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(54) **TURFGRASS FUNGICIDE FORMULATION WITH PIGMENT**

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See application file for complete search history.

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(57) **ABSTRACT**

Oil-in-water fungicidal formulations are prepared having pigment dispersed therein, the pigment being stable within the oil-in-water emulsion as a result of the addition of suitable silicone surfactants and suitable emulsifiers. The formulations can be prepared either as a 2-pack formulation or as a single formulation. In the case of the single formulation polyethylene glycol is also added. In either case, the formulations show a synergistic effect through the addition of the pigment, the resulting formulations having an increased efficacy. Further, the formulations show a synergistic effect when mixed with conventional chemical fungicides, both being added in reduced amounts compared to recommended rates.

16 Claims, 17 Drawing Sheets

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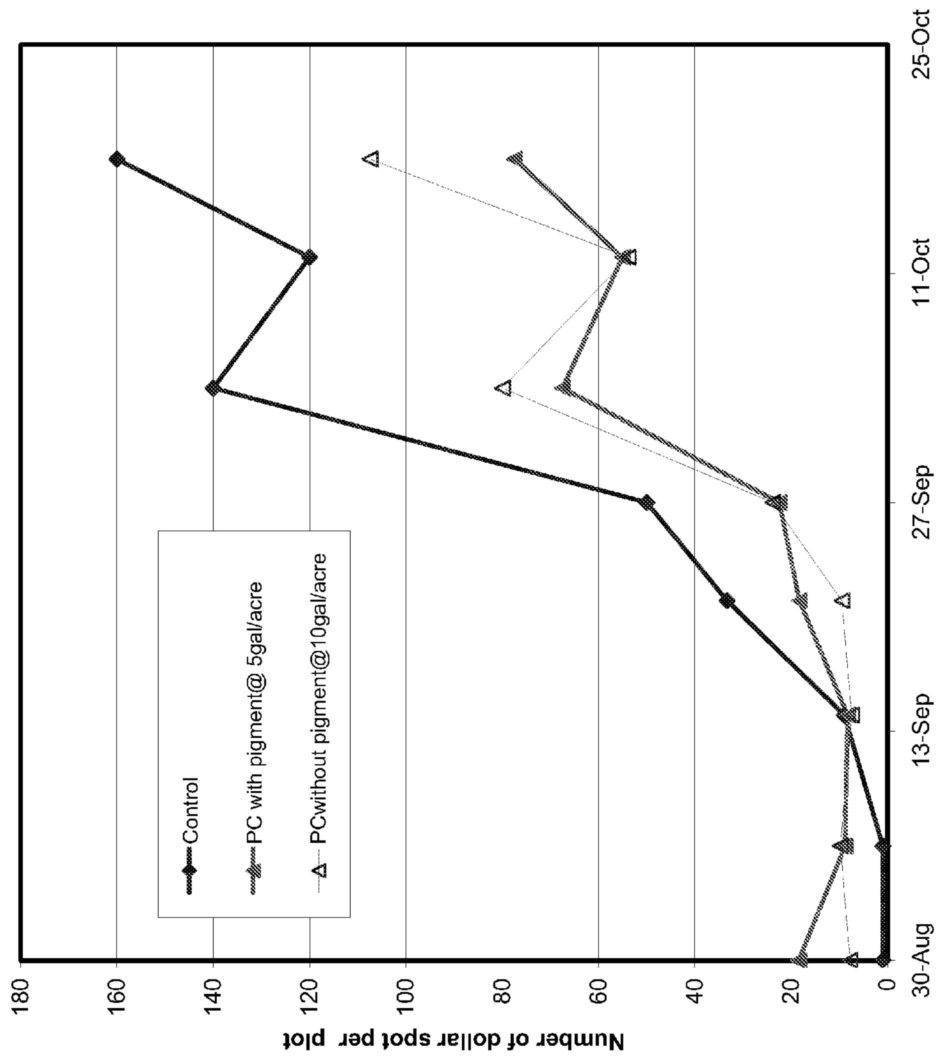
U.S. Appl. No. 15/074,919, filed Mar. 18, 2016.
Martin, "DMI (demethylation inhibitor) management strategy," Pesticide resistance: Prevention and management strategies 2005, pp. 21-25, 2005.

Fig. 1



Control
PC with pigment@ 5gal/acre
PCwithout pigment@10gal/acre
Number of dollar spot per plot
180
160
140
120
100
80
60
40
20
0
30-Aug
13-Sep
27-Sep
11-Oct
25-Oct

Fig. 2

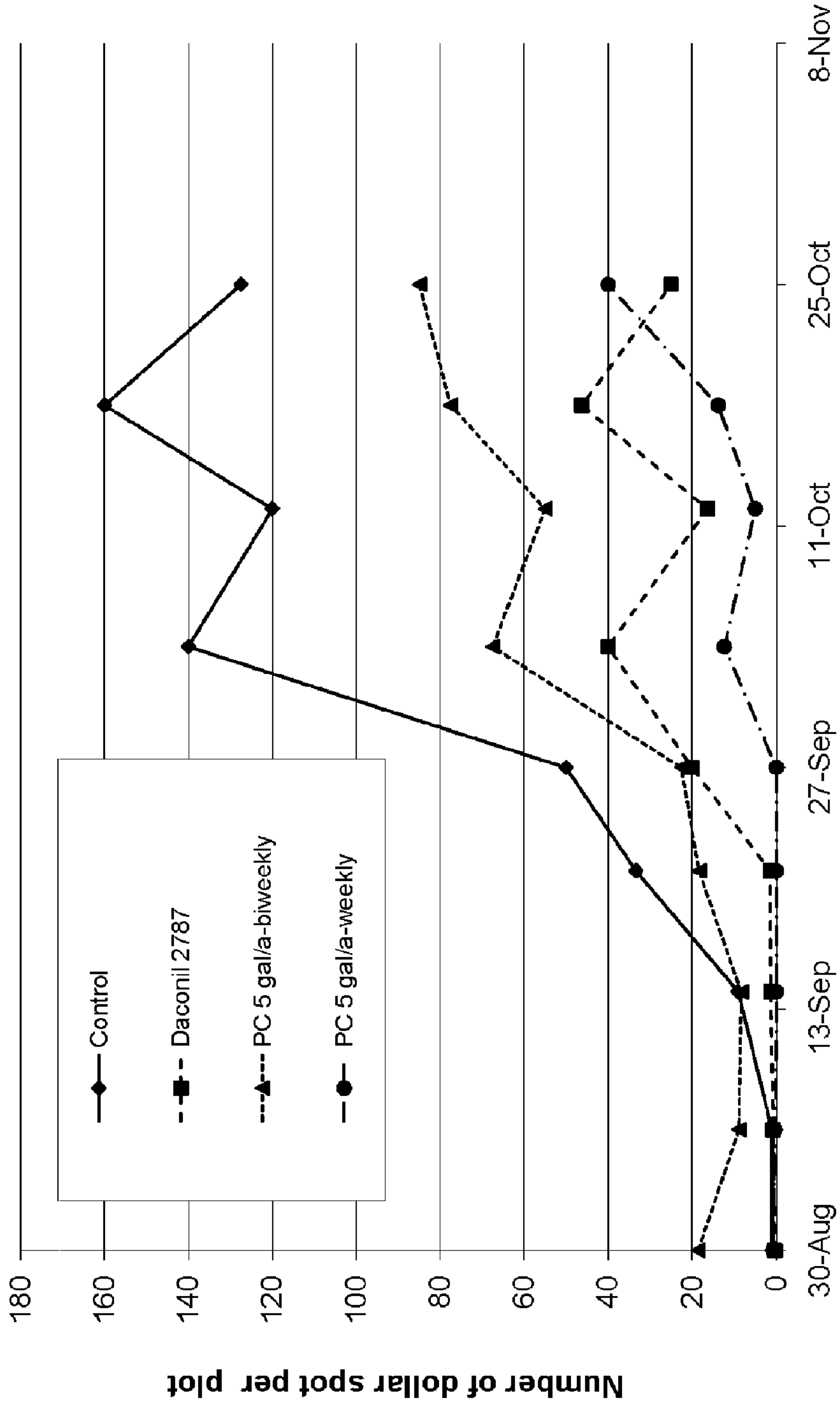

Control
Daconil 2787
PC 5 gal/a-biweekly
PC 5 gal/a-weekly
Number of dollar spot per plot
180
160
140
120
100
80
60
40
20
0
30-Aug
13-Sep
27-Sep
11-Oct
25-Oct
8-Nov

Fig. 3

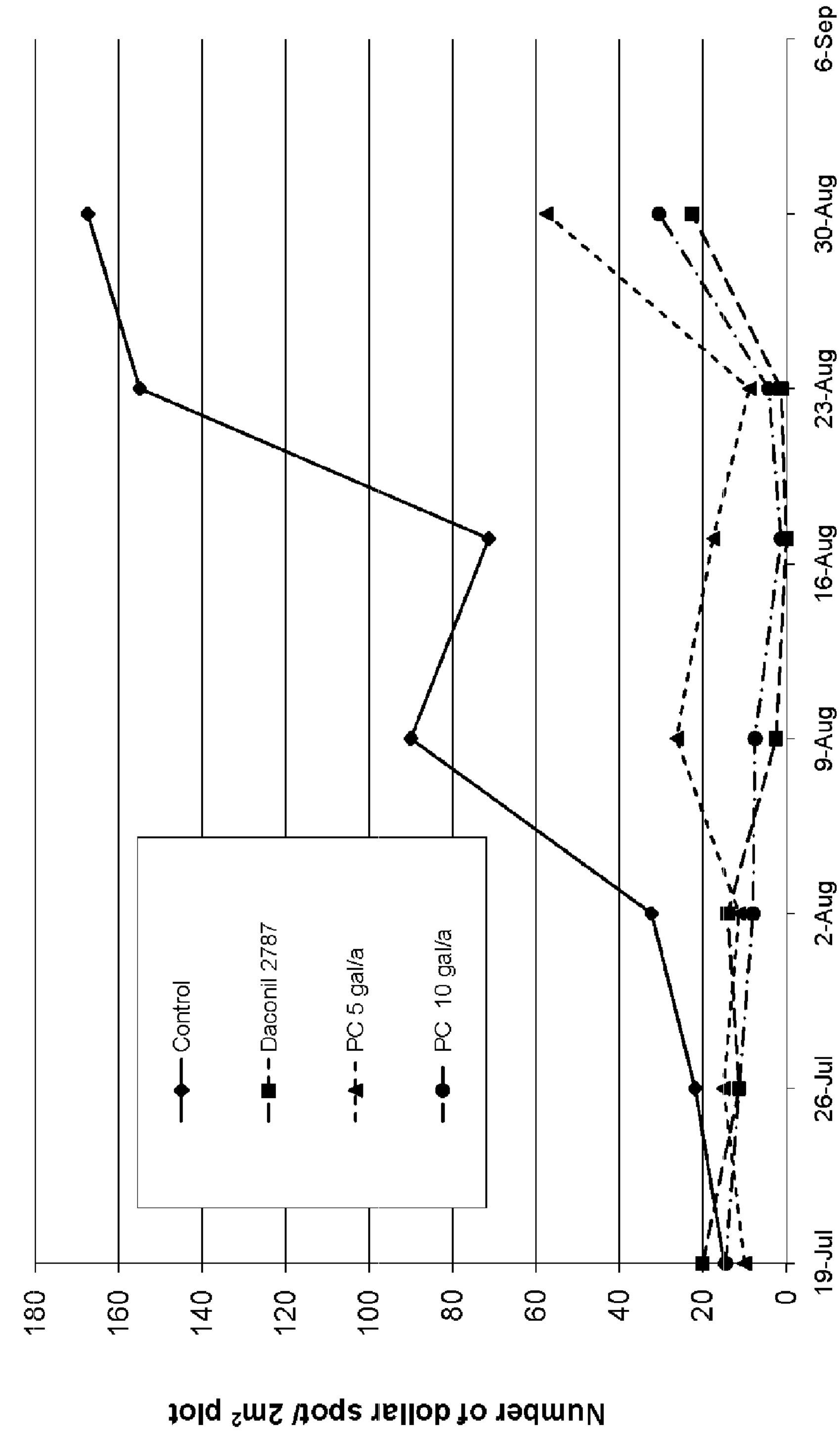

Number of dollar spot/ 2m² plot
180
160
140
120
100
80
60
40
20
0
19-Jul
26-Jul
2-Aug
9-Aug
16-Aug
23-Aug
30-Aug
6-Sep
Control
Daconil 2787
PC 5 gal/a
PC 10 gal/a

Fig. 4

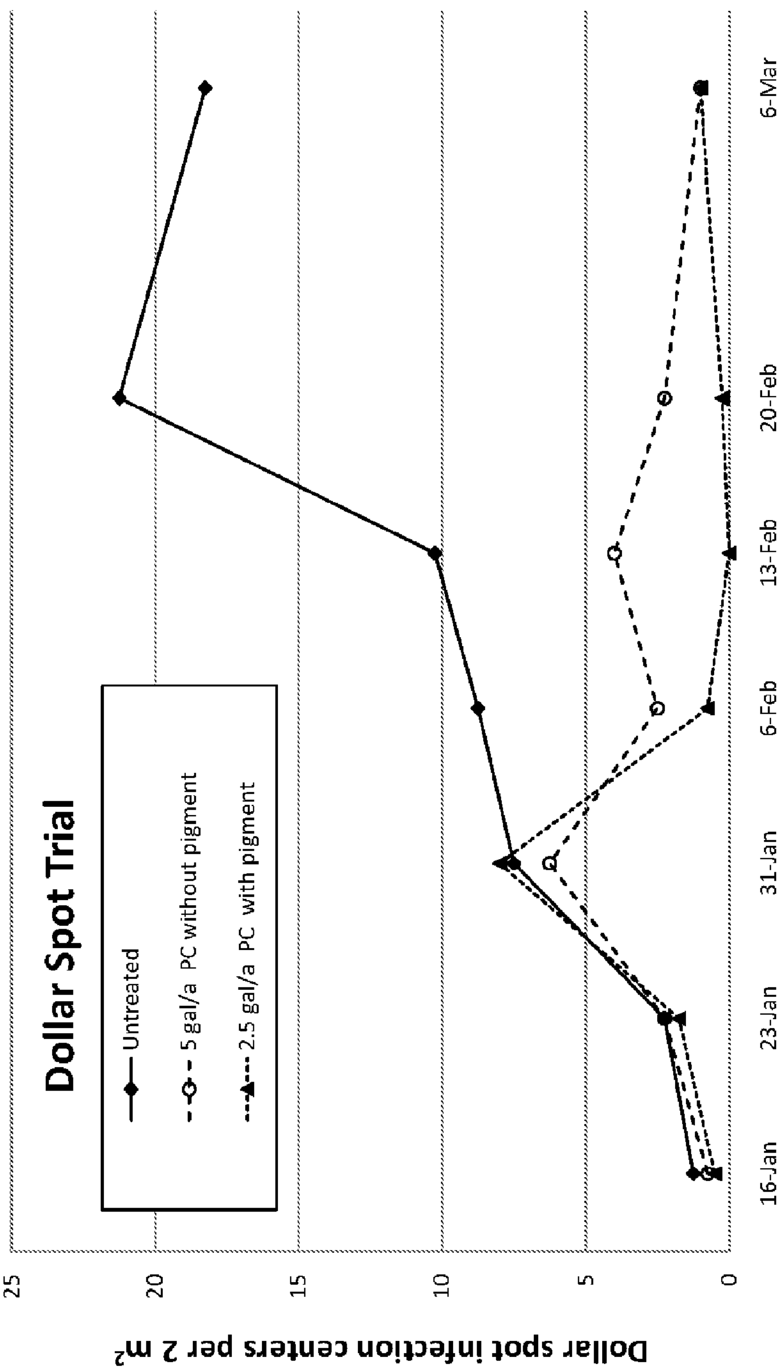
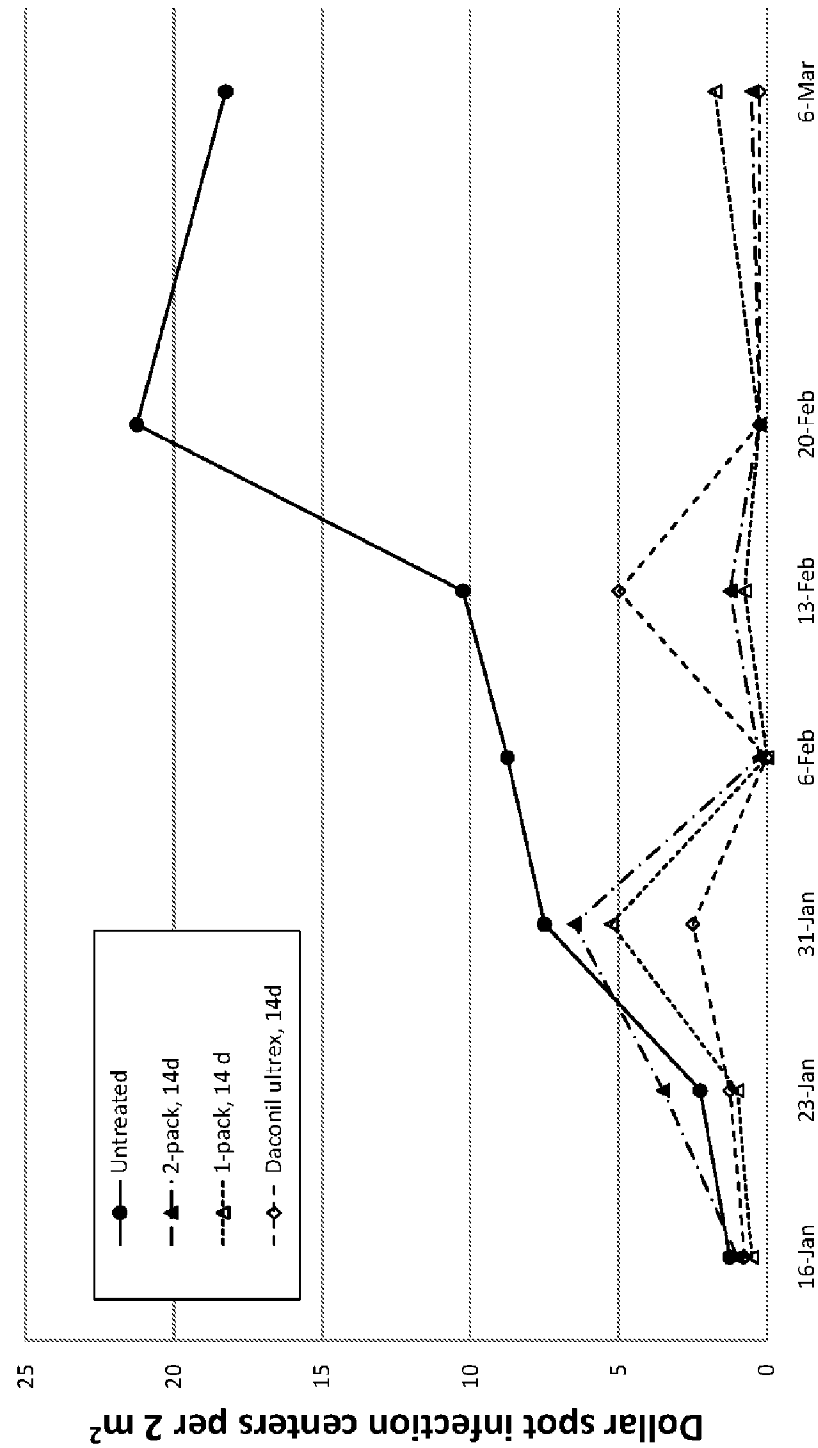

Dollar Spot Trial
Untreated
5 gal/a PC without pigment
2.5 gal/a PC with pigment
Dollar spot infection centers per 2 m2
0
5
10
15
20
25
16-Jan
23-Jan
31-Jan
6-Feb
13-Feb
20-Feb
6-Mar

Fig. 5



Dollar spot infection centers per 2 m²
0
5
10
15
20
25
16-Jan
23-Jan
31-Jan
6-Feb
13-Feb
20-Feb
6-Mar
Untreated
2-pack, 14d
1-pack, 14 d
Daconil ultrex, 14d

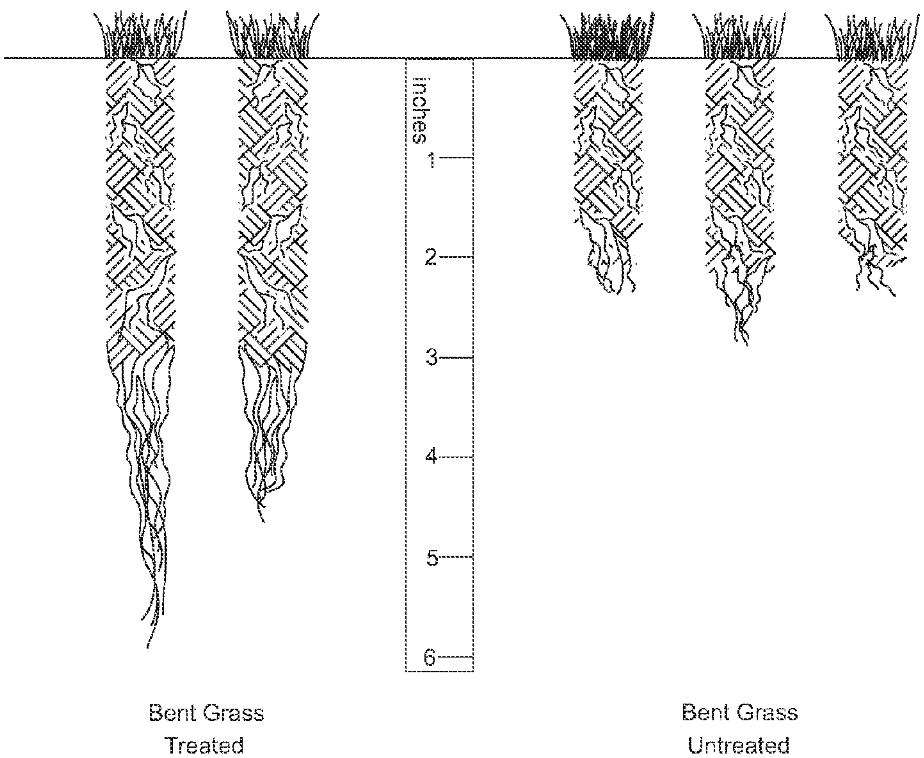


Fig. 6

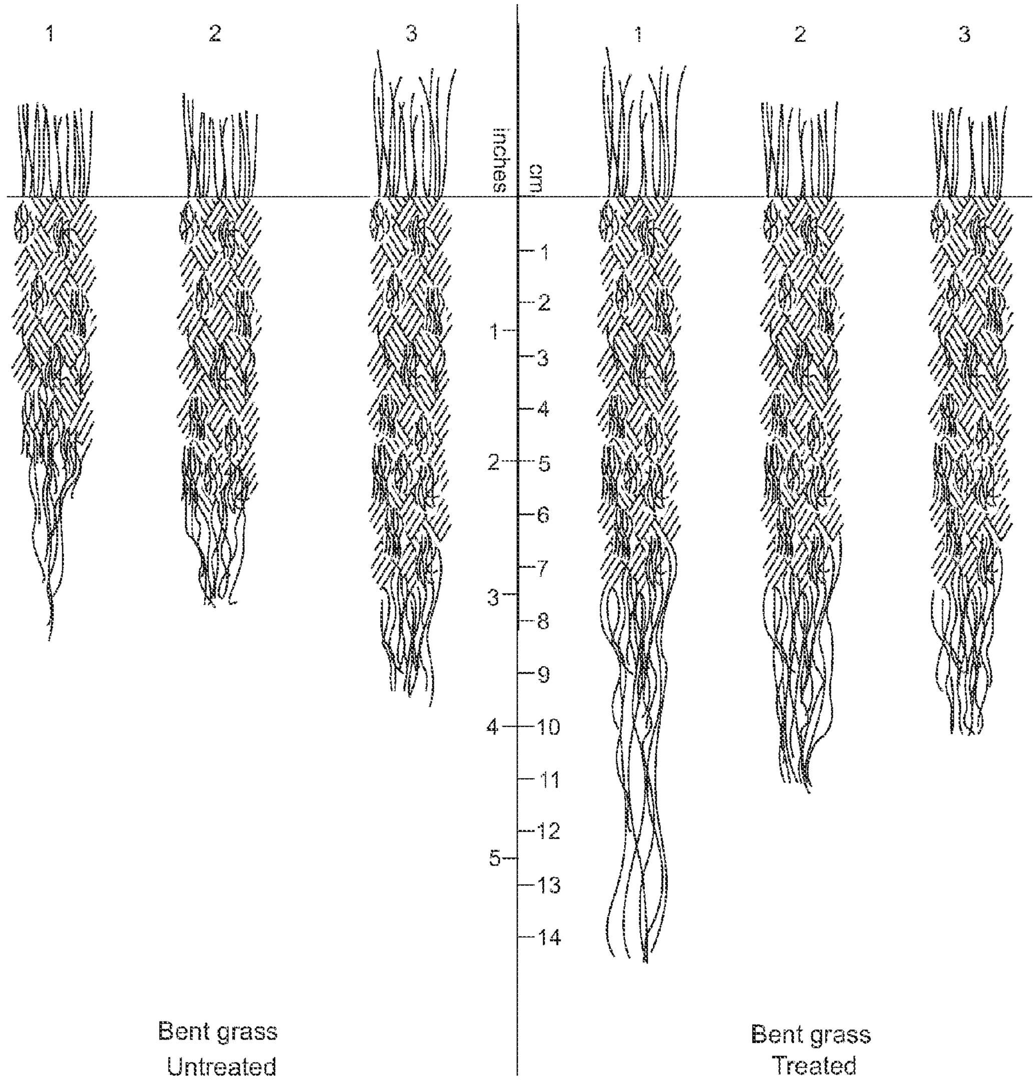

1
2
3
1
2
3
inches
cm
1
2
3
4
5
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Bent grass
Untreated
Bent grass
Treated

Fig. 7

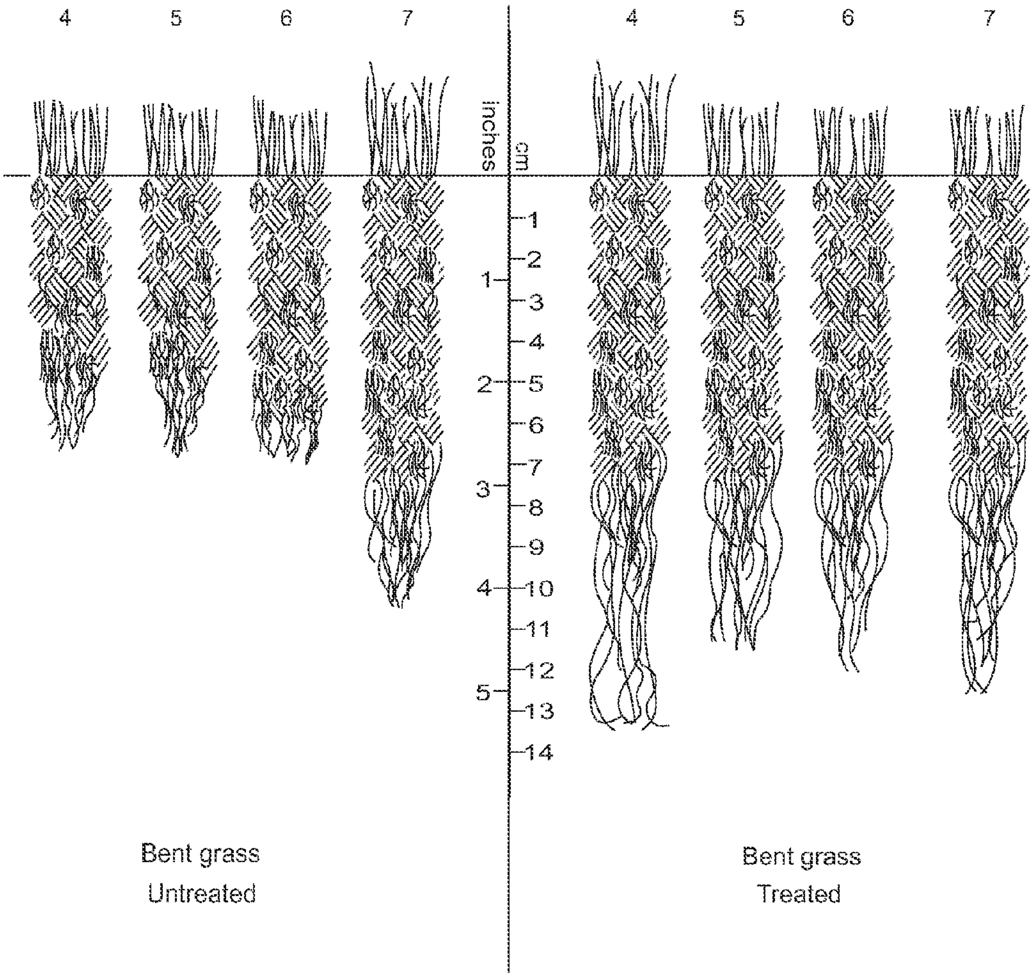

4
5
6
7
4
5
6
7
inches
cm
1
2
3
4
5
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Bent grass
Untreated
Bent grass
Treated

Fig. 8

Fig. 9A

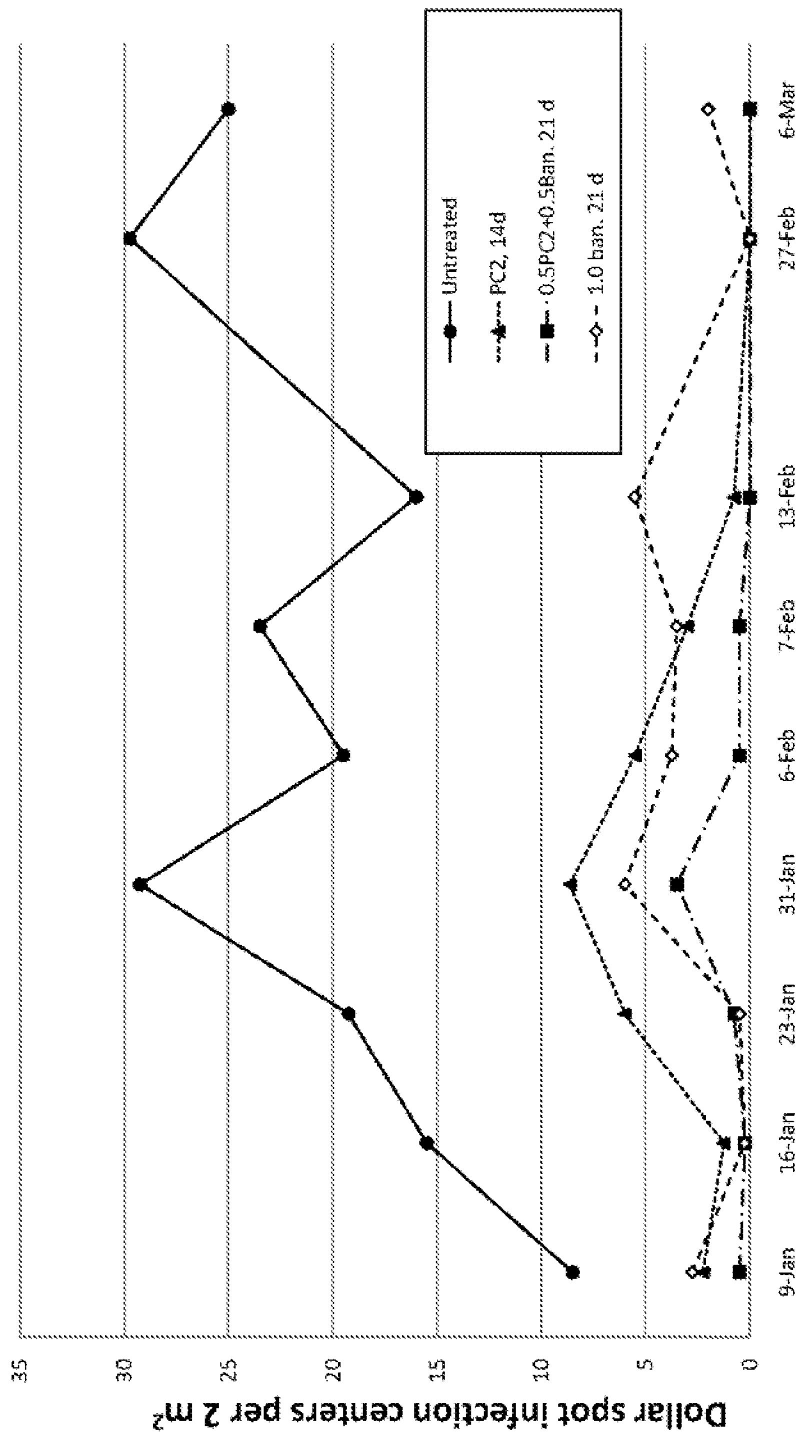

Untreated
PC2, 14d
0.5PC2+0.5Ban. 21 d
1.0 ban. 21 d
Dollar spot infection centers per 2 m²
0
5
10
15
20
25
30
35
9-Jan
16-Jan
23-Jan
31-Jan
6-Feb
7-Feb
13-Feb
27-Feb
6-Mar

Fig. 9B

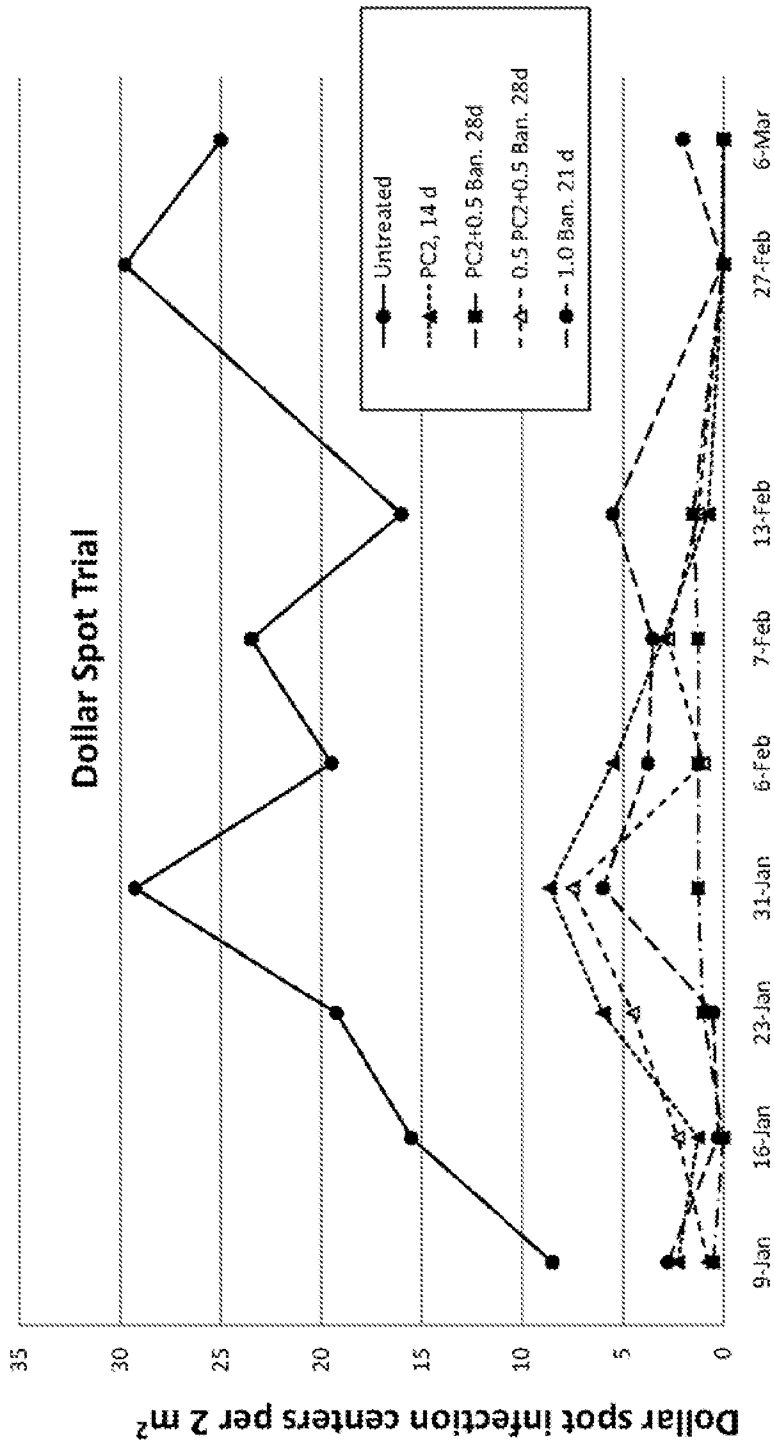

Dollar Spot Trial
Dollar spot infection centers per 2 m²
35
30
25
20
15
10
5
0
9-Jan
16-Jan
23-Jan
31-Jan
6-Feb
7-Feb
13-Feb
27-Feb
6-Mar
Untreated
PC2, 14 d
PC2+0.5 Ban. 28d
0.5 PC2+0.5 Ban. 28d
1.0 Ban. 21 d

Fig. 10

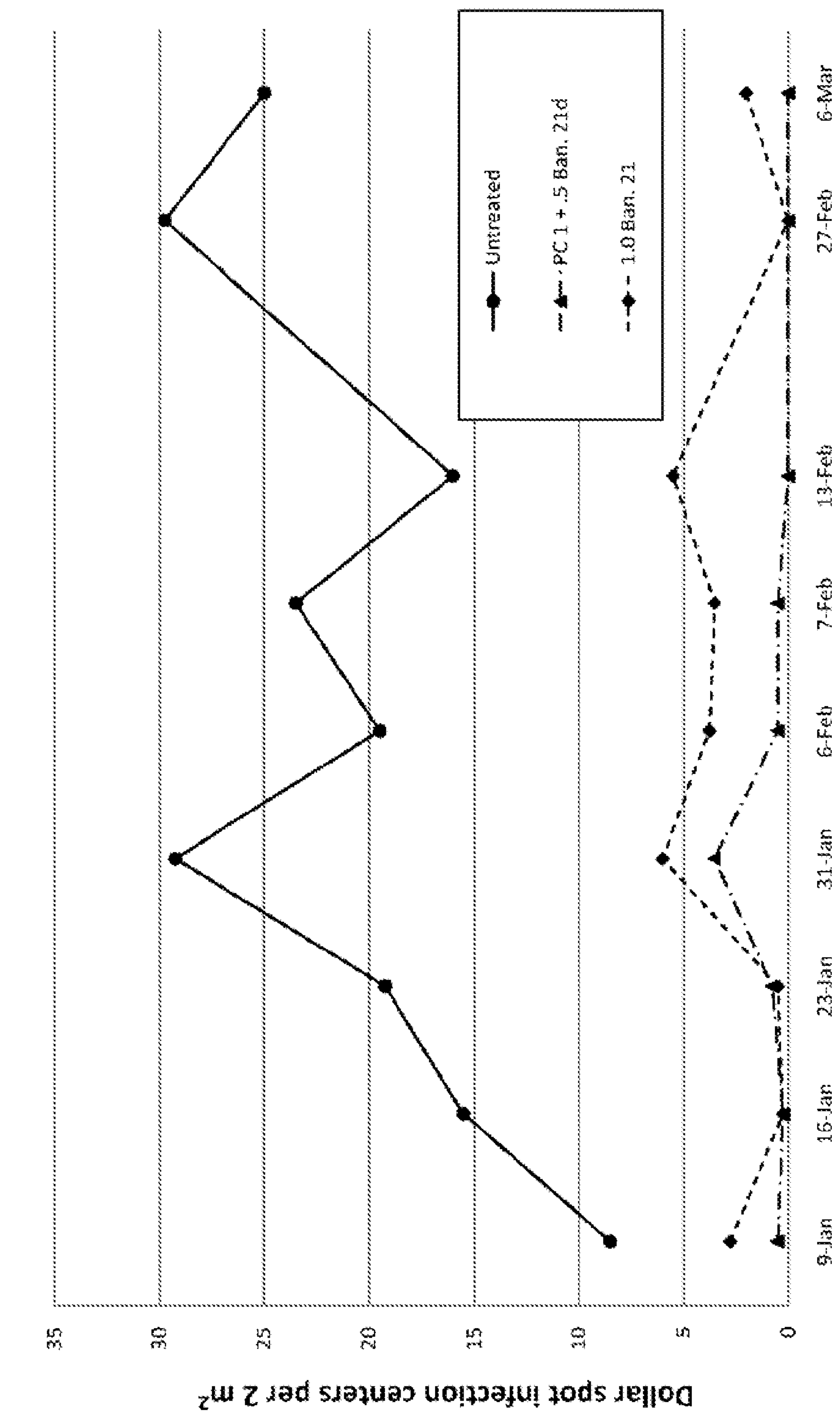

Dollar spot infection centers per 2 m²
0
5
10
15
20
25
30
35
9-Jan
16-Jan
23-Jan
31-Jan
6-Feb
7-Feb
13-Feb
27-Feb
6-Mar
Untreated
PC 1 + .5 Ban. 21d
1.0 Ban. 21

Fig. 11

Typhula ishikariensis plots

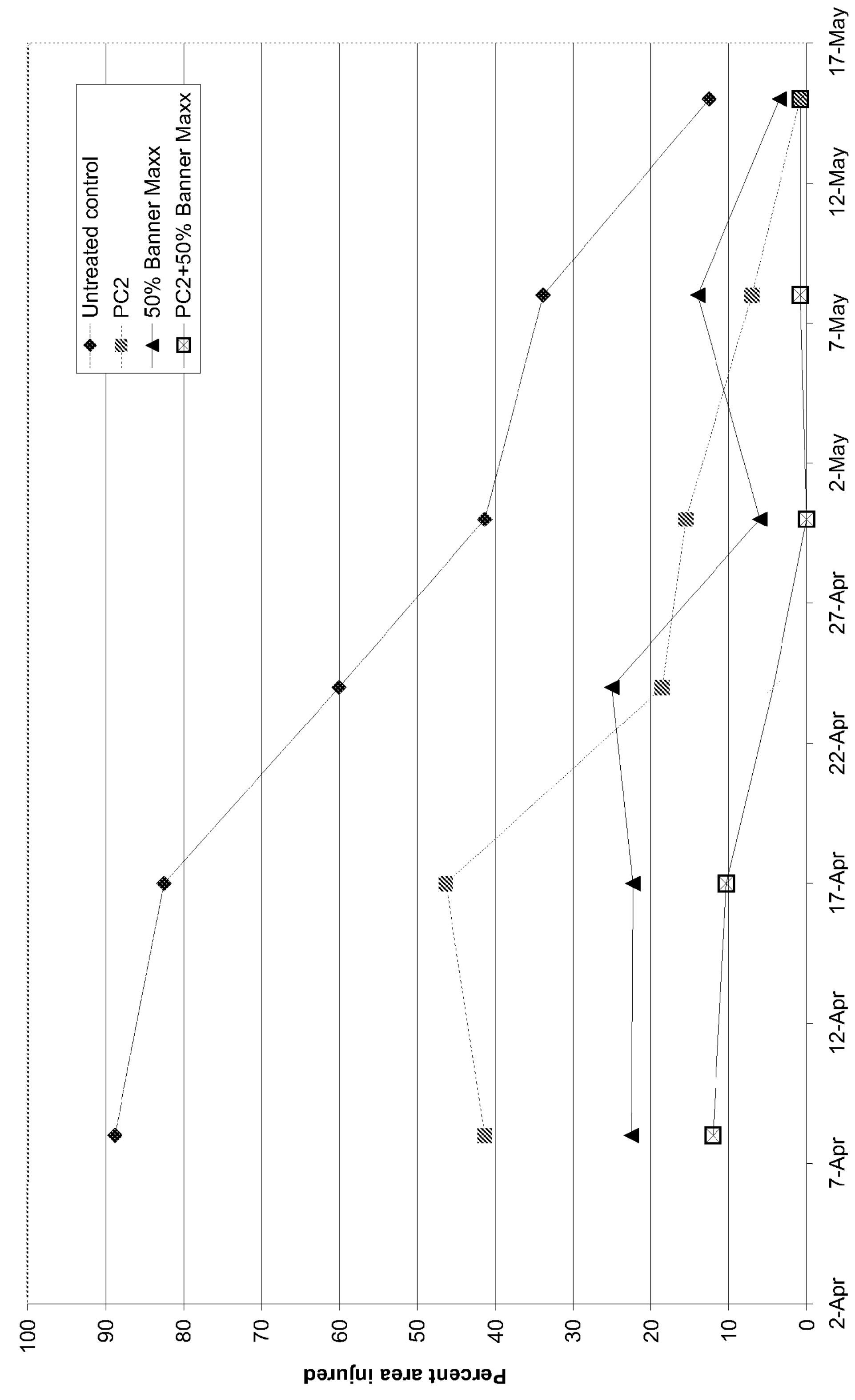


Fig. 12

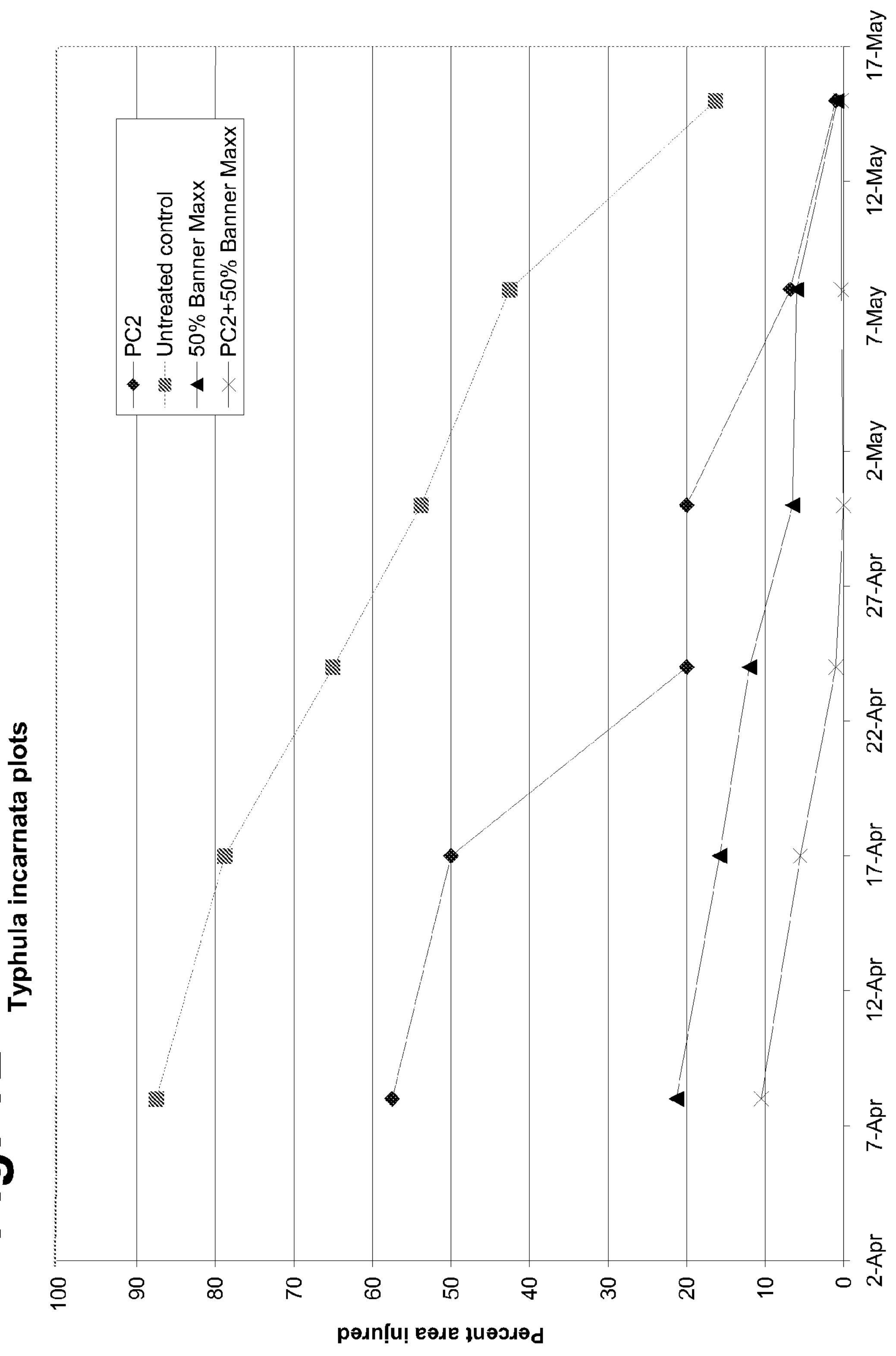

Typhula incarnata plots
PC2
Untreated control
50% Banner Maxx
PC2+50% Banner Maxx
Percent area injured
100
90
80
70
60
50
40
30
20
10
0
2-Apr
7-Apr
12-Apr
17-Apr
22-Apr
27-Apr
2-May
7-May
12-May
17-May

Fig. 13

Microdochium nivale plots

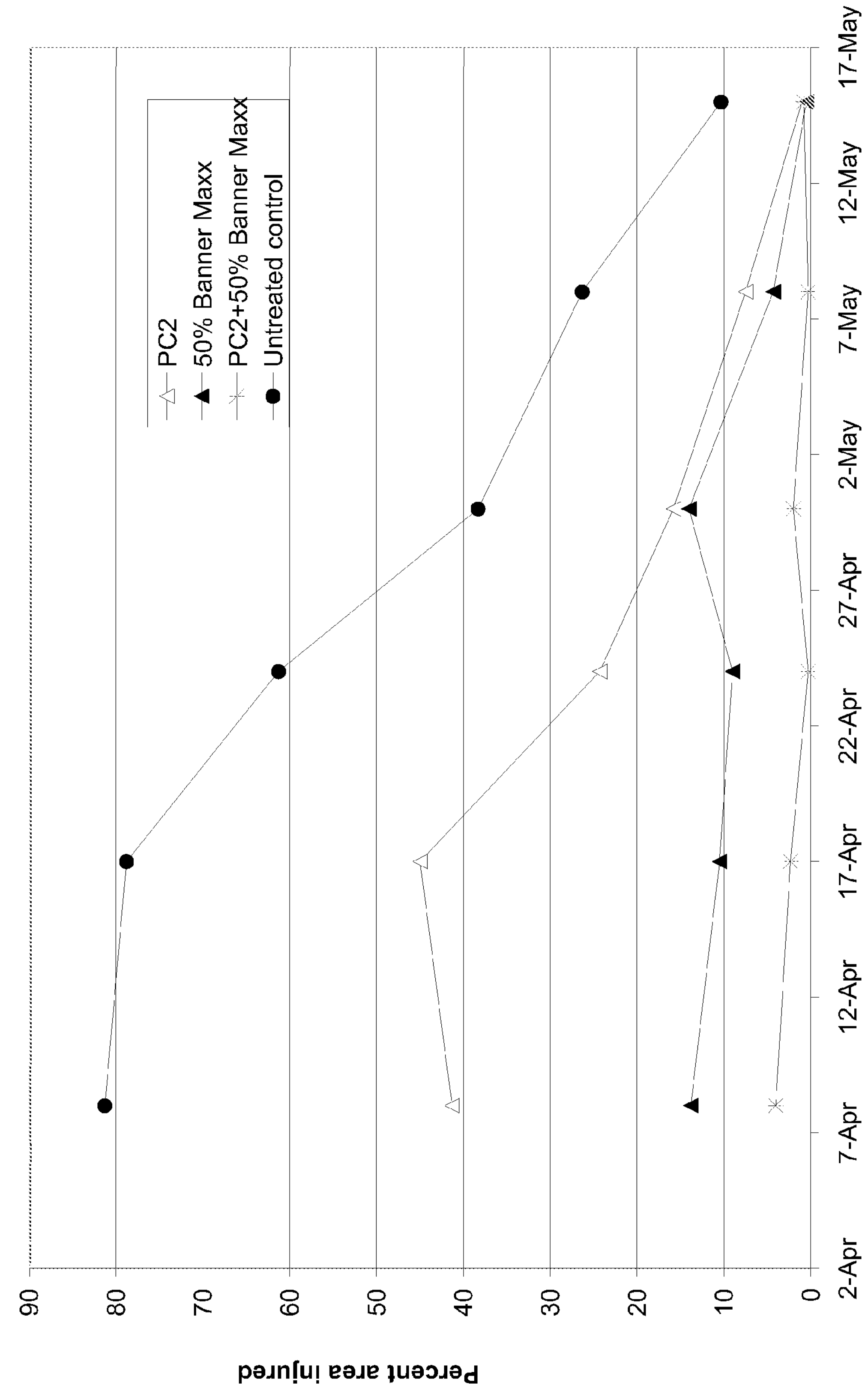


Fig. 14

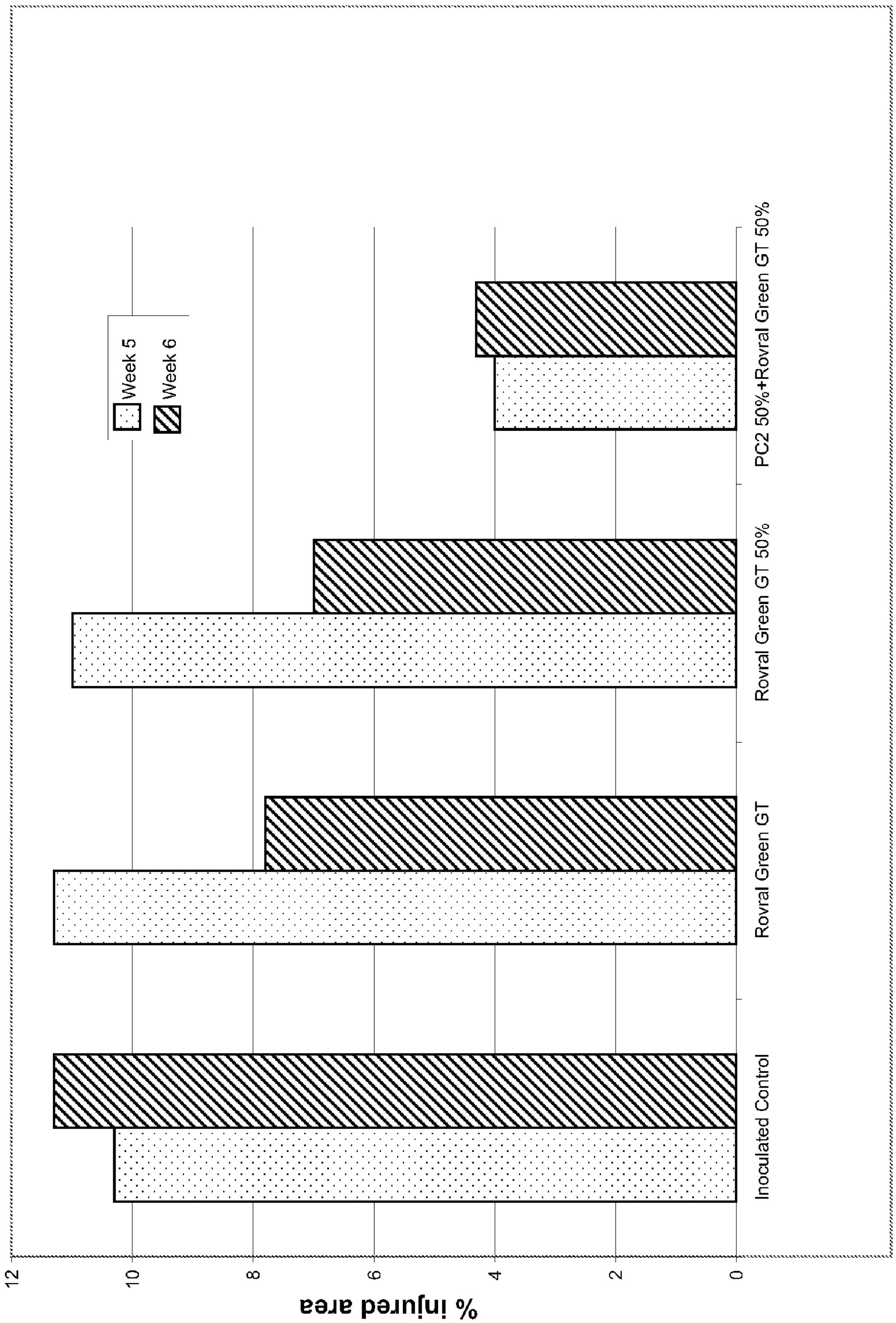

Week 5
Week 6
% injured area
0
2
4
6
8
10
12
Inoculated Control
Rovral Green GT
Rovral Green GT 50%
PC2 50%+Rovral Green GT 50%

Fig. 15

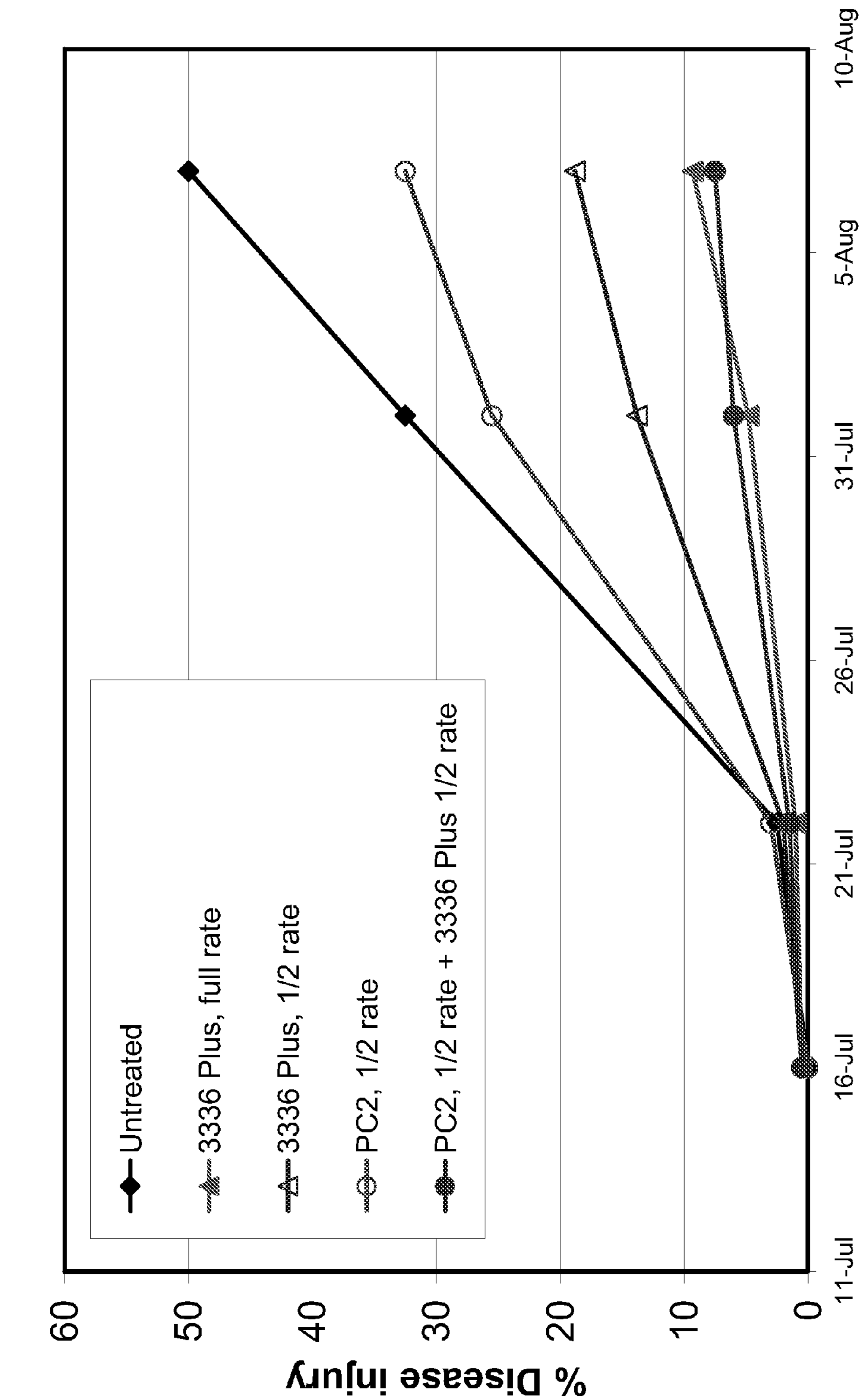
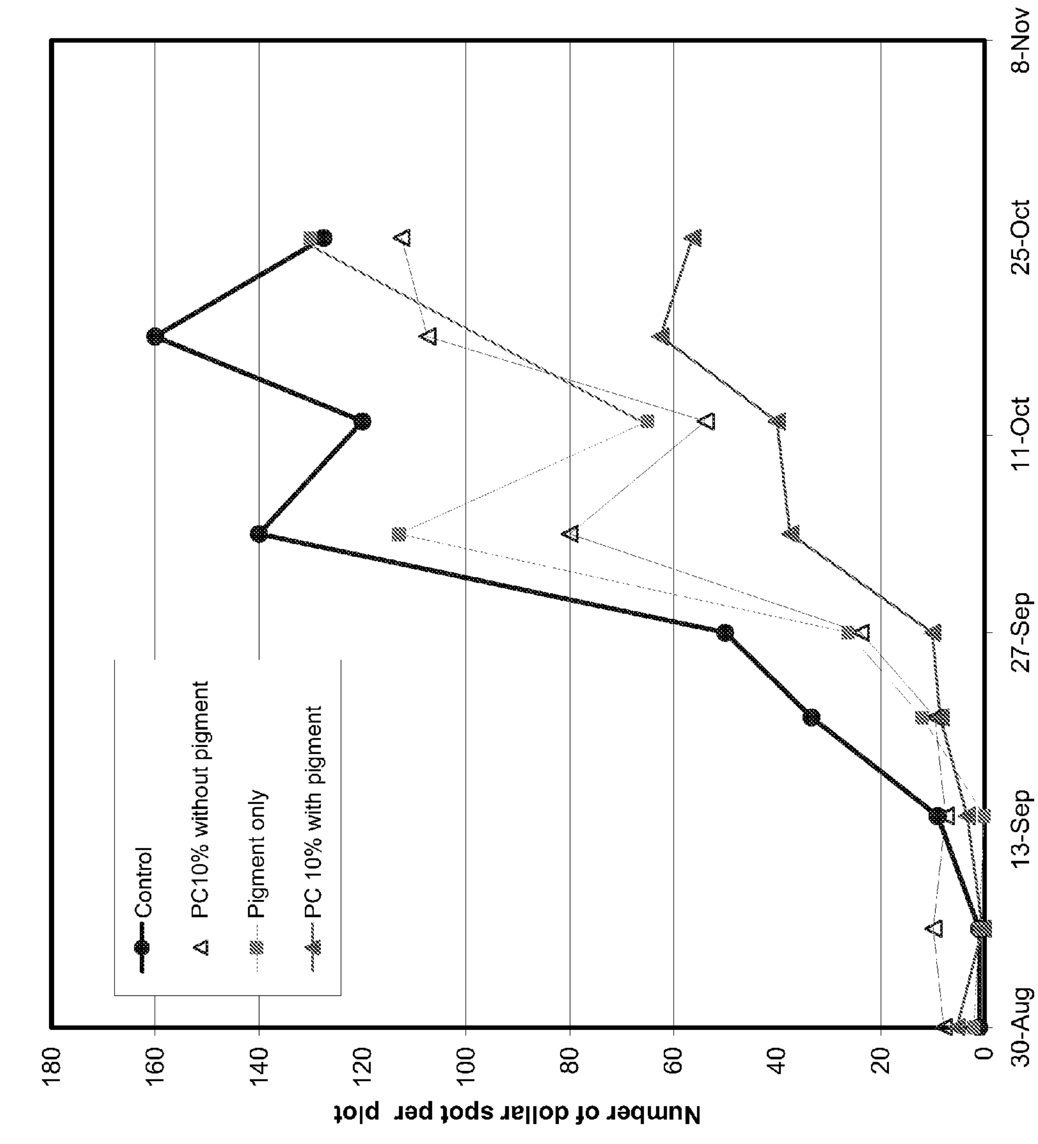

Untreated
3336 Plus, full rate
3336 Plus, 1/2 rate
PC2, 1/2 rate
PC2, 1/2 rate + 3336 Plus 1/2 rate
% Disease injury
60
50
40
30
20
10
0
11-Jul
16-Jul
21-Jul
26-Jul
31-Jul
5-Aug
10-Aug

Fig. 16



Number of dollar spot per plot
180
160
140
120
100
80
60
40
20
0
30-Aug
13-Sep
27-Sep
11-Oct
25-Oct
8-Nov
Control
PC10% without pigment
Pigment only
PC 10% with pigment

TURFGRASS FUNGICIDE FORMULATION WITH PIGMENT

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation of U.S. patent application Ser. No. 13/832,808, filed Mar. 15, 2013, which is a continuation of U.S. patent application Ser. No. 12/492,863, filed Jun. 26, 2009, which claims the benefit of U.S. Provisional Patent application Ser. No. 61/075,821, filed Jun. 26, 2008 and U.S. Provisional Patent application Ser. No. 61/147,523, filed Jan. 27, 2009, the entirety of each of the above-referenced applications are incorporated herein by reference.

FIELD OF THE INVENTION

Embodiments of the invention relate to oil-in water emulsions having fungicidal properties when applied to turfgrass and more particularly, to oil-in-water emulsions having stable dispersions of pigment therein for enhancing fungicidal activity and for imparting color to the turfgrass when applied thereon.

BACKGROUND OF THE INVENTION

In Applicant's previous applications, such as in co-pending US-2005-0261379-A1, the entirety of which is incorporated herein by reference, the Applicant has previously described the use of an oil-in-water emulsion as means of controlling turf diseases. A disadvantage may be that certain grasses such as varieties of bentgrass are sensitive to oil-in-water formulations which can often have the undesired effect of discolouring the grass especially under the heat of summer. Although the health of the plant is not negatively affected, the discolouration can be problematic from an aesthetic perspective.

Pigment colorants, such as phthalocyanine compounds, are known to have been used in the turf industry, both in the presence and the absence of fungicide. The known literature teaches the use of pigment color, such as non-chlorinated copper phthalocyanine as a means of colouring the grass or turf. One such example is US 2006/0293188 A1 to Norton (Bayer Cropscience LP), the entirety of which is incorporated herein by reference. Additional references include U.S. Pat. No. 5,336,661 to Lucas, U.S. Pat. No. 5,643,852 to Lucas and U.S. Pat. No. 5,599,804 to Mudge, the entirety of which are incorporated herein by reference.

Others references of interest include German application DE 2511077 published in 1978, which teaches cobalt phthalocyanine as a colourant in the absence of an acid. In an English abstract for JP 03-221576 to Nippon Chemical Works, published Sep. 30, 1991, the disclosed formulation uses phthalocyanine "green", an anionic dispersant, and acrylic acid ester-styrene and water.

Unfortunately, none of the teachings provide a solution for use of pigment in oil-in-water emulsion systems as Applicant has found that pigments, such as polychlorinated copper phthalocyanine, appear to clump or coagulate and thereafter quickly fall out of suspension rendering the formulation unworkable.

Clearly, there is a need to provide an oil-in-water fungicidal formulation which contains a dispersion of pigment or colorant therein in which the colorant remains stably dispersed for application to turfgrass.

SUMMARY OF THE INVENTION

Applicant has discovered that one can generate stable compositions of pigment in a high oil-in-water emulsion environment by the addition of a small amount of a silicone surfactant of a specific chemistry in combination with a small amount of an emulsifier of specific chemistry. The silicone surfactant and emulsifier are thought to act as dispersants for the pigment within the oil-based formulation, prior to dilution for forming the oil-in-water emulsion and in the final oil-in-water emulsion. Formulations according to embodiments of the invention have an enhanced efficacy in treating turfgrass disease.

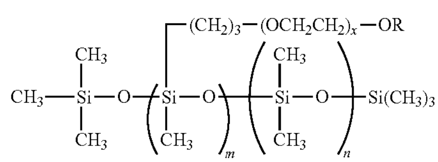
In addition, Applicant has found that the incorporation of a pigment dispersed into the oil-in-water emulsion disclosed herein has a synergistic impact and improves the overall efficacy of disease control of the active fungicidal components. At the same time, the amount of oil required to achieve adequate disease control can be reduced to about half the amount of oil compared to the amount required if the oil is used alone, thus further reducing the possibility of phytoxicity. Further, discolouration issues which may occur on certain grasses, such as varieties of bentgrass that are sensitive to oil-in-water formulations especially under the heat of summer, are overcome by formulations prepared according to embodiments of the invention.

In addition, Applicant has determined that embodiments of the present invention have an unexpected synergistic effect when mixed with conventional chemical fungicides such as demethylation inhibitors (such as propiconazole), methyl benzimidazole carbamate (such as thiophanate-methyl) and dicarboximide (such as iprodione). When mixed with formulations according to embodiments of the invention, the dosage of such conventional chemical fungicides can be reduced significantly, such as to about 50% the recommended label rates, as well permitting significant reduction in the required dosage of the formulations of the present invention.

Advantageously, the present invention also acts to suppress certain turf insects such as fall armyworms and sod webworms.

In a broad aspect of the invention, a fungicidal formulation for application to turfgrass comprises: an oil-in water emulsion comprising a paraffinic oil, a suitable emulsifier and water; polychlorinated (Cu II) phthalocyanine; and a silicone surfactant selected from the group consisting of trisiloxanes and silicone polyethers of Formula I

(Formula I)



where: R=H, CH_3 or $COCH_3$; x=1 to 24; n=0 or 1; m=1, wherein the polychlorinated (Cu II) phthalocyanine is maintained in dispersion in the oil-in-water emulsion for delivery to turgrass.

In another broad aspect, a method for preparing the fungicidal formulation comprises: preparing a first composition having the paraffinic oil; and the suitable emulsifier selected from the group consisting of natural and synthetic alcohol ethoxylates, including polyoxyethylene (4 to 12) lauryl ether (C_{12}), polyoxyethylene (10) cetyl ether (C_{16}), polyoxyethylene (10) stearyl ether (C_{18}), polyoxyethylene (10) oleyl ether (C_{18} monounsaturated), polyoxyethylene (2 to 11) C_{12}-C_{15} alcohols, polyoxyethylene (3 to 9) C_{11}-C_{14} alcohols, polyoxyethylene (9) C_{12}-C_{14} alcohols; polyoxyethylene (11) C_{16}-C_{18} alcohols, and polyoxyethylene (20) C_{12}-C_{15} alcohols; alcohol alkoxylates including butyl polyoxyethylene/polyoxypropylene block copolymer; alkyl polysaccharides including C_8-C_{11} alkylpolysaccharides; glycerol oleate; polyoxyethylene-polyoxypropylene block copolymers of MW 1100 to 11400 and 10 to 80% EO; nonyl phenol ethoxylates including polyoxyethylene (2 to 8) nonylphenol; polymeric surfactants including graft copolymer such as polymethacrylic acid and acrylate with polyoxyethylene chains and random copolymer with ester and ether group; polyethylene glycols including MW: 200 to 8000, MW: 400 PEG dioleate, and MW: 600 PEG dioleate; sorbitan fatty acid ester ethoxylates including polyoxyethylene (20) sorbitan tristearate, polyoxyethylene (20) sorbitan monooleate, polyoxyethylene (5) sorbitan monooleate, and polyoxyethylene (20) sorbitan trioleate; and mixtures thereof; preparing a second composition being and aqueous dispersion of the polychlorinated (Cu II) phthalocyanine; adding the silicone surfactant to one or both of the first and second compositions; and thereafter prior to use; and mixing an effective amount of the first composition with an effective amount of the second composition, the polychlorinated (Cu II) phthalocyanine being dispersed and stable therein.

In another broad aspect, a method for preparing the fungicidal formulation comprises: preparing a single composition having the paraffinic oil; the suitable emulsifier selected from the group consisting of natural or synthetic alcohol ethoxylates including polyoxyethylene (4 to 7) lauryl ether (C_{12}); polyoxyethylene (10) cetyl ether (C_{16}); polyoxyethylene (2 to 11) C_{12}-C_{15} alcohols; polyoxyethylene (3 to 9) C_{11}-C_{14} alcohols; polyoxyethylene (9) C_{12}-C_{14} alcohols; polymeric surfactants including graft copolymer such as polymethacrylic acid and acrylate with polyoxyethylene chains; and random copolymer with ester and ether group; sorbitan fatty acid esters including sorbitan tristearate; and sorbitan trioleate; and mixtures thereof; the polychlorinated (Cu II) phthalocyanine being dispersed in oil; and the silicone surfactant, wherein the silicone surfactant further comprises polyethylene glycols (PEG) according to Formula (IV):

$$R_1{-}O{-}(CH_2{-}CH_2{-}O)_n{-}R_2 \qquad \text{Formula (IV)}$$

where: R_1=H or CH_2=CH—CH_2 or $COCH_3$.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a graphical representation of the results of Example 7 showing a synergistic effect resulting from the addition of pigment to an oil-in-water fungicidal formulation prepared as a 2-pack formulation, permitting use of the formulation at rates lower than predicted rates when treating turfgrass infected with dollar spot disease;

FIG. **2** is a graphical representation of the results of Example 8 showing the efficacy of the 2-pack fungicide applied at 5 gal/acre (non-aqueous portion) compared to conventional chemical fungicide, DACONIL® 2787, applied at the same rate for treating turfgrass infected with Dollar Spot disease;

FIG. **3** is a graphical representation of the results of Example 9 showing the efficacy of the 2-pack fungicide, applied at both 5 gal/acre (non-aqueous portion) and 10 gal/acre (non-aqueous portion), compared to the chemical fungicide, DACONIL® 2787, for treating turfgrass infected with Dollar Spot disease;

FIG. **4** is a graphical representation of the results of Example 10 showing the efficacy of weekly use of 2.5 gal/acre (non-aqueous portion) of 2-pack fungicide compared to an oil-in-water formulation without the addition of the polychlorinated Cu (II) phthalocyanine pigment, emulsifier and silicone additives applied weekly at 5 gal/acre (non-aqueous portion);

FIG. **5** is a graphical representation of the results of Example 18 comparing the efficacy of the 2-pack formulation, a 1-pack formulation and convention chemical fungicide DACONIL® Ultrex for treating turgrass infected with Dollar Spot disease;

FIG. **6** is a picture of increased root length as a result of the application of a 2-Pack formulation prepared according to Example 6 when applied to a golf course fairway;

FIG. **7** is a picture of increased root length as a result of the application of a 2-Pack formulation, prepared according to Example 6, to areas of bentgrass;

FIG. **8** is a picture of increased root length as a result of the application of a 2-Pack formulation, prepared according to Example 6, to areas of bentgrass;

FIG. **9**A is a graphical representation of the results of Example 21 comparing the efficacy of a 2-pack formulation and a 2-pack formulation tank mixed at 50:50 with chemical fungicide BANNER MAXX™ for treating turf infected with Dollar Spot disease;

FIG. **9**B is a graphical representation of the results of Example 21 showing a synergistic effect of a 2-pack formulation tank mixed at 50:50 with chemical fungicide BANNER MAXX™ compared to the 2-pack formulation alone for treating turf infected with Dollar Spot disease, the residue period extending from 21 days to 28 days;

FIG. **10** is a graphical representation of the results of Example 22 showing a synergistic effect of a 1-pack formulation tank mixed 50:50 with chemical fungicide BANNER MAXX™ compared to the 1-pack formulation alone for treating turf infected with dollar spot disease;

FIG. **11** is a graphical representation of the results of Example 23 illustrating the effectiveness of a 2-pack formulation with 50% of the recommended label rate of BANNER MAXX™ compared to the 2-pack formulation alone, 50% of the recommended label rate of BANNER MAXX™ alone and an untreated control for treating turf infected with *Typhula ishikariensis;*

FIG. **12** is a graphical representation of the results of Example 24 illustrating the effectiveness of a 2-pack formulation with 50% of the recommended label rate of BANNER MAXX™ compared to the 2-pack formulation alone, 50% of the recommended label rate of BANNER MAXX™ alone and an untreated control for treating turf infected with *Typhula incarnate;*

FIG. **13** is a graphical representation of the results of Example 25 illustrating the effectiveness of a 2-pack formulation with 50% of the recommended label rate of BANNER MAXX™ compared to the 2-pack formulation alone, 50% of the recommended label rate of BANNER MAXX™ alone and an untreated control for treating turf infected with *Microdochium nivale;*

FIG. **14** is a graphical representation of the results of Example 26 comparing the efficacy of a 2-pack formulation enhanced with 50% of the recommended label rate of ROVRAL® Green GT to ROVRAL® Green GT at full label rate alone and ROVRAL® Green GT applied alone at 50% of the recommended label rate for the control of *Fusarium* Patch disease on bentgrass;

FIG. **15** is a graphical representation of the results of Example 27 comparing the efficacy of a 2-Pack formulation prepared according to Example 6 and applied at the full rate, conventional chemical fungicide Cleary 3336™ Plus at the full recommended label rate, the 2-pack formulation mixed 50:50 with Cleary 3336™ Plus, the 2-pack formulation alone at 50% of the recommended rate, and Cleary 3336™ Plus alone at 50% the recommended label rate, when applied to perennial ryegrass for control of Gray Leaf Spot disease; and

FIG. **16** is a graphical representation of the results of Example 28 illustrating a synergistic effect of the addition polychlorinated Cu(II) phthalocyanine when compared to oil/emulsifier alone and pigment alone, when compared to an untreated control.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Prior Art

Applicant has found that the addition of colorants or pigments, based upon the teachings in the prior art, to oil-in-water emulsion formulations resulted in unstable dispersions of the pigment therein.

In the following Examples 1 through 3, polychlorinated Cu(II) phthalocyanine pigment (available from Sun Chemical as SUNSPERSE® Green 7, ~60% polychlorinated Cu (II) phthalocyanine dispersed in water or as Pigment Green 7 powder available from Hercules Exports, Mumbai, India) was added to a synthetic isoparaffinic oil (N65DW available from Petro-Canada, Calgary, AB, Canada), with or without polyoxyethyene lauryl ether, C_{10} to C_{16} alcohol ethoxylates, and glycerol oleate as an emulsifier (available as PC Emuls Green, from Petro-Canada, Calgary, AB, Canada) and was diluted in water to form the oil-in-water emulsion suitable for application to turfgrass.

In each of Examples 1-3, the pigment coagulated or formed clumps which rapidly separated out and/or resulted in phase separation of the formulations. Thus, the pigment did not remain dispersed in the formulations and therefore the formulations were not usable to reliably and evenly impart color to turfgrass.

Example 1

a. 0.3 to 0.5 wt % polychlorinated Cu (II) phthalocyanine (SUNSPERSE® Green 7)
b. 10 wt % synthetic isoparaffinic oil (N65DW)
c. 89.5 wt % water

Example 2

a. 0.3-0.5 wt % polychlorinated CU (II) phthalocyanine (SUNSPERSE® Green 7)
b. 10 wt % isoparaffinic oil (N65DW)
c. 0.1 wt % emulsifier (PC Emuls Green)
d. 89.4 wt % water

Example 3

a. 0.5 wt % polychlorinated Cu (II) phthalocyanine (Pigment Green 7 powder)
b. 10 wt % isoparaffinic oil (N65DW)
c. 0.1 wt % emulsifier (PC Emuls Green)
d. 89.4 wt % water

Embodiments of the Invention

As shown in Example 4, Applicant has found that the incorporation of specific silicone surfactants and emulsifier dispersants added to an oil-in-water emulsion, having a significant portion of oil therein and containing pigment, results in the pigment being stably dispersed therein for application, such as by spraying, to turfgrass.

The non-aqueous portion of the oil-in-water portion is typically applied at rates from about 1 gal/acre (0.093 L/100 m^2) to about 15 gal/acre (1.395 L/100 m^2). The total spray volume of the oil-in-water emulsion is typically from about 20 gal/acre (1.9 L/100 m^2) to about 200 gal/acre (18.6 L/100 m^2).

Example 4

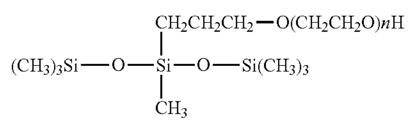
A formulation according to an embodiment of the invention was prepared as follows:

a. 0.5 wt % polychlorinated Cu (II) phthalocyanine (SUNSPERSE® Green 7)
b. 10 wt % isoparaffinic oil (N65DW)
c. 0.1 wt % emulsifier (PC Emuls Green)
d. 89.3 wt % water
e. 0.1 wt % silicone surfactant (Lambent MFF-199 SW)

An exemplary silicone super-wetting agent, such as Lambent MFF-199 SW (available from Lambent Technologies, a division of Petroferm, Inc., Gurnee, Ill., USA. MFF-199-SW) is a silicone copolyol, containing a hydrogen end group and one pendant polyethylene oxide group and has an average molecular weight between 600 to 1000 Daltons.

Lambent MFF-199 is a totally different class of silicone oil compared to common linear or cyclic polydimethylsiloxane. Lambent MFF-199 is a trisiloxane with an ethoxylated alkyl group having a hydrogen end group (H-End). The number of ethoxylation group is in the range of 1-20.

The suggested structure is as follows:



where: n=1-20 and average n=8

2-Pack Formulation

In an embodiment of the invention, a first composition (Pack A) is prepared containing the paraffinic oil and a suitable emulsifier. A second composition (Pack B) is prepared comprising a polychlorinated Cu (II) phthalocyanine. The polychlorinated Cu (II) phthalocyanine can be provided as a powder dispersed in water or as a ready to use aqueous dispersion. A silicone surfactant, such as Lambent MFF 159-100 or MFF 199 SW or other suitable silicone surfactant as described below can be added entirely to Pack A or to Pack B. Alternatively, the silicone surfactant can be split between Pack A and Pack B.

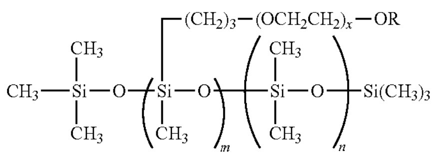
Immediately prior to use, an effective amount of each of Pack A and Pack B are mixed together to form the fungicidal dispersion which is further diluted in water to the desired concentration, as described below, for delivery to turfgrass at a predetermined dosage rate.

More particularly, in embodiments of the invention, the effective amount of Pack A is mixed with some or all of the water which would be required to obtain a desired concentration so as to form an emulsion. Thereafter, the effective amount of Pack B and any remaining water are added to the emulsion and the mixture is delivered to turfgrass as an oil-in-water emulsion at a predetermined dosage rate.

The silicone and emulsifier are selected to provide an intermolecular hydrophilic and lipophilic balance upon mixing of Pack A and Pack B so as to substantially prevent the polychlorinated Cu (II) phthalocyanine from clumping and rapidly separating out of suspension in the presence of the oil phase during application to the turfgrass.

Suitable silicone surfactants comprise trisiloxanes or silicone polyethers having a suitable alkoxy group with hydrogen end groups (H-capped), methyl end groups (CH_3 capped) or acetyl end groups ($COCH_3$ capped) according to the following formula (I):

(Formula I)



Where:

R═H; x=1 to 24; n=0; m=1; H-capped trisiloxane

R═H; x=1 to 24; n 1; m=1; H-capped silicone polyethers

R═CH_3; x=1 to 24; n=0; m=1; CH_3-capped trisiloxane

R═CH_3; x=1 to 24; n 1; m=1; CH_3-capped silicone polyethers

R═$COCH_3$; x=1 to 24; n=0; m=1; $COCH_3$-capped trisiloxane

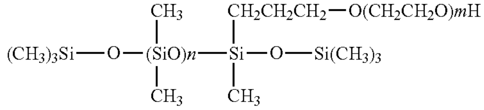
R═$COCH_3$; x=1 to 24; n 1; m=1; $COCH_3$-capped silicone polyethers

Commercial preparations of the silicone surfactants above may or may not contain small amounts of polyethylene glycols (PEG) or other low molecular weight polydimethyl siloxanes (PDMS).

In embodiments of the invention, silicone surfactant is added in a range of about 0.1 wt % to about 5 wt % in the non-aqueous portion of the oil-in-water emulsion.

In an embodiment of the invention, the silicone surfactant, added in an amount of about 2 wt % in the non-aqueous portion of the oil-in-water emulsion, is an H-capped dimethyl methyl (polyethylene oxide) silicone polymer having a molecular weight from 200-6000 as shown below in Formula (II):

Formula (II)



where: n=2-70, the average n=44; m=2-16 and the average m=10.

Suitable emulsifiers are selected and added in amounts so as to generate a stable emulsion and to prevent phytotoxicity. The emulsifier is added in a range from about 0.5 wt % to about 5 wt % in the non-aqueous portion of the oil-in-water emulsion. More particularly, in embodiments of the invention, the emulsifier is added in a range from about 1 wt % to about 3 wt % in the non-aqueous portion of the oil-in-water emulsion. In an embodiment of the invention, the emulsifier is added at about 2 wt % in non-aqueous portion of the oil-in-water emulsion.

The emulsifier is selected from the group consisting of:

Alcohol ethoxylates (natural and synthetic) including polyoxyethylene(4 to 12) lauryl ether (C12); polyoxyethylene (10) cetyl ether (C16); polyoxyethylene (10) stearyl ether (C18); polyoxyethylene (10) oleyl ether (C18 monounsaturated); polyoxyethylene (2 to 11) C12-C15 alcohols; polyoxyethylene (3 to 9) C11-014 alcohols; polyoxyethylene (9) C12-C14 alcohols; polyoxyethylene (11) C16-C18 alcohols; and polyoxyethylene (20) C12-C15 alcohols;

Alcohol al koxylates including butyl polyoxyethylene/polyoxypropylene block copolymer;

Alkyl polysaccharides including C_8-C_{11} alkylpolysaccharides;

Glycerol oleate;

Polyoxyethylene-polyoxypropylene block copolymers of MW 1100 to 11400 and 10 to 80% EO;

Nonyl phenol ethoxylates including polyoxyethylene (2 to 8) nonylphenol;

Polymeric surfactants including graft copolymer such as polymethacrylic acid and acrylate with polyoxyethylene chains and random copolymers with ester and ether groups;

Polyethylene glycols including MW: 200 to 8000; MW: 400 PEG dioleate; and MW: 600 PEG dioleate; and

Sorbitan fatty acid ester ethoxylates including polyoxyethylene (20) sorbitan tristearate; polyoxyethylene (20) sorbitan monooleate; polyoxyethylene (5) sorbitan monooleate; and polyoxyethylene (20) sorbitan trioleate.

Examples of 2-Pack Embodiment

In embodiments of the invention, a sufficient volume of Pack A was added to a volume of water required to obtain a desired concentration in the final formulation and was mixed to form an emulsion. Sufficient Pack B was added to the emulsion to result in a fungicidal dispersion which comprised:

an effective amount of paraffinic oil, being about 5 wt %;

about 0.1 wt % emulsifiers;

about 0.3 wt % polychlorinated Cu (II) phthalocyanine; and

about 0.1 wt % silicone surfactant.

The fungicidal dispersion was sprayed onto turfgrass at a rate of from about 50 gal/acre (4.7 L/100 m^2) to about 100 gal/acre (9.3 L/100 m^2).

Example 5

In an example of the 2-Pack embodiment of the invention, the following compositions (Pack A and Pack B) were prepared and mixed together as described to achieve the sprayable dispersion.

Pack A					
	Components	Chemical Description	Supplier Name	% by weight	Purpose in Formulation
1	N65DW	Highly saturated paraffinic oils with a carbon number distribution in the range of about C_{16} to about C_{35}	Petro-Canada	96	Active Ingredient
2	PC Emuls Green	1. Ethoxylated alcohols having primary C5-C20 carbon chains with an average of about 2 to about 7 ethoxylation groups 2. Glycerol Oleate	Petro-Canada	2	Emulsifier
3	Lambent MFF199 SW	Methyl (propylhydroxide, ethoxylated) bis (trimethylsiloxy) silane	Lambent Technologies Corp., Gumee IL USA	2	Wetting agent/dispersant

Pack B					
	Components	Chemical Description	Supplier Name	% by weight	Purpose in Formulation
1	SUNSPERSE ® Green 7 (GCD9957)	58% polychlorinated Cu(II) phthalocyanine (C32HCl15CuN8) dispersed in water	Sun Chemical Corp Performance Pigment Cincinnati OH USA	100	Colorant

In the embodiment of the invention described in Example 5, all of the silicone surfactant was added to Pack A.

Example 6

In an example of the 2-Pack embodiment of the invention, the following components or compositions were prepared and mixed together as described to achieve the sprayable dispersion.

Pack A					
	Components	Chemical Description	Supplier Name	% by weight	Purpose in Formulation
1	N65DW	Highly saturated paraffinic oils with a carbon number distribution in the range of about C_{16} to about C_{35}	Petro-Canada	98	Active Ingredient
2	PC Emuls Green	1. Ethoxylated alcohols having primary C_5-C_{20} carbon chains with an average of about 2 to about 7 ethoxylation groups 2. Glycerol Oleate	Petro-Canada	2	Emulsifier

Pack B					
	Components	Chemical Description	Supplier Name	% by weight	Purpose in Formulation
1	SUNSPERSE ® Green 7 (GCD9957)	58% polychlorinated Cu(II) phthalocyanine ($C_{32}HCl_{15}CuN_8$) dispersed in water	Sun Chemical Corp Performance Pigment Cincinnati, OH USA	83.8	Colorant
2	Lambent MFF159-10	Dimethyl, methyl (polyethylene oxide) silicone polymer	Lambent Technologies Corp., Gumee IL USA	16.2	Wetting agent/dispersant

In the embodiment of the invention described in Example 6, all of the silicone surfactant was added to Pack B.

Examples 7 to 10

2-Pack Formulation

Examples 7 to 10 were performed using a formulation prepared according to Example 5.

Example 7

Comparison of the Efficacy of the 2-Pack Formulation to a Formulation Without Pigment

An embodiment of the invention was applied to creeping bentgrass (*Agrostis stolonifera*) at a close cut putting green height of 5 mm to determine the efficacy of an embodiment of the invention to control dollar spot. Dollar spot is caused by *Sclertinia Homeocarpa* and is the most common disease requiring control on golf courses throughout most of the world.

The embodiment of the invention, applied to the turfgrass at 5 gal/acre (0.5 L/100 m^2) of the non-aqueous portion of the oil-in-water emulsion, was compared to the use a higher concentration of oil-in-water emulsion without pigment, applied at 10 gal/acre (1 L/100 m^2) of the non-aqueous portion of the oil-in-water emulsion, and an inoculated control. The plots were inoculated with five strains of *Sclertinia Homeocarpa*, one week after initial chemical application.

The fungicides were applied in water at a total spray volume rate of about 129 gal/acre (12 L/100 m^2) using a wheel-mounted compressed air boom sprayer at 140 kPa. Applications were made at 14 day intervals. Weekly counts of dollar spot infection were conducted over the 6 week period.

Chemical Treatment List

Treatment	Product per 100 m^2	No. of Applications	Treatment Interval
Fungicide with pigment (2-pack)	465 mL	3	14 days
Fungicide without pigment	930 mL	3	14 days

Conclusions

As shown in FIG. **1**, acceptable control of dollar spot was achieved using the 2-pack fungicide at 5 gal/acre (0.5 L/100 m^2) with the addition of the polychlorinated Cu (II) phthalocyanine pigment dispersion, emulsifier and silicone additives.

The use of 5 gal/acre (0.5 L/100 m^2) of the non-aqueous portion of the 2-pack fungicide formulation performed substantially the same as using the oil-in-water emulsion alone at 10 gal/acre (1 L/100 m^2) of the non-aqueous portion. The data suggests a synergistic effect resulting from the addition of pigment, permitting use of the formulation at rates lower than predicted rates.

An additional benefit of the lower treatment rate is the reduced propensity for phytotoxicity which may be observed at high oil rates.

Example 8

A 2-Pack embodiment of the invention was applied to creeping bentgrass (*Agrostis stolonifera*) at a close cut putting green height of 5 mm to determine the efficacy of an embodiment of the invention to control dollar spot. Close cut turf is highly susceptible to dollar spot.

The 2-pack embodiment of the invention was compared to a chemical fungicide, DACONIL® 2787, also known as WEATHERSTIK™, available from Syngenta Crop Protection Canada, Inc. Guelph, Ontario, Canada, and an inoculated control. The trials were conducted on 8 year old PENNCROSS® creeping bentgrass (*Agrostis stolonifera*). The treatments were applied over a 7-week period and the turf and disease were monitored over a 9-week period to examine residual effects and grass recovery. A randomized complete block design having four replications was used and each treatment plot measure 1 m×2 m. The plots were inoculated with five strains of *Sclertinia Homeocarpa*, one day after initial chemical application.

Due to the close cutting of the turf in this example the disease pressure was extreme. The fungicides were applied in water at a total spray volume rate of 118 gal/acre (11 L/100 m^2) using a wheel-mounted compressed air boom sprayer at 140 kPa. Applications were made at 14 day intervals for both the DACONIL® and the 2-pack formulation. An additional plot was treated with applications of the 2-pack formulation at 7 day intervals. Weekly counts of dollar spot infection were conducted over the 7 week period.

Chemical Treatment List

Treatment	Product per 100 m^2	No. of Applications	Treatment Interval
DACONIL ® 2787	95 mL	4	14 days
2-pack fungicide	465 mL	4	14 days
2-pack fungicide	465 mL	7	7 days

Results

As shown in FIG. **2**, low levels of dollar spot disease were present on all of the plots at the start of the trial. Nearing the end of the trial, the disease levels in the control exceeded 100 spots per plot on the inoculated areas. All three chemical treatments showed significant suppression of dollar spot disease when compared to the control. The suppression of disease continued for about two weeks following the last application.

It was noted that when applied weekly, the 2-pack formulation performed substantially better than the 2-pack formulation or the DACONIL® applied at the recommended rate of biweekly. One of skill in the art would recognize therefore that, in cases of extreme dollar spot disease, efficacy of the 2-pack formulation is improved if applied more frequently.

Phytotoxicity was not observed in any of the treatments.

Conclusions

The 2-pack fungicide, applied at 5 gal/acre (0.5 L/100 m^2) of the non-aqueous portion performed substantially the same as the chemical fungicide, DACON ILO 2787.

In cases of extreme disease pressure the 2-pack formulation should be applied more frequently.

Example 9

An embodiment of the invention was applied to creeping bentgrass (*Agrostis stolonifera*) at a fairway height of 11 mm to determine the efficacy of an embodiment of the invention to control dollar spot. Dollar spot is caused by *Sclertinia Homeocarpa* and is the most common disease requiring control on golf courses throughout most of the world.

The embodiment of the invention was compared to a chemical fungicide, DACONIL® 2878, also known as WEATHERSTIK™, available from Syngenta Crop Protection Canada, Inc. Guelph, Ontario, Canada, and an inoculated control. The trials were conducted on 13 year old PENNCROSS® creeping bentgrass (*Agrostis stolonifera*). The treatments were applied over a 6-week period and the turf and disease were monitored to examine residual effects and grass recovery. A randomized complete block design having four replications was used and each treatment plot measure 1 m×2 m. The plots were inoculated with five strains of *Sclertinia Homeocarpa*, one week after initial chemical application.

The fungicides were applied in water at a total spray volume rate of 129 gal/acre (12 L/100 m^2) using a wheel-mounted compressed air boom sprayer at 140 kPa. Applications were made at 14 day intervals. Weekly counts of dollar spot infection were conducted over the 6 week period.

Chemical Treatment List

Treatment	Product per 100 m^2	No. of Applications	Treatment Interval
DACONIL ® 2787	95 mL	3	14 days
2-pack fungicide	465 mL	3	14 days
2-pack fungicide	930 mL	3	14 days

Results

As shown in FIG. **3**, dollar spot disease was present on all of the plots at the start of the trial. All three treatments showed significant suppression of dollar spot disease when compared to the control. The suppression of disease continued for about two weeks following the last application.

Phytotoxicity was not observed in any of the treatments.

Conclusions

The 2-pack fungicide, applied at both 5 gal/acre (0.5 L/100 m^2) of the non-aqueous portion and 10 gal/acre (1 L/100 m^2) of the non-aqueous portion, performed substantially the same as the chemical fungicide, DACON ILO 2787.

Example 10

An embodiment of the 2-pack formulation was used to treat dollar Spot on *Poa Trivialis* (rough stalk bluegrass) overseeded Bermudagrass plot cut at putting green height. The 2-pack formulation was applied at 2.5 gal/acre (0.2 L/100 m^2) of the non-aqueous portion and was compared to a formulation prepared without the pigment, the silicone surfactant and the particular emulsifier and which was applied at 5 gal/acre (0.5 L/100 m^2) of the non-aqueous portion and to an untreated control.

The formulations were applied using a CO_2 backpack boom sprayer calibrated to deliver products in 2 gallons of water per 1000 sq ft (8 L/100 m^2) through two 8003 TEEJETO flat fan nozzles.

The turfgrass plots were divided into 4 blocks and treatments were assigned in a randomized complete block design. The plots were inoculated with 1 L of wheat seed infested with *Sclerotinia homoeocarpa*. Fungicide formulations were applied weekly for 8 weeks.

Having reference to FIG. **4**, dollar spot counts were made throughout the 8 week period.

Conclusions:

Acceptable control of dollar spot was obtained through weekly use of 2.5 gal/acre (0.2 L/10 m^2) of the non-aqueous portion of 2-pack fungicide which represents approximately one half the amount required to achieve the same result using a formulation without the addition of the polychlorinated Cu (II) phthalocyanine pigment dispersion, emulsifier and silicone additives (5 gal/acre (0.5 L/100 m^2) of the non-aqueous portion, weekly).

Advantageously, the use of a lower treatment rate reduces the propensity for phytotoxicity which may be observed at high rate oil rates.

Example 11

Example 11 was performed using a formulation prepared according to Example 6.

Kentucky bluegrass was mowed three times per week at a cutting height of 2 inches. Applications of the 2-pack formulation were made at 14-day intervals beginning April 10. Assessment of Spring leaf spot or Melting-out disease was made using a “0 to 10” severity index, where 10 is equivalent to greater than 90% symptomatic turf area.

For the purposes of comparison to conventional treatment, DACONIL® ULTREX, available from Syngenta Crop Protection Canada, Inc. Guelph, Ontario, Canada, was used as a control.

Results

Treatment	Application rate (oz/1000 ft^2)	Disease Severity 14-May	22-May	28-May	4-Jun
Untreated		2.7ab	4.3a	5.3a	6.7a
2-pack	21.75	0.0e	0.3ef	0.3ef	0.3hi
DACONIL ® Ultrex	3.2	0.0e	0.0f	0.0f	0.0i
LSD (P = 0.05)		1.45	0.96	1.38	1.28
Std Deviation		0.89	0.59	0.85	0.78

Means in a row followed by the same letter are not significantly different (alpha = 0.05) using LSD test.

No phytotoxicity was observed in any treatment plot.

Conclusions:

The 2-Pack formulation, used at 7.5 gal/acre (0.7 L/100 m^2) of the non-aqueous portion) provided excellent disease control.

1-Pack Formulation

In another embodiment of the invention, Applicant has surprisingly found that pigment, such as polychlorinated Cu (II) phthalocyanine, can be prepared in a single, stable dispersion in an oil-based fungicidal composition, prior to dilution in water to form a sprayable dispersion. Thus, the user does not need to handle two separate components for preparing a stable fungicidal application.

More specifically, the pigment is dispersed in a compatible oil, such as a paraffinic oil or the same paraffinic oil as is used used to provide the fungicidal properties as described in embodiments of the invention, for additional to the formulation. Use of specific silicone surfactant and emulsifier chemistries stabilizes the colorant in the oil-based composition.

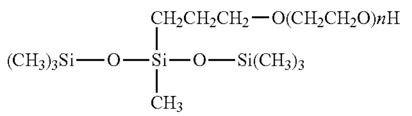
In examples of the 1-pack formulation, polychlorinated Cu(II) phthalocyanine is dispersed in a paraffinic oil, such as N65DW (available from Petro-Canada) to provide about 18% polychlorinated CU(II) phthalocyanine (SUNSPERSE® EXP 006-102, available from Sun Chemical Corp. Performance Pigments, Cincinnati, Ohio USA) prior to mixing with the remaining constituents.

In embodiments of the invention, the 1-pack formulation comprises silicone surfactant, emulsifier and polyethylene glycols which are selected to provide an intermolecular hydrophilic and lipophilic balance within the fungicidal formulation so as to substantially prevent the polychlorinated Cu(II) phthalocyanine from separating out of suspension during application to the turf grass.

Applicant believes that suitable silicone surfactants are those previously identified for the 2-pack formulation, as described in Formula (I). In embodiments of the invention the silicone surfactants are H-capped, CH_3-capped and

$COCH_3$-capped trisiloxanes. In an embodiment of the invention, the silicone is an H-capped trisiloxane as shown below in Formula (III):

Formula (III)



Where: n=1-24, average n=8-10.

Suitable emulsifiers for the 1-Pack formulation are selected from the following:

- Alcohol ethoxylates (natural and synthetic) including polyoxyethylene (4 to 7) lauryl ether (C12); polyoxyethylene (10) cetyl ether (C16); polyoxyethylene (2 to 11) C12-C15 alcohols; polyoxyethylene (3 to 9) C11-C14 alcohols; polyoxyethylene (9) C12-C14 alcohols;
- Polymeric surfactants including graft copolymer such as polymethacrylic acid and acrylate with polyoxyethylene chains and random copolymers with ester and ether groups; and
- Sorbitan fatty acid esters including sorbitan tristearate and sorbitan trioleate.

The emulsifier is added to the formulation in a range of about 0.5 wt % to about 5 wt % in the non-aqueous portion of the formulation.

In embodiments of the invention, Applicant has noted that the silicone surfactants used typically comprise 10-30% polyethylene glycols (PEG) according to Formula (IV) shown below.

$$R_1—O—(CH_2—CH_2—O)_n—R_2 \qquad \text{Formula (IV)}$$

Where:

R_1=H or CH_2=CH—CH_2 or $COCH_3$

R_2=H or CH_2=CH—CH_2 or $COCH_3$

n≥1

In embodiments of the invention, the PEG has a low molecular weight, typically about 300 to about 1500 Daltons. In embodiments of the invention, the PEG is a low molecular weight polyethylene glycol allyl ether. In embodiments of the invention, the PEG is a low molecular weight polyethylene glycol mono-allyl ether having an average molecular weight of from about 300 to about 600 Daltons and having from 1 to 20 moles of ethylene glycol with an average ethoxylation (EO) of 8 to 10.

Examples 12 to 14

1-Pack Formulations

Example 12

28 wt % SUNSPERSE® EXP 006-102 containing 18 wt % polychlorinated Cu(II) phthalocyanine, dispersed in N65DW;

2 wt % silicone surfactant according to Formula (I) where: m=1, n=0, X=1-24 (average 8-10) and R=H; and PEG according to Formula (IV) where: R_1=CH_2=CH—CH_2, R_2=H and n=1-20 with an average n=8 (Lambent MFF199);

2 wt % polyoxyethylene (11) C_{16-18} alcohols such as LUTENSOL® AT11 available from BASF; and

68 wt % N65DW.

Example 13

28 wt % SUNSPERSE® EXP 006-102 containing 18 wt % polychlorinated Cu(II) phthalocyanine, dispersed in N65DW;

2 wt % silicone surfactant according to Formula (I) where: m=1, n=0, X=1-24 (average 8-10) and R=H; and PEG according to Formula (IV) where: R_1=CH_2=CH—CH_2, R_2=H and n=1-20 with an average n=8 (Lambent MFF199);

2 wt % sorbitan tristearate such as SPAN65 available from Uniqema or S-MAZ® 65K available from BASF; and

68 wt % N65DW.

Example 14

28 wt % SUNSPERSE® EXP 006-102 containing 18 wt % polychlorinated Cu(II) phthalocyanine, dispersed in N65DW;

1.8 wt % silicone surfactant as described in Formula (I) where m=1, n=0, X=1-24 (average 8-10) and R=$COCH_3$, and Polyethylene Glycols as described in Formula (IV) where R_1=CH_2=CH—CH_2 or $COCH_3$, R_2=$COCH_3$ (SYLGARD® 309, available from Dow Corning, USA)

0.2% Polyethylene Glycols as described in Formula (IV) where R_1=CH_2=CH—CH_2, R_2=H (Polyglykol A500, available from Clariant);

2 wt % polyoxyethylene (11) C_{16-18} alcohols, such as LUTENSOL® AT11 available from BASF; and

68 wt % N65DW.

The formulations disclosed in Examples 12-14 were further diluted to 6% in water prior to application to the turfgrass. The resulting oil-in-water formulations comprised:

about 5 wt % paraffinic oil;

about 0.12 wt % emulsifier;

about 0.3 wt % polychlorinated Cu(II) phthalocyanine;

about 0.1 wt % silicone surfactant;

about 0.01-0.03 wt % polyethylene glycol; and

the balance being water.

The resulting oil-in-water emulsion/pigment dispersions were found to be stable until applied, typically within one day and can be applied to turfgrass. The oil-in-water emulsions were applied at a conventional total spray volume rate of about 50 gal/acre (4.7 L/100 m^2) to about 100 gal/acre (9.3 L/100 m^2).

Examples 15-17

Additional testing was performed to determine the stability of 1-pack formulations without the presence of silicone surfactant and/or PEG.

In Examples 15-17, the formulations were further diluted to 6% in water to form the oil-in-water emulsion prior to application to turfgrass.

Example 15

A 1-pack formulation was prepared with neither silicone surfactant nor PEG according to the following formula:

28 wt % SUNSPERSE® EXP 006-102 containing 18 wt % polychlorinated Cu(II) phthalocyanine, dispersed in N65DW;

2 wt % polyoxyethylene (11) C_{16-18} alcohols such as LUTENSOL® AT11 available from BASF; and

70% N65DW.

Example 16

A 1-pack formulation was prepared with insufficient PEG according to the following formula:

28 wt % SUNSPERSE® EXP 006-102 containing 18 wt % polychlorinated Cu(II) phthalocyanine, dispersed in N65DW;

2 wt % silicone surfactant as described in Formula (I) where m=1, n=0, X=1-24 (average 8-10) and R=H (SILTECH® SILSURF® A008-UP);

2 wt % polyoxyethylene (11) O_{16-18} alcohols such as LUTENSOL® AT11 available from BASF; and

68% N65DW.

Example 17

A 1-pack formulation was prepared without silicone surfactant according to the following formula:

28 wt % SUNSPERSE® EXP 006-102 containing 18 wt % polychlorinated Cu(II) phthalocyanine, dispersed in N65DW;

2 wt % Polyethylene Glycols as described in Formula (IV) where $R_1{=}CH_2{=}CH{-}CH_2$, $R_2{=}H$ (Polyglykol A500, available from Clariant);

2 wt % polyoxyethylene (11) C_{16-18} alcohols such as LUTENSOL® AT11 available from BASF; and

68% N65DW.

Results:

The pigment aggregated and fell out of suspension in all of the formulations tested in Examples 15-17, rendering the formulations unusable.

Conclusions:

As shown in Examples 12-17, without both silicone surfactant and sufficient amounts of PEG, the resulting 1-pack formulations, diluted to form oil-in-water emulsions, are not stable and are therefore not usable for turf application.

As demonstrated in Examples 12-17, the presence of silicone surfactants and polyethylene glycols improve the stability and dispersibility of the 1-Pack formulation resulting in a commercially viable fungicidal dispersant for turf application and management of disease therein.

Example 18

Embodiments of the 1-pack and 2-pack formulations, according to the invention, and a conventional fungicide, DACONIL® Ultrex, were used to treat dollar Spot on *Poa Trivialis* (rough stalk bluegrass) overseeded Bermudagrass plot cut at putting green height. As with Example 10, the formulations were applied with a CO_2 backpack boom sprayer calibrated to deliver products in 2 gallons of water per 1000 sq ft (8 L/100 m^2) through two 8003 TEEJET® flat fan nozzles.

The plots were divided into 4 blocks and treatments were assigned in a randomized complete block design. The plot was inoculated with 1 L of wheat seed infested with *Sclerotinia homoeocarpa*. The formulations were applied biweekly for 8 weeks.

As shown in FIG. **5**, dollar spot counts were made throughout the 8 week period.

Conclusions:

Both the 1-pack and 2-pack formulations had substantially the same efficacy as the DACONIL® Ultrex.

Example 19

A 2-Pack formulation was prepared according to Example 6 an applied on a fairway and an area of rough at the Saginaw Golf Course in Cambridge, Ontario, Canada for an 8 week period using a 14-day application interval.

At the end of 8 weeks, core samples of the treated and untreated areas were obtained to compare root development.

Results

As shown in FIG. **6**, the grass on the treated areas (left) was much denser and healthier than on the untreated areas (right). Further, the treated areas had a darker green color than the untreated areas.

It was found that the roots of the bentgrass on the treated area were longer by approximately twice the length of the roots of the untreated bentgrass. Further, the roots were observed to be denser than the roots of untreated bentgrass.

Conclusions:

The 2-Pack and 1-Pack formulations promote the growth of bentgrass and bluegrass.

Example 20

Having reference to FIGS. **7** and **8**, areas of bentgrass were treated using a 2-Pack formulation prepared according to Example 6. Seven (7) core samples were randomly taken from treated areas and from untreated areas for comparison. The core samples were soaked overnight in water in a glass tray. Subsequently, soil from the roots was washed away with water to reveal the root structure, as shown in FIGS. **7** and **8** and summarized in Table A below.

Results

TABLE A

Core sample #	Untreated root length (inches)	Treated root length (inches)
1	3.5	5.5
2	3.0	4.5
3	3.75	4.0
4	2.75	5.25
5	2.75	4.5
6	2.75	4.75
7	4.25	4.75
Average	3.25	4.75

Conclusions:

On the average, the root length of the treated bentgrass is approximately 50% longer than that of the untreated bentgrass. Further it was noted that the root mass was considerably greater for the treated bentgrass.

Enhanced Formulation

Applicant has determined that embodiments of the present invention have a surprising synergistic effect when mixed with some conventional systemic chemical fungicides selected from the group consisting of demethylation inhibitors (such as propiconazole), methyl benzimidazole carbamate (such as thiophanate-methyl) and dicarboximide (such as iprodione). As an example, a suitable propiconazole fungicide is BANNER MAXX™ (available from Syngenta Crop Protection Canada, Inc. Guelph, Ontario, Canada), a thiophanate-methyl fungicide is Cleary 3336™ (available from Cleary Chemical Corporation, Dayton, N.J., USA) and an iprodione fungicide is ROVRAL® Green (available from Bayer Environmental Science-Canada, Guelph, Ontario, Canada).

Applicant has found however that, despite predictions to the contrary, the synergistic effect was not observed with all conventional chemical fungicides, such as some contact fungicides, one of which was chlorothalonil (such as DACONIL® Ultrex, available from Syngenta Crop Protection Canada, Inc. Guelph, Ontario, Canada).

As shown in the following additional examples for treatment of Dollar Spot, snow moulds and gray leaf spot, mixing an embodiment of the present invention at half the predicated recommended label rate in equal parts with certain conventional chemical fungicides at half the amount of the label rate resulted in an equivalent or improved efficacy of the mixture when compared to each of the fungicides used alone at full label rate.

As one of skill would understand and as taught by Burpee and Latin, Plant Disease Vol. 92 No. 4, April 2008, pp 601-606., knowing that the efficacy of fungicides is not additive, the addition of half the label rate of each of the two fungicidal formulations would not conventionally be thought to result in high efficacy. Surprisingly this was not the case with embodiments of the present invention. Mixtures of formulations of the present invention and certain conventional chemical fungicides, at rates not thought to be useful, resulted synergistically in a highly efficacious formulation.

Applicant believes that the amount of formulations according to embodiments of the invention can be reduced to a range from about 25% to about 75% of the amount used if used alone, when mixed with the conventional chemical fungicide, also reduced to from about 25% to about 75% of the recommended label rate.

Examples 21 and 22

Examples 21 and 22 illustrate results of use of the 1-pack formulation, the two pack formulation and the enhanced formulation on the treatment of Dollar Spot on *Poa Trivialis* (rough stalk bluegrass) cut at putting green height.

Example 21

Having reference to FIGS. **9**A and **9**B, the 2-pack formulation was tank mixed at 50:50 with chemical fungicide BANNER MAXX™ and applied to turf infected with dollar spot disease.

The mixture of the 2-pack fungicide and the chemical fungicide exhibited a synergistic effect compared to using either of the fungicides alone. As shown in FIG. **9**B, the residue period can be extended from 21 days to 28 days.

Example 22

Having reference to FIG. **10**, the 1-pack formulation was tank mixed 50:50 with chemical fungicide BANNER MAXX™ and applied to turf infected with dollar spot disease.

The 1-pack formulation with the addition of chemical fungicide exhibited a synergistic effect when compared to use of the 1-pack formulation or BANNER MAXX™ alone, when applied at the full label rate.

Examples 23-25

Embodiments of the invention were mixed 50:50 with conventional chemical fungicide BANNER MAXX™ to form an enhanced formulation and were applied to creeping bentgrass (*Agrostis stolonifera*) at fairway height which was infected with a variety of snowmolds.

An enhanced formulation containing the 2-pack formulation and chemical fungicide was compared to use of the fungicides alone. BANNER MAXX™ was applied at 50% the recommended label rate for comparison to the enhanced formulation.

Example 23

As shown in FIG. **11**, the effectiveness of the enhanced formulation was compared to the 2-pack formulation, 50% of the recommended label rate of BANNER MAXX™ alone and an untreated control for treating turf infected with *Typhula ishikariensis.*

Example 24

As shown in FIG. **12**, the effectiveness of the enhanced formulation was compared to the 2-pack formulation, 50% of the recommended label rate of BANNER MAXX™ alone and an untreated control for treating turf infected with *Typhula incarnata.*

Example 25

As shown in FIG. **13**, the effectiveness of the enhanced formulation was compared to the 2-pack formulation, 50% of the recommended label rate of BANNER MAXX™ alone and an untreated control for treating turf infected with *Microdochium nivale.*

Conclusions:

It is clear from Examples 23-25 that use of the enhanced formulation comprising 50% of the recommended rate of an embodiment of the invention and 50% of the recommended label rate of BANNER MAXX™ is as effective, or more effective, than using either the 2-pack formulation or the chemical fungicide alone.

Example 26

A 2-Pack formulation was prepared according to Example 6 using half the recommended rate (i.e. 232.5 ml per 100 m^2 for the non-aqueous portion) and was mixed with a commercial fungicide ROVRAL® Green GT (available from Bayer Environmental Science-Canada, Guelph, Ontario, Canada) at 50% the recommended label rate (i.e., applied at 125 ml per 100 m^2) to form the enhanced formulation.

The enhanced formulation was applied to creeping bentgrass (*Agrostis stolonifera*) cut to greens height for the control of *Fusarium* Patch disease. ROVRAL® Green GT was also applied alone at 50% the recommended rate ((i.e., applied at 125 ml per 100 m^2) for comparison.

The treatments were applied over a 6-week period and disease was monitored weekly.

Conclusions:

As shown in FIG. **14**, the enhanced formulation ("PC2 50%+ROVRAL® Green GT 50%") provided significant suppression of injury by *Fusarium* Patch disease.

Example 27

One half (50%) of the recommended rate of a 2-Pack formulation (i.e., at 2.5 gal per acre of the non-aqueous portion), prepared according to Example 6, was mixed 50:50 with a conventional chemical fungicide Cleary 3336™ Plus at 50% the recommended rate (i.e., at 2 oz per 1000 ft^2).

The enhanced formulation (PC2, ½ rate+Cleary 3336™ Plus, ½ rate), as well as the individual formulations at full rate and at half rate, were applied to perennial ryegrass cut to fairway height for control of Gray Leaf Spot disease.

Conclusions:

As shown in FIG. **15**, the enhanced formulation provided excellent control of Gray Leaf Spot disease on Ryegrass.

Synergistic Effect of the Oil/Emulsion and Pigment Dispersion

Example 28

As shown in FIG. **16**, Applicant believes that in all formulations according to embodiments of the invention, the addition of the polychlorinated Cu(II) phthalocyanine has a synergistic effect when compared to oil/emulsifier alone or pigment alone, when compared to an untreated control.

Turf infected with Dollar Spot disease was treated with 10% oil/emulsifier alone, 0.5% SUNSPERSE® Green 7 alone and an embodiment of the invention comprising both 10% oil/emulsifier and 0.5% SUNSPERSE® Green 7.

Conclusions:

Clearly, it appears that addition of pigment to the fungicidal oil component enhances the fungicidal properties of the dispersion.

Use of Embodiments of the Invention for Controlling Additional Pests in Turfgrass

Example 29

Fall Armyworms

The efficacy of an embodiment of the 2-pack formulation against different larval stages of fall armyworms (*Spodoptera frugiperda*) was determined under laboratory conditions. Embodiments of the invention were compared to a conventional pesticide Cyfluthrin.

Methods:

1) Larvae were obtained from Benzon Research Inc.
2) 5 larvae/container and 3 containers=1 replication
3) Treatments=1) Control
   2) 2-pack formulation at 5% dilution
   3) Cyfluthrin (insecticide), Al=0.75%, 3 fl oz/gal H_2O (22 mL/L)
4) Container=760 ml plastic bowl with lid containing moist filter paper on bottom and grass clippings
5) St. Augustinegrass clippings dipped into respective fungicide treatment, drained to dry and put into container
6) Hold 4 days at 25° C. and measure survival
7) 7 replications of small larvae (2-10 mm) tested
8) 6 replications of medium larvae (11-20 mm) tested
9) 6 replications of large larvae (21-30 mm) tested
10) Statistical analysis=Least Significant Difference (LSD) test

Results:

Fall army	Mean survival[a]		
worms Larvae	control	Cyfluthrin	2-pack formulation
Small	3.86 A	0 B	0.43 B
Medium	3.50 A	0 B	1.17 B
Large	3.00 A	0 B	2.50 A

[a]Means in a row followed by the same letter are not significantly different (alpha = 0.05) using LSD test.

Conclusions:

The data indicates that embodiments of the 2-pack formulation are effective to kill small and medium larvae of fall army worms.

Tropical Sod Webworms

Similar testing was conducted to determine the efficacy of embodiments of the 2-pack formulation to kill all sizes larvae (small, medium and large) of tropical sod webworms.

Sodweb	Mean survival[a]		
worms Larvae	control	Cyfluthrin	PC
Small	3.0 A	0 B	0.3 B
Medium	4.8 A	0 B	0 B
Large	4.0 A	0.3 B	1.0 B

[a]Means in a row followed by the same letter are not significantly different (alpha = 0.05) using LSD test.

Conclusions:

The data indicates that embodiments of the 2-pack formulation are effective to kill small, medium and large larvae of tropical sod webworms.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A formulation comprising:

a paraffinic oil comprising an isoparaffinic oil;

one or more emulsifiers, each of which is independently selected from the group consisting of natural and synthetic alcohol ethoxylates, alcohol alkoxylates, glycerol oleate, and nonyl phenol ethoxylates;

a polychlorinated (Cu II) phthalocyanine;

a silicone surfactant; and

water,

wherein the silicone surfactant represents from about 0.1 wt % to about 5 wt % of the total weight of the paraffinic oil, the one or more emulsifiers, the polychlorinated (Cu II) phthalocyanine, and the silicone surfactant;

wherein the one or more emulsifiers represent from about 0.5 wt % to about 5 wt % of the total weight of the paraffinic oil, the one or more emulsifiers, the polychlorinated (Cu II) phthalocyanine, and the silicone surfactant;

wherein the polychlorinated (Cu II) phthalocyanine represents from about 1 wt % to about 10 wt % of the total weight of the paraffinic oil, the one or more emulsifiers, the polychlorinated (Cu II) phthalocyanine, and the silicone surfactant; and

wherein the formulation is an oil-in-water emulsion and the one or more emulsifiers and the silicone surfactant are selected such that the polychlorinated (Cu II) phthalocyanine is maintained in dispersion in the oil-in-water emulsion.

2. The formulation of claim **1**, wherein the isoparaffinic oil is a synthetic isoparaffinic oil.

3. The formulation of claim **1**, wherein the isoparaffinic oil has an independently selected carbon number distribution of from C16 to C35.

4. The formulation of claim **1**, wherein each of the one or more emulsifiers is independently selected from the group consisting of polyoxyethylene(4 to 7) lauryl ether (C_{12}); polyoxyethylene (10) cetyl ether (C_{16}), polyoxyethylene (2 to 11) C_{12}-C_{15} alcohols, polyoxyethylene (3 to 9) C_{11}-C_{14} alcohols, and polyoxyethylene (9) C_{12}-C_{14} alcohols.

5. The formulation of claim **1**, wherein each of the one or more emulsifiers is independently selected from the group consisting of natural or synthetic alcohol ethoxylate, glycerol oleate, and nonyl phenol ethoxylates.

6. The formulation of claim **5**, wherein each of the one or more emulsifiers is independently selected from the group consisting of polyoxyethylene (4 to 12) lauryl ether (C12); polyoxyethylene (10) cetyl ether (C16); polyoxyethylene (10) stearyl ether (C18); polyoxyethylene (10) oleyl ether (C18 monounsaturated); polyoxyethylene (2 to 11) C12-C15 alcohols; polyoxyethylene (3 to 9) C11-C14 alcohols; polyoxyethylene (9) C12 C14 alcohols; polyoxyethylene (11) C16-C18 alcohols; polyoxyethylene (20) C12 C15 alcohols, glycerol oleate, and polyoxyethylene (2 to 8) nonylphenol.

7. The formulation of claim **1**, wherein each of the one or more emulsifiers is independently selected from a natural or synthetic alcohol ethoxylate and a glycerol oleate.

8. The formulation of claim **7**, wherein each of the one or more emulsifiers is independently selected from the group consisting of polyoxyethylene (4 to 12) lauryl ether (C12); polyoxyethylene (10) cetyl ether (C16); polyoxyethylene (10) stearyl ether (C18); polyoxyethylene (10) oleyl ether (C18 monounsaturated); polyoxyethylene (2 to 11) C12-C15 alcohols; polyoxyethylene (3 to 9) C11-C14 alcohols; polyoxyethylene (9) C12 C14 alcohols; polyoxyethylene (11) C16-C18 alcohols; polyoxyethylene (20) C12 C15 alcohols, and glycerol oleate.

9. The formulation of claim **1**, wherein the one or more emulsifiers represent from about 1 wt % to about 3 wt % of the total weight of the paraffinic oil, one or more emulsifiers, polychlorinated (Cu II) phthalocyanine, and silicone surfactant.

10. The formulation of claim **1**, wherein the one or more emulsifiers represent about 2 wt % of the total weight of the paraffinic oil, one or more emulsifiers, polychlorinated (Cu II) phthalocyanine, and silicone surfactant.

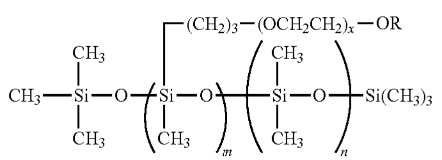
11. The formulation of claim **1**, wherein the silicone surfactant comprises polyethylene glycols (PEG) according to Formula (IV):

$$R_1—O—(CH_2—CH_2—O)_n—R_2 \quad \text{Formula (IV)}$$

where: R_1=H or CH_2=CH—CH_2 or $COCH_3$
R_2=H or CH_2=CH—CH_2 or $COCH_3$
n is greater than or equal to 1.

12. The formulation of claim **1**, wherein:
the silicone surfactant is selected from the group consisting of trisiloxanes and silicone polyethers of Formula I

(Formula I)



where R=H, CH_3, or $COCH_3$; x=1 to 24; n=0 or 1; and m=1.

13. The formulation of claim **1**, wherein
the one or more emulsifiers are selected from the group consisting of polyoxyethylene(4 to 7) lauryl ether (C_{12}); polyoxyethylene (10) cetyl ether (C_{16}), polyoxyethylene (2 to 11) Cu-Cis alcohols, polyoxyethylene (3 to 9) C_{11}-C_{14} alcohols, and polyoxyethylene (9) C_{12}-C_{14} alcohols, and
the silicone surfactant comprises polyethylene glycols (PEG) according to Formula (IV):

$$R_1—O—(CH_2—CH_2—O)_n—R_2 \quad \text{Formula (IV)}$$

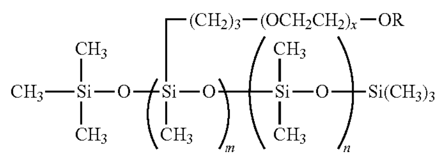
where: R_1=H or CH_2=CH—CH_2 or $COCH_3$
R_2=H or CH_2=CH—CH_2 or $COCH_3$
n is greater than or equal to 1.

14. The formulation of claim **1**, wherein the formulation further comprises one or more chemical fungicides.

15. The formulation of claim **14**, wherein each of the one or more chemical fungicides is independently selected from the group consisting of a demethylation inhibitor, a methyl benzimidazole carbamate, and a dicarboximide.

16. A formulation comprising:
a synthetic isoparaffinic oil;
one or more emulsifiers, each of which is independently selected from the group consisting of natural or synthetic alcohol ethoxylate, glycerol oleate, and nonyl phenol ethoxylates;
a polychlorinated (Cu II) phthalocyanine; and
a silicone surfactant, which is independently selected from the group consisting of trisiloxanes and silicone polyethers of Formula I

(Formula I)



where R=H, CH_3, or $COCH_3$; x=1 to 24; n=0 or 1; and m=1; and
water;
wherein the silicone surfactants represents from about 0.1 wt % to about 5 wt % of the total weight of the paraffinic oil, one or more emulsifiers, polychlorinated (Cu II) phthalocyanine, and silicone surfactant;
wherein the one or more emulsifiers represent from about 0.5 wt % to about 5 wt % of the total weight of the paraffinic oil, one or more emulsifiers, polychlorinated (Cu II) phthalocyanine, and silicone surfactant;
wherein the polychlorinated (Cu II) phthalocyanine represents from about 1 wt % to about 10 wt % of the total weight of the paraffinic oil, one or more emulsifiers, polychlorinated (Cu II) phthalocyanine, and silicone surfactant; and
wherein the formulation is an oil-in-water emulsion and the one or more emulsifiers and the silicone surfactant are selected such that the polychlorinated (Cu II) phthalocyanine is maintained in dispersion in the oil-in-water emulsion.

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