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(54) Title: ENHANCEMENT OF THE EFFICACY OF FUNGICIDES

(57) Abstract

Compounds from the group of mono- or polyunsaturated fatty acids with 10-24 C-atoms, their C_{1-4} alkylesters and the C_{1-4} alkyl esters of saturated C_{10-24} fatty acids enhance the curative efficacy and/or bioavailability of systemic fungicides; they can be incorporated into formulations of the fungicidal compounds or be added to spray mixtures (tank mix) as separately formulated additives in order to raise or improve the curative efficacy of the fungicides.

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ENHANCEMENT OF THE EFFICACY OF FUNGICIDES

BACKGROUND OF THE INVENTION

This invention concerns the enhancement of the efficacy and/or bioavailability of various systemic fungicidal compounds by addition of certain longer chain fatty acids and/or their lower alkyl esters, preparations through which this effect can be exploited as well as the combined use of the new additives and the fungicidal compounds in the control of phytopathogenic fungi.

The bioavailability is defined as the capability of a plant to take up active ingredients.

As a rule formulation ingredients must be used to bring crop protection agents, for example fungicidal compounds, into such a form that the user can apply them either as such or after dilution with water. The right choice of suitable formulation ingredients and carriers for the formulation often determines to a significant extent whether the active ingredient can display its full efficacy on application. The necessity to select suitable formulation ingredients means that not every active ingredient can be processed to any formulation without losses in efficacy having to be taken into account.

The efficacy of the active components can often be improved by addition of other (active) ingredients. The observed efficacy of the combination of ingredients can sometimes be significantly higher than that

would be expected from the amounts of the individual ingredients used (synergism).

The usual components of formulations such as carriers and formulation ingredients (e.g. organic solvents, suspension agents, emulgators, wetting agents, solubilizing agents) which do not themselves possess pesticidal activity, however, do not usually lead to an unexpected increase in efficacy.

In the case of the fungicidal compound dimethomorph, however, EP 520385 describes fungicidally inactive additives by means of which an unexpected enhancement of dimethomorph efficacy could be found in the experiments described.

These additives are alkoxylates of aliphatic alcohols, for example, of aliphatic alcohols with 8 to 20 C-atoms and, on average, 2 - 9 ethylene oxide units per molecule, with a terminal free or alkylated OH group. The enhancement in activity due to the described additives is, however, not always satisfactory. For example, under certain climatic conditions, phytotoxicity is observed.

In the US Patent 4,834,908, preparations ("Crop Oil Concentrates") are suggested or referred to which, as well as certain anionic surfactants containing an acidic group (also as salt) are characterised by their containing a long chain carbonic acid or a lower alkyl ester of the same as well as an aliphatic and/or aromatic hydrocarbon. These preparations are intended as additives to herbicides for post-emergence treatments. The patent does not contain any reference to the use of the preparations in connection with other crop protection agents, in particular not with fungicides.

The German patent application DE 33 09 765 teaches that the preventive fungicidal activity of triadimefon against *Puccinia* of cereals can be enhanced by the addition of linoleic acid.

The international patent application WO 92/19104 discloses a method for the curative control of fungal plant diseases by applying

fungicidal effective amounts of certain fatty acids or the derivatives thereof. Moreover, this international patent application suggests to add conventional fungicides, in order to achieve additional preventive protection of said plants.

However, there are no reports of fatty acids enhancing the curative activity and/or bioavailability of systemic fungicides.

SUMMARY OF THE INVENTION

The present invention relates to the use of mono- or polyunsaturated fatty acids with 10 - 24 C-atoms and/ or their C_{1-4} alkyl esters and/or the C_{1-4} alkyl esters of saturated C_{10-24} carbonic acids to enhance the curative activity of systemic fungicides

Furthermore, the additives used according to the present invention increase the bioavailability of the active ingredient(s) and thus improve the efficacy profile of the said fungicides in so far as they can be successfully applied, with normal application amounts, against such fungal diseases for the curative control of which they had previously been less suitable. Yet further, the use of the new additives makes it possible to process the fungicides to or use them as such formulations as had previously been looked upon as less satisfactory, for example the solid formulation of triforine.

Those and other objects and features of the invention will become more apparent from the detailed description set forth hereinbelow.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

It has now been found that, surprisingly, the effective amounts of systemic fungicides which must be applied can be lowered considerably with respect to the amounts usually required to achieve the same curative effect, if these fungicidal compounds or their formulations are applied in combination with certain unsaturated fatty acids and/or their lower alkyl esters and/or the lower alkyl esters of longer chain saturated fatty acids.

Moreover, it has been found that, surprisingly, the yields of crops which are infected by certain diseases, in particular caused by Oomycete fungi, can be increased by treating the infected plants with an effective amount of fungicidal composition in combination with certain unsaturated fatty acids and/or their lower alkyl esters and/or the lower alkyl esters of longer chain saturated fatty acids, in particular linoleic acid.

These additives are unsaturated fatty acids with 10 - 24, preferably 12 - 22 and in particular 14 - 20 C-atoms with 1 - 5 double bonds and/or C_{1-4} alkyl esters of the said unsaturated fatty acids or of saturated fatty acids with the same number of C-atoms. The aliphatic moieties of the said acids and esters may be straight or branched. Of particular interest are those unsaturated fatty acids, which are liquids at temperatures below 20°C such as linoleic acid, linolenic acid, arachidonic acid and oleic acid and their respective methyl, ethyl and propyl esters and of the esters of saturated fatty acids, mainly the methyl, ethyl and propyl esters of C_{14-22} carbonic acids. One or several of the acids and/or esters together can be used according to the invention. Linoleic acid (including technical material, which is a mixture consisting of about 70 % by weight of linoleic acid and about 30 % by weight of linolenic acid, as for example commercially available Edenor SB0.5) has been proved to be especially advantageous.

The enhancement in efficacy by addition of the said fatty acids and/or esters can, in particular, be observed for the fungicidal compounds dimethomorph, azoxystrobin, triforine, metalaxyl, cymoxanil, tebuconazol and triadimenol or compositions comprising at least one of these systemic

fungicides in combination with at least another systemic or non-systemic fungicidal compound.

Preferably any of said systemic fungicidal compounds is combined with at least one compound selected from mancozeb, fentinhydroxid, fluazinam, cymoxanil and propamocarb.

Most preferred is the combined use of linoleic acid with dimethomorph, in particular in combination with mancozeb, which is commercially available under the trademark ACROBAT® MZ or ACROBAT® PLUS, or triforine.

The fatty acids and fatty acid esters which are usable according to the invention can be included in the formulation or also added in a suitable form with the preparation of the spray mix (tank mix). In this latter case, they are added preferably as a separate preparation in a mixture with a dispersing agent and, where desirable, with further formulation ingredients so as to ensure that they are as evenly distributed as possible in the spray mix.

It is expedient to add an antioxidant to preparations containing unsaturated fatty acids or their esters so as to improve the storage stability. Preferred antioxidants are di-*tert*-butylhydroxytoluene (BHT), ascorbic acid 6-palitate, hydroquinone, butylhydroxyanisol (BHA), isoascorbic acid, sodium ascorbate and alkyl gallates, in particular BHT.

Therefore, the invention relates to a fungicidal formulations with at least one systemic fungicidal compound, formulation ingredients and/or carrier substances characterised by their containing, in addition to the conventional formulation ingredients and carriers, one or more compounds from the group of mono- or polyunsaturated fatty acids with 10-24 C-atoms, their C_{1-4} alkyl esters and the C_{1-4} alkylesters of C_{10-24} fatty acids and one or more antioxidants.

The appropriate relative amounts of antioxidant and unsaturated fatty acids lie, in accordance with the invention, between 1:2 and 1:1000,

preferably between 1:5 and 1:200 and, in particular, between 1:10 and 1:100.

The fungicidal compounds can be applied as normal commercial formulations with which the fatty acids and esters according to the invention, and where desirable, additional formulation ingredients such as antioxidants and emulgators, are mixed in. New formulations containing the fatty acids and esters can also be prepared.

Alkylphenoloxyethylates, alkyloxyalkylates (alkyloxyethylates) preferably ethopropoxylated tristyrylphenol are suitable emulgators or surfactants. Suitable products are available commercially, for example the SOPROPHOR product line. Under suitable conditions, alkoxylates in accordance with EP 520585 can also be used.

The appropriate relative amounts of active ingredient and unsaturated fatty acids lie, in accordance with the invention, between 5:1 and 1:100, preferably between 2:1 and 1:50 and, in particular, between 1:1 and 1:10. In general and within certain limits, the fungicidal efficacy can be enhanced to a higher degree by the addition of larger amounts of the fatty acids and/or esters as is shown in the experimental results described below.

The amounts of surfactants which, according to the invention, can be used in the formulations can be varied within a broad range. This lies in general between 2 and 20 percent by weight of the active ingredient-containing formulation and can rise to 60 percent by weight when the additives in accordance with the invention are formulated separately, for example, with the alkoxylates according to EP 520585 and formulation ingredients. In general, however, 2 to 30, preferably 3 to 20 percent by weight of surfactants are used for the separate formulations of the fatty acids and esters. In a preferred embodiment the additive, in particular linoleic acid, is added as a formulation comprising conventional formulation ingredients and an antioxidant to the tank mix together with a conventional, preferably commercially available, fungicide.

Therefore, the present invention relates to a kit for the preparation of a spray mixture comprising at least two separate containments:

(a) a containment which comprises at least one systemic fungicide, conventional formulation ingredients and carriers;

(b) a containment which comprises at least one compound selected from the group of mono- or polyunsaturated fatty acids with 10-24 C-atoms, their C_{1-4} alkyl esters and the C_{1-4} alkylesters of C_{10-24} fatty acids, in particular linoleic acid, and one or more antioxidants.

In a preferred embodiment the said kit consists of two bottles, which are preferably connected with each other, with dispensing means which allow the easy and correct addition of the active ingredient (a) and the additive (b) to the tank mix.

Another aspect of the invention is a pre-mixture for the enhancement of the curative efficacy of systemic fungicidal formulations which comprises one or more compounds from the group of mono- or polyunsaturated fatty acids with 10-24 C-atoms, their C_{1-4} alkylesters and the C_{1-4} alkyl esters of saturated C_{10-24} carbonic acids, in particular linoleic acid, one or more antioxidants and one or more surfactants as emulgators or dispersion agents and, where appropriate organic solvents.

Recommended doses for various applications are known for those fungicidal substances where the efficacy can be enhanced in accordance with the invention. Addition of the fatty acids and/or esters suggested here can (depending on the active ingredient, the fatty acids and/or ester and their amounts) reduce the amount of active ingredient per hectare required in these recommendations by one third or more. By using somewhat higher application doses, it is possible to treat other fungal diseases for the control of which the said fungicides without the new additives would not be suitable.

In a preferred embodiment linoleic acid in combination with the curative systemic fungicide is applied at rates of 100 to 3000 ml/ha, preferably 500 to 2000 ml/ha, in particular 700 to 1400 ml/ha.

An important advantage is the rapid onset and the high persistency of activity on use of the new additives. This enlarges the period for application of the fungicide making its use more versatile.

The fungicidal formulations according to the present invention can be used in combination with said additives and one ore more antioxidants prophylactically and curatively, preferably curatively.

The fatty acids and/or esters according to the invention, the fungicidal compounds, the antioxidant and usual formulation ingredients and carriers can be processed to the preferably fluid or dispersible solid formulations known in the art, for example, solutions, emulsions, WPs (wettable powders), suspension concentrates, emulsion concentrates, low volume or ultra low volume preparations and granulates.

As well as fluid and/or solid carriers or solubilising agents such as organic solvents like ketones, alcohols, fluid aliphatic, araliphatic or aromatic compounds, fine natural or synthetic silicates or carbonates, the preparations usually contain ionic and/or non-ionic surfactants which function as emulsifiers, disperging agents or wetting agents. Antifoam, and antifreeze agents may be added. Suitable adjuvant and carrier substances are described in the literature and well known to the persons skilled in the art.

Examples of formulations according to the invention:

1. Dimethomorph DC

dimethomorph	75g
linoleic acid	75g
di-tert.-butylhydroxytoluene	10g
SOPROPHOR FL	150g
benzyl alcohol	to 1000ml

2. Triforine EC

triforine (100% TM)	100g

linoleic acid	100g
di-tert.-butylhydroxytoluene	10g
dodecylbenzenesulfonic acid	206g
triethylamine	64g
isooctadecylalcohol	20g
Luviskol VA 55 I	20g
N-methylpyrrolidone	256g
dimethylformamide	to 1000ml

The formulation described above is mixed for use with water to give a spray mix having the desired concentration of active ingredient.

If the fatty acids and/or esters according to the invention are to be formulated separately (as additive for a tank mix) this can be carried out as in the following example:

Linoleic acid for tank mix

Recipe (A)

linoleic acid	100g
di-tert.-butylhydroxytoluene	10g
Emcol 4210	100g
solvent naphtha	to 1000ml

Recipe (B)

Soprophor 796/B	100 g
Edenor SB 0.5	to 1000 ml

In order to improve the stability of this formulation 10 g of di-tert.-butylhydroxytoluene are added to Recipe (B) as a rule.

It is also an object of the invention to suggest a method for the curative control of phytopathogenic fungi, preferably Oomycete fungi, in particular *Phytophtora infestans*, characterised by the use of systemic

fungicidal compounds, in particular, dimethomorph, triforine and metalaxyl in combination with one or more compounds selected from the group comprising mono- or polyunsaturated fatty acids with 10-24 C-atoms, their C_{1-4} alkyl esters and the C_{1-4} alkyl esters of saturated C_{10-24} fatty acids, in particular linoleic acid.

Examples of plant diseases which can be combated with the fungicidal formulations according to the present invention are the following: *Plasmopara viticola* (grape dawny mildew), *Phytophtora infestans* (potato late blight, tomato late blight), *Sphaerotheca fuliginea*, *Podosphaera leuctricha*, *Uromyces phaseoli*.

Another aspect of the invention is a method of increasing the yields of crops which are infected by diseases caused by fungi, preferably Oomycete fungi, in particular *Phytophtora infestans* which comprises treating the infected plants with an effective amount of fungicidal composition, in particular comprising dimethomorph and mancozeb, in combination with mono- or polyunsaturated fatty acids with 10-24 C-atoms, in particular with linoleic acid.

In a preferred embodiment the tuber and starch yields of potatoes which are infected by potato late blight can be increased with the aid of the method according to the present invention.

For a more clear understanding of the invention, specific examples are set forth below. These examples are merely illustrations and are not to be understood as limiting the scope and underlying principles of the invention in any way. Various modifications of the invention in addition to those shown and described herein will become apparent to those skilled in the art from the following examples and foregoing description. Such modifications are also intended to fall within the scope of the appended claims.

The test results described below demonstrate the enhancement in efficacy of various fungicidal substances by addition of certain fatty acids and esters.

Biological Investigations

A Spray treatment

Spray mixtures to which (with the exception of comparative tests) 500 ppm linoleic acid had been added were sprayed to just before run off onto the upper side of the leaves of various plant species. Forty eight hours after the treatment, the plants were inoculated with a fungal spore suspension (80,000 spores/ml) and incubated for 24 hrs at 22°C and 98% relative humidity.

Cucumbers and apples were inoculated with dry spores of *Sphaerotheca fuligenea* or *Podosphaera leucotricha* respectively. The infection was determined as % leaf area infected in comparison with the control.

1. *Plasmopara viticola* on Vines (Müller-Thurgau)
(Infection in % leaf area at active ingredient dose in ppm)

active ingredient	without linoleic acid			with 500 ppm linoleic acid		
	2.5ppm	10ppm	25ppm	2.5ppm	10ppm	25ppm
dimethomorph	76	61	18	39	3	0
cymoxanil	83	65	30	79	32	6
----- (control)	100	100	100	100	100	100

2. *Phytophthora infestans* on Tomatoes (Rheinlands Ruhm)
(Infection in % leaf area at active ingredient dose in ppm)

active ingredient	without linoleic acid			with 500ppm linoleic acid		
	2.5ppm	10ppm	25ppm	2.5ppm	10ppm	25ppm
dimethomorph	92	66	29	66	7	2
cymoxanil	96	83	43	79	51	15
----- (control)	100	100	100	100	100	100

3. *Sphaerotheca fuliginea* on Cucumbers (Hoffmanns Producta)

(Infection in % leaf area at active ingredient dose in ppm)

active ingredient	without linoleic acid			with 500ppm linoleic acid		
	5ppm	10ppm	20ppm	5ppm	10ppm	20ppm
triforine	96	82	66	95	59	33
----- (control)	100	100	100	100	100	100

4. *Podosphaera leucotricha* on Apples (Golden Delicious)

(Infection in % leaf area at active ingredient dose in ppm)

active ingredient	without linoleic acid			with 500ppm linoleic acid		
	5ppm	10ppm	20ppm	5ppm	10ppm	20ppm
triforine	93	79	53	91	40	2
triadimenol	83	65	30	79	32	6
----- (control)	100	100	100	100	100	100

5. Treatment of potato late blight

Curative activity of dimethomorph applied at different doses (g of a.i./ha) together with 1000g/ha of isopropylmyristate (a) or 1000g/ha of linoleic acid (b) plus emulsifier as additives. The plants were sprayed 2 days after inoculation. Percent infected leaf areas of plants 5 days after inoculation were as follows:

Additive	dimethomorph dose (g a. i./ha)					
	0	3.3	10	30	90	270
(control)	100	99	98	88	84	77
(a)	100	100	98	75	59	52
(b)	99	92	67	31	18	13

The following table shows the curative activity of various dimethomorph doses (g a.i./ha) in combination with different doses (g/ha) of linoleic acid. Plants were sprayed 2 days after inoculation. Percent of infected leaf areas of the plants 6 days after inoculation were as follows:

dose (g/ha) linoleic acid	dimethomorph dose (g a. i./ha)	
	0	270
0	71	46
100	---	35
300	---	27

1000	68	15

6. Effect of 200ppm a.i. of triforine in combination with 1000ppm of isopropyl myristate or 1000ppm of linoleic acid against cucumber powdery mildew. The compounds were applied the leaves, two days after inoculation.

Percent of infected leaf areas of the plants at 6 days after inoculation were as follows:

additive	without triforine	with triforine
isopropyl myristate	100	61
linoleic acid	100	49
without	100	84

7. Effect of fungicidal SC formulations with dimethomorph and propamocarb as active ingredients in tank mixed with linoleic acid formulated as described in Recipe B (500 g/ha) against potato late blight. The formulations were applied on the leaves, 5 days before inoculation. Percent of infected leaf areas of the plants at 11 days after treatment were as follows:

active ingredient	dose (g/ha)	infected leaf area (%)
dimethomorph + propamocarb	25 25	49
dimethomorph + propamocarb + linoleic acid	25 25 500	25
linoleic acid	500	91
control		100

8. Effect of fungicidal formulations comprising a SC formulation of dimethomorph and and a WP formulation of fentinhydroxid as active

ingredients tank mixed with linoleic acid formulated as described in Recipe B (500 g/ha) against potato late blight. The formulations were applied in a small band on the leaves, 5 days before inoculation. Percent of infected leaf areas of the plants at 11 and 15 days after treatment were as follows:

		11 days	15 days
active ingredient	dose (g/ha)	infected leaf area (%)	infected leaf area (%)
dimethomorph +	25 25	49	62
dimethomorph + fentinhydroxid + linoleic acid	25 25 500	22	50
linoleic acid	500	91	100
control		100	100

9. Effect of azoxystrobin as active ingredient applied as an SC formulation in combination with linoleic acid formulated as described in Recipe B (500 g/ha) against potato late blight. The formulations were applied on the leaves, 5 days before inoculation.
Percent of infected leaf areas of the plants at 11 and 15 days after treatment were as follows:

		11 days	15 days
active ingredient	dose (g/ha)	infected leaf area (%)	infected leaf area (%)
azoxystrobin	12.5	6	47
azoxystrobin + linoleic acid	12.5 500	7	17
azoxystrobin	50	2	7
azoxystrobin + linoleic acid	50 500	2	2
linoleic acid	500	91	100
control		100	100

B Systemic test

One drop containing 15 or 45 g active ingredient was applied to the base on the upper side of either grape or bean leaves. Linoleic acid had been added to the active ingredient at a 1:1 proportion (except in comparative experiments). The leaves were inoculated with a spore suspension (80,000 spores/ml) forty eight hours after the treatment and incubated for 24 hrs at 22°C or 98% relative humidity. Infection was determined as % infected leaf area in comparison to the control.

1. *Plasmopara viticola* on Vines (Müller-Thurgau)

(Infection in % leaf area)

active ingredient	without linoleic acid			with linoleic acid 15µg 45µg		
	15µg	45µg		15µg	45µg	
dimethomorph	83	68		43	6	
cymoxanil	88	70		52	18	
metalaxyl	70	49		39	10	
----- (control)	100	100		100	100	

2. *Uromyces phaseoli* on Beans (Saxa)

(Infection in % leaf area at active ingredient dose in g)

active ingredient	without linoleic acid			with linoleic acid 15µg 45µg		
	15µg	45µg		15µg	45µg	
triforine	80	64		45	16	
tebuconazol	64	33		51	11	
triadimenol	66	24		55	11	
----- (control)	100	100		100	100	

The following experiments were carried out as with experiments 1 and 2 above but with differences in the amounts of active ingredients and additives:

3. Effect of various unsaturated fatty acids together with triforine (45 g fatty acid and 45 g triforine). Systemic test against *Uromyces phaseoli* on beans (Saxa). Infection in percent leaf area.

fatty acid	triforine	infection
without	45µg	79
linoleic acid (45µg]	45µg	21
arachidonic acid (45µg)	45µg	26
control	-----	100

4. As 3 but with dimethomorph (45 g fatty acid and 45 g dimethomorph). Systemic test against Plasmopara viticola on Vines (Müller-Thurgau). Infection in percent leaf area.

fatty acid	dimethomorph	infection
without	45µg	70
linoleic acid (45µg)	45µg	10
arachidonic acid (45µg)	45µg	17
control	-----	100

5. Dose-dependence of the effect of linoleic acid exemplified as effect of triforine against *Uromyces phaseoli* on beans (Saxa). Systemic test. Infection in percent leaf area.

linoleic acid	triforine	infection
without	45µg	71
15µg	45µg	26
45µg	45µg	20

90µg	45µg	12
control	---	100

6. Dose-dependence of the effect of linoleic acid exemplified as effect of dimethomorph against *Plasmopara viticola* on Vines (Müller-Thurgau). Systemic test. Infection in percent leaf area.

linoleic acid	dimethomorph	infection
without	45µg	74
15µg	45µg	31
45µg	45µg	17
90µg	45µg	8
control	---	100

C Field Tests

1. *Phytophthora infestans* on Potatoes

ACROBAT® MZ is a commercially available WG formulation comprising 9 % by weight of dimethomorph and 60 % by weight of mancozeb. Potatoes of the varieties „Mentor" and „Ponto" are planted in the field. The treatment with the active ingredient (ACROBAT® MZ, ACROBAT® MZ + linoleic acid formulated as described in Recipe (B) or untreated control) was carried out 55, 67, 83, 96, 109 and 122 days after the planting date. The infection with phytophtora infestans was monitored by assessing the infected leaf area 109, 122 and 149 days after the planting date. The potatoes were harvested 171 days after the planting date. The results of these field tests are shown in the following tables:

Variety „Mentor"

		day 109	day 122	day 149	day 171	day 171
active ingredient	dose (g/ha)	infected leaf area (%)	infected leaf area (%)	infected leaf area (%)	Tuber yields (dt/ha)	Starch yields (dt/ha)

20

ACROBAT® MZ	2000	9	18	81	564	102.7
ACROBAT® MZ + Linoleic acid	2000 + 1000	6	11	73	603	112.1
control		28	96	100	394	63

Variety „Ponto"

		day 109	day 122	day 149	day 171	day 171
active ingredient	dose (g/ha)	infected leaf area (%)	infected leaf area (%)	infected leaf area (%)	Tuber yields (dt/ha)	Starch yields (dt/ha)
ACROBAT® MZ	2000	7	14	85	421	73.7
ACROBAT® MZ + Linoleic acid	2000 + 1000	6	10	70	473	82.7
control		20	87	100	278	43.4

2. *Phytophthora infestans* on Tomatoes

FORUM® is a commercially available DC formulation comprising 15 % by weight of dimethomorph. Tomatoes of the variety „Brigade" are planted in the field.The treatment with the active ingredient (FORUM®, FORUM® + linoleic acid formulated as described in Recipe (B) or untreated control) was carried out at different days (1st, 8th, 16th, 24th). The infection with phytophtora infestans was monitored by assessing the infected leaf area and the infected fruits at the 24th and 36th day after the first treatment. The results of these field tests are shown in the following table:

		day 24	day 36	day 24	day 36
active ingredient	dose (g/ha)	infected leaf area (%)	infected leaf area (%)	infected fruit (%)	infected fruit (%)
FORUM®	1250	11.7	14.7	0.3	0.3
FORUM® + Linoleic acid	750 + 1000	10.0	14.0	0.3	0.3
control		75	77	23	26

What is claimed is:

1. A method of use comprising mono- or polyunsaturated fatty acids with 10 - 24 C-atoms and/ or their C_{1-4} alkyl esters and/or the C_{1-4} alkyl esters of saturated C_{10-24} carbonic acids to enhance the curative activity and/or bioavailability of systemic fungicides.

2. The method of claim 1 wherein said fatty acids contain 12 - 22 C-atoms and the unsaturated fatty acids contain 1-5 double bonds.

3. The method of claim 1 wherein said unsaturated fatty acids are selected from the group comprising linoleic acid, linolenic acid, arachidonic acid and oleic acid.

4. The method of claim 1 wherein the ratio of fungicidal ingredient to said fatty acids and/or esters is between 5:1 and 1:100.

5. The method of claim 1 wherein the fatty acids/fatty acid esters are incorporated into a fungicide formulation consisting of at least one systemic fungicidal compound, one or more antioxidants, and adjuvant and carrier substances.

6. The method of claim 1 wherein the fatty acids/fatty acid esters or their formulations are added only when preparing the spray mixture (tank mix).

7. A composition comprising Fungicidal formulations with at least one systemic fungicidal compound, adjuvants an/or carrier substances characterised by their containing, in addition to the conventional adjuvants and carriers, one or more compounds from the group of mono- or polyunsaturated fatty acids with 10-24 C-atoms, their

C_{1-4} alkyl esters and the C_{1-4} alkylesters of C_{10-24} fatty acids and one or more antioxidants.

8. The composition of claim 7 comprising at least two different fungicidal compounds, at least one of which being a systemic fungicide.

9. The composition of claim 7 wherein the systemic fungicidal compound is selected from the group consisting of dimethomorph, cymoxanil, azoxystrobin, triforine or metalaxyl and the fatty acid linoleic acid, linolenic acid, arachidonic acid or oleic acid or a C_{1-3} alkyl ester of these acids or of a saturated C_{14-18} fatty acid.

10. The composition of claim 9 wherein the systemic fungicide is selected from the group consisting of dimethomorph, azoxystrobin, triforine and metalaxyl and at least one fungicidal compound selected from mancozeb, fentinhydroxid, fluazinam, cymoxanil and propamocarb.

11. The composition of claim 10 comprising dimethomorph and mancozeb.

12. The compositions of claim 7 wherein the relative proportion of active ingredient/unsaturated fatty acid is being 5:1 to 1:100.

13. A composition for the enhancement of the curative efficacy and/or bioavailability of systemic fungicidal formulations which comprises one or more compounds from the group of mono- or polyunsaturated fatty acids with 10-24 C-atoms, their C_{1-4} alkylesters and the C_{1-4} alkyl esters of saturated C_{10-24} carbonic acids, one or more antioxidants and one or more surfactants as emulgators or dispersion agents and, where appropriate organic solvents.

14. A method for the curative control of phytopathogenic fungi comprising the use of an effective amount of a systemic fungicidal compound, in particular dimethomorph, cymoxanil, azoxystrobin, triforine and metalaxyl, in combination with mono- or polyunsaturated fatty acids with 10-24 C-atoms, their C_{1-4} alkyl esters and/or the C_{1-4} alkyl esters of saturated C_{10-24} fatty acids.

15. A method according to claim 14 for the curative control of diseases caused by Oomycete fungi.

16. A method for increasing the yield of crops which are infected by fungal diseases comprising treating the infected plants with an effective amount of a fungicidal composition in combination with mono- or polyunsaturated fatty acids with 10-24 C-atoms.

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/US 97/07693

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A01N37/06 A01N37/02

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 6 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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 92 19104 A (MYCOGEN CORP.) 12 November 1992 cited in the application see claims 1,6,10,11 see page 5, line 23 - line 25 see page 11, line 17 see page 13, line 18 - line 25 ---	1-16
X	DE 33 09 765 A (BAYER AG) 20 September 1984 cited in the application see claims see page 4, paragraph 1 see page 8, line 15 --- -/--	1-16

[X] Further documents are listed in the continuation of box C.

[X] 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

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Date of the actual completion of the international search	Date of mailing of the international search report
17 September 1997	30 -09- 1997

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INTERNATIONAL SEARCH REPORT

Intern ıal Application No
PCT/US 97/07693

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	EP 0 729 700 A (ISAGRO) 4 September 1996 see claims see page 4, line 32 see page 4, line 51 - line 53 -----	1-16

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INTERNATIONAL SEARCH REPORT

...ormation on patent family members

Interna ·al Application No
PCT/US 97/07693

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		AU 673496 B	14-11-96
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