polysulfones, polyisoprenes, poly-chloroprenes, polytetrafluoroethylenes and polyterephthalate and copolymers thereof.
8. A method according to claim 1 wherein the fungicidal polymer is obtained by the copolymerization of a monomer of the formula (3):



wherein X is O or NH, Y is a C₁₋₅ branched or straight chain aliphatic hydrocarbyl group, Z is NR⁵R⁶ or N⁺R⁵R⁶R⁷A⁻, R³ and A⁻ have the meanings defined above and R⁵, R⁶ and R⁷ are independently H or a C₁₋₅ branched or straight chain aliphatic hydrocarbyl group; with at least one other aliphatic unsaturated monomer.

9. A method according to claim 8 wherein
- (a) X is O, Y is C₁₋₄ alkylene and Z is NR⁵R⁶ wherein R⁵ and R⁶ are independently H or C₁₋₄ alkyl; or
- 10 (b) X is NH, Y is C₁₋₄ alkylene and Z is NR⁵R⁶ wherein R⁵ and R⁶ are independently H or C₁₋₄ alkyl; or
- (c) X is O, Y is C₁₋₄ alkylene and Z is N⁺R⁵R⁶R⁷A⁻ wherein R⁵, R⁶ and R⁷ are independently H or C₁₋₄ alkyl and A⁻ is a halide anion or methosulphate; or
- (d) X is NH, Y is C₁₋₄ alkylene and Z is N⁺R⁵R⁶R⁷A⁻ wherein R⁵, R⁶ and R⁷ are
- 15 independently H or C₁₋₄ alkyl and A⁻ is a halide anion or methosulphate.
10. A method according to claim 8 wherein the other aliphatic unsaturated monomer or monomers used to form the copolymer with the monomer of the formula (3) is an acrylate, a methacrylate, styrene, vinyl chloride, vinyl ether, acrylamide,
- 20 acrylonitrile, an olefin, an allyl compound, vinyl ketone, vinyl acetic acid, vinyl acetate or a vinyl ester.

11. A method according to claim 1 wherein the fungicidal polymer is obtained by the polymerization of a monomer of the general formula (4):



(4)

wherein Y, R¹, R², R³ and R⁸ have the meanings defined above and R⁴ is H or a C₁₋₅ branched or straight chain aliphatic hydrocarbonyl group.

12. A method according to any one of the preceding claims wherein the fungicidal polymer is used in admixture with one or more other polymers selected from the group consisting of polyurethanes, PVCs, polyolefins, polysiloxanes, polystyrenes, polyacrylates, polymethacryates, polyamides and polyterephthalates.
- 5
13. A method according to any one of the preceding claims wherein the fungicidal polymer is used in admixture with one or more other compounds having biological activity.
- 10
14. A method according to claim 13 wherein the other compound is another fungicide.
15. A plant fungicidal composition that comprises a fungicidally effective amount of a polymer as defined in claim 1 and an agriculturally acceptable carrier.
- 15
16. A composition according to claim 15 which additionally comprises another active ingredient.
17. A composition according to claim 16 wherein the other active ingredient is a fungicidal compound.
- 20
18. The use of a polymer as defined in claim 1 for combating phytopathogenic diseases on plants and harvested food crops.

INTERNATIONAL SEARCH REPORT

national Application No

T/GB2004/003458

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 A01N41/04 A01N37/20 A01N37/12		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 A01N		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 331 528 A (SUMITOMO CHEMICAL CO) 6 September 1989 (1989-09-06)	1,2,4-6, 8-10, 13-18
Y	page 2, line 21 - page 6, line 25 page 6, line 52 - line 61 Reference examples 1-8 Preparation examples 1, 2 Test examples 1,3, 5 claims	3,7,11, 12
Y	WO 01/85813 A (KOSSMANN BEATE ; CREAVIS TECH & INNOVATION GMBH (DE); OTTERSBACK PETER) 15 November 2001 (2001-11-15)	3,7,12
X	page 1, paragraph 1 - paragraph 2 page 3, line 12 - page 5, line 19 page 10, line 28 - page 12, line 3; claims 1-12 ----- -/--	15
☒ Further documents are listed in the continuation of box C. ☒ Patent family members are listed in annex.		
° Special categories of cited documents :		
A document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *&* document member of the same patent family		
Date of the actual completion of the international search 29 November 2004		Date of mailing of the international search report 09/12/2004
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Muellners, W

INTERNATIONAL SEARCH REPORT

national Application No

T/GB2004/003458

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 01/72859 A (KOSSMANN BEATE ; CREAVIS TECH & INNOVATION GMBH (DE); OTTERSBAACH PETER) 4 October 2001 (2001-10-04)	11
X	page 1, line 3 - line 12 page 3, line 18 - page 5, line 15 page 10, line 3 - line 8 -----	15
X	DATABASE WPI Section Ch, Week 199046 Derwent Publications Ltd., London, GB; Class A18, AN 1990-345637 XP002307850 & JP 02 250803 A (SUMITOMO CHEM IND KK) 8 October 1990 (1990-10-08) abstract -& PATENT ABSTRACTS OF JAPAN vol. 0145, no. 71 (C-0790), 19 December 1990 (1990-12-19) -& JP 2 250803 A (SUMITOMO CHEM CO LTD), 8 October 1990 (1990-10-08) abstract -----	1-6, 8-10,15, 18
X	DE 24 46 449 A (HYDROPHILICS INT INC) 10 April 1975 (1975-04-10) page 1, paragraph 1 page 4, paragraph 2 page 4, last paragraph - page 5, paragraph 2; examples 1,5 page 13, last paragraph - page 14, paragraph 1; examples 10-17 -----	1-3,5,6, 8-10, 13-17
X	PATENT ABSTRACTS OF JAPAN vol. 0135, no. 46 (C-661), 6 December 1989 (1989-12-06) & JP 1 224301 A (HOKKO CHEM IND CO LTD), 7 September 1989 (1989-09-07) abstract -----	1,13-17
A	WO 01/18077 A (KOSSMANN BEATE ; SOSNA FRIEDRICH (DE); CREAVIS TECH & INNOVATION GMBH) 15 March 2001 (2001-03-15)	1-18
X	page 1, line 3 - line 11 page 2, line 18 - page 4, line 12 page 7, line 6 - line 32; claims 1,6,17,19-21 -----	15

INTERNATIONAL SEARCH REPORT

national Application No
T/GB2004/003458

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0331528	A	06-09-1989	EP 0331528 A1	06-09-1989
			JP 2036106 A	06-02-1990
			JP 2661241 B2	08-10-1997
			US 5208016 A	04-05-1993
WO 0185813	A	15-11-2001	DE 10022406 A1	15-11-2001
			AU 5623001 A	20-11-2001
			WO 0185813 A2	15-11-2001
WO 0172859	A	04-10-2001	DE 10014726 A1	27-09-2001
			AU 4062701 A	08-10-2001
			WO 0172859 A1	04-10-2001
			EP 1268580 A1	02-01-2003
JP 2250803	A	08-10-1990	NONE	
DE 2446449	A	10-04-1975	DE 2446449 A1	10-04-1975
			FR 2246572 A1	02-05-1975
			IL 45712 A	31-10-1977
			JP 50077496 A	24-06-1975
JP 1224301	A	07-09-1989	JP 2530201 B2	04-09-1996
WO 0118077	A	15-03-2001	DE 10022453 A1	15-03-2001
			AU 5826600 A	10-04-2001
			CA 2384531 A1	15-03-2001
			CN 1387542 T	25-12-2002
			WO 0118077 A1	15-03-2001
			EP 1218425 A1	03-07-2002
			JP 2003508604 T	04-03-2003
			NO 20021183 A	10-05-2002
			US 6790910 B1	14-09-2004