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(54) FUNGICIDAL COMPOSITIONS FOR THE ENHANCEMENT OF TURF QUALITY

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(57) ABSTRACT

Fungicidal compositions for the protection of turfgrass against crown and root rot are disclosed. The compositions comprise, as the active material, (a) a first active agent selected from the group consisting of (i) a monoester salt of a phosphorous acid (preferably aluminum ethyl phosphite), and (ii) phosphorous acid or an alkali or alkali earth metal salt thereof; and (b) a benzoporphyrin compound. Preferred compositions comprise 1 part by weight of the first active agent, and between about 0.01 and about 0.1 parts by weight of the benzoporphyrin compound.

34 Claims, No Drawings

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FUNGICIDAL COMPOSITIONS FOR THE ENHANCEMENT OF TURF QUALITY

Matter enclosed in heavy brackets [] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

FIELD OF THE INVENTION

The present invention relates to methods and compositions for the enhancement of turf quality and the control or crown and root rot in turfgrass, and more particularly to synergistic combinations of fungicides useful therefore.

BACKGROUND OF THE INVENTION

Crown and root rot is a serious disease of turfgrasses, especially highly maintained turfgrasses as found in lawns, golf courses, nursery crops, and other landscape architecture applications. Current techniques for controlling this disease are not entirely satisfactory, and there is a continuing need for new treatments thereof.

U.S. Pat. No. 4,698,334 to Horriere et al. and U.S. Pat. No. 4,806,445 to Horriere et al. propose fungicidal compositions based on alkyl phosphites in combination with various contact fungicities such as Mancozeb. These compositions are useful for treating mildew in vines. U.S. Pat. No. 4,139,616 to Ducret et al. describes fungicidal compositions based on alkyl phosphites. None of these references relate to the treatment of 30 turfgrasses.

U.S. Pat. No. 5,336,661 to Lucas discloses methods of enhancing turf quality of bentgrass using compositions comprising a mixture of a monoester salt of a phosphorous acid, and an ethylenebisdithiocarbamate contact fungicide.

High quality, healthy turfgrass is essential to the golfing industry. Accordingly, there remains a need in the art for fungicidal compositions which enhance turf quality and protect against crown and root rot in turfgrass to provide high quality, healthy turfgrass.

SUMMARY OF THE INVENTION

As a first aspect, the present invention provides a fungicidal composition for enhancing the quality of turfgrass and protecting against crown and root rot. The compositions com- 45 prise a synergistic combination of:

(a) a first active agent selected from the group consisting of

(i) a monoester salt of a phosphorous acid of Formula (I):

$$\begin{bmatrix} R - O - P - O \end{bmatrix}_{n} Me^{n+}$$

wherein:

R is an alkyl radical having 2 to 4 carbon atoms,

Me is an alkali metal, alkaline earth metal, or aluminum atom, and

n is a whole number from 1 to 3 equal to the valence of Me: and

(ii) phosphorous acid or an alkali or alkali earth metal salt

thereof: and

(b) a benzoporphyrin compound.

As a second aspect, the present invention provides a 65 method of enhancing turf quality and protecting against crown and root rot. The method comprises applying

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(a) a first active agent selected from the group consisting of

(i) a monoester salt of a phosphorous acid of Formula (I) above, and

(ii) phosphorous acid or an alkali or alkali earth metal salt thereof, and

(b) a benzoporphyrin compound.

The compounds are applied in an amount effective to enhance turf quality and/or protect against crown and root rot. In one embodiment, the active agents applied consist essentially of the monoester salt and the benzoporphyrin compound.

The benzoporphyrin compounds useful in the method of the present invention include substituted and unsubstituted benzoporphyrins and derivatives thereof. Suitable benzoporphyrins include tetrabenzoporphyrine, alkyl-substituted benzoporphyrins, halo-substituted benzoporphyrins, and the like. According to one embodiment, the benzoporphyrin is a coordination complex of the Formula L_1L_2 — X_1X_2 — L_3L_4 , wherein X_1 and X_2 are each H or X_1 and X_2 together are a transition metal, and L_1 , L_2 , L_4 , and L_4 are each substituted or unsubstituted isoindole groups, and wherein L_1 , L_2 , L_3 , and L_4 are covalently joined to one another. In one preferred coordination complex, L_1 , L_2 , L_3 , and L_4 together form a ligand of Formula (II)

$$(R_1)_a$$

$$(R_2)_b$$

$$(R_3)_c$$

$$(R_4)_d$$

$$(R_3)_c$$

wherein a, b, c, and d are each independently selected from positive integers 0-4, and R_1 , R_2 , R_3 , and R_4 are each independently selected from the group consisting of H, halogen, C_{1-20} substituted or unsubstituted, saturated or unsaturated, linear, branched or cyclic alkyl, alkoxy, alkylamino, alkylthio, onium, sulphonium, sulphate, and carboxylate.

The foregoing and other aspects of the present invention are explained in detail in the detailed description set forth below.

DETAILED DESCRIPTION OF THE INVENTION

The methods and compositions described herein are useful for improving turf quality and color in turfgrasses. In addition, the methods and compositions described herein are useful for treating crown and root rot in turfgrass. Crown and root rot, which causes a decline in turfgrass quality during hot, wet weather, is a disease complex apparently caused by Pythium species and Rhizoctonia species in combination with environmental and management stresses.

The first active agent is selected from the group consisting of monoester salts of phosphorous acid and phosphorous acid or alkali or alkali earth metal salts thereof. Monoester salts of phosphorus acids useful for carrying out the present invention, as given in Formula (I) above, are known. See, e.g., U.S. Pat. No. 4,139,616 to Ducret et al. U.S. Pat. No. 4,698,334 to Horriere et al. and U.S. Pat. No. 4,806,445 to Horriere et al. (the disclosures of all U.S. patents cited herein are to be

incorporated herein by reference). Examples include calcium ethyl phosphite, sodium ethyl phosphite, aluminum ethyl phosphite, magnesium isopropyl phosphite, calcium isopropyl phosphite, magnesium ethyl phosphite, magnesium isobutyl phosphite, magnesium sec-butyl phosphite, calcium isobutyl phosphite, aluminum N-butyl phosphite, aluminum sec-butyl phosphite, and aluminum isobutyl phosphite. Most preferred is aluminum ethyl phosphite also called aluminum Iris (0-ethyl phosphonate)).

Alternatively, the first active agent may be phosphorous acid or an alkali or alkali earth metal salt thereof. Suitable alkali or alkali earth metal salts include, for example, lithium, sodium, polassiu, rubidium, cesium, beryllium, magnesium, calcium, strontium, and barium salts of phosphorous acid. The sodium, potassium and calcium salts or phosphorous acid are currently preferred.

Benzoporphyrin compounds are the preferred class of porphine compounds and derivatives thereof, which are useful in the methods of the present invention. Examples of useful porphine compounds include substituted and unsubstituted porphines and derivatives thereof. Suitable derivatives of porphines include substituted and unsubstituted porphyrins. The porphyrins may be benzoporphyrins such as tetrabenzoporphyrins, alkyl-substituted benzoporphyrins, halo-substituted 25 benzoporphyrins, and the like. According to one embodiment, the benzoporphyrin is a coordination complex of the Formula L_1L_2 — X_1X_2 — L_3L_4 , wherein X_1 and X_2 are each H or X_1 and X_2 together are a metal selected from the group consisting of alkali metals, alkali earth metals and transition 30 metals, and L_1 , L_2 , L_3 , and L_4 are each substituted or unsubstituted isoindole groups, and wherein L_1 , L_2 , L_3 , and L_4 are covalently joined to one another (e.g., through a nitrogen or carbon atom, preferably a nitrogen atom). As will be apparent, they are covalently joined as a cyclic structure, i.e. 35 $-L_1-L_3-L_4$ —cy, where 0 means L_4 is covalently joined to L_1 . Preferably, X_1 and X_2 together are a transition metal from Groups IB and VIIIB. The isoindole groups represented by L_1, L_2, L_3 , and L_4 may be unsubstituted, or alternatively, they may be each independently substituted from 1 to 4 times with 40 a substituent selected from the group consisting of halogen, C_{1-20} substituted or unsubstituted, saturated or unsaturated, linear, branched or cyclic alkyl, alkoxy, alkylamino, alky-Ithio, onium, sulphonium, sulphate, and carboxylate.

In one preferred embodiment of the coordination complex 45 of L_1L_2 — X_1X_2 — L_3L_4 , L_1 , L_2 , L_3 , and L_4 together form a ligand of Formula (II)

wherein a, b, c, and d are each independently selected from positive integers 0-4, and R_1 , R_2 , R_3 , and R_4 are each independently selected from the group consisting of H, halogen, C_{1-20} substituted or unsubstituted, saturated or unsaturated, linear, branched or cyclic alkyl, alkoxy, alkylamino, alkylthio, onium, sulphonium, sulphate, and carboxylate.

Examples of suitable benzoporphyrins of the coordination complex L_1L_2 — X_1X_2 — L_3L_4 include phthalocyanine dyes. Suitable phthalocyanine dyes may be metal-free phthalocyanines, or metal phthalocyanines. The metal of metal phthalocyanines may be selected from alkali metals, alkali earth metals and transition metals, with transition metals being preferred. Examples of suitable metals include but are not limited to, lithium, sodium, potassium, rubidium and cesium from the alkali metal family; berillium, magnesium, calcium, strontium, barium, and radium from the alkali earth metal family; and copper, silver, gold, zinc, cadmium, mercury, scandium, yittrium, lanthanum, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molyb-20 denum, tungsten, manganese, technetium, rhenium, iron, ruthenium, osmium, cobalt, rhodium, iridium, nichel, palladium, and platinum from the transition metal family. Copper, nickel, cobalt, iron and zinc phthalocyanine dyes are particularly preferred in the methods of the present invention.

Phthalocyanine dyes which are useful in the methods of the present invention include subsituted and unsubstituted dyes. Suitable substituted phthalocyanine dyes may be metal-tree phthalocyanines, or metal phthalocyanines, and may be substituted from 1 to 4 times on each isoindole group independently. Examples of suitable substituents for the isoindole groups of phthalocyanine dyes include but are not limited to, halogens, substituted or unsubstituted, saturated or unsaturated, linear, branched or cyclic alkyl, alkoxy, alkylamino, alkylthio, onium, sulphonium, sulphate, and carboxylate. Suitable phthalocyanine dyes are commercially available and include but are not limited to Pigment Blue 16, Vat Blue 29. Pigment Blue 15, Heliogen Green GG, Ingrain Blue 14, Ingrain Blue 5, Ingrain Blue 1, Pigment Green 37, and Pigment Green 7. In one preferred embodiment, the phthalocyanine dye is Pigment Blue 15. In another preferred embodiment, the phthalocyanine dye is any phthalocyanine dye other than Pigment Blue 15.

Synergistic combinations of the foregoing two active ingredients (the two together being referred to herein as the "active material") are, in general, 1 part by weight of the compound of Formula (I) above in combination with from 0.01 to 0.1, preferably 0.04 to 0.05. parts by weight of the benzoporphyrin compound. More preferably, the active material includes 1 part by weight of the compound of Formula (I) above in combination with from 0.01 to 0.1 parts by weight of the benzoporphyrin compound. A particularly preferred combination is 1 part by weight of the compound of Formula (I) above in combination with from 0.04 to 0.05 parts by weight of Pigment Blue 15.

The synergistic combinations according to the invention may be used with advantage in admixture with one another or with other known fungicides, such as basic salts or hydroxides of copper (oxychloride, oxysulphate), (tetrahydro)phthalimides (Captan, Captafol, Folpel), methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate (Benomyl), thiophanates such as dimethyl (1,2-phenylene)bis(iminocarbonothioyl)bis(carbamate) (Thiophanate-methyl), tetrachloroisophthalonitrile (Chlorothalonil), 3-(3,5-dichlorophenyl)-N-(1-methylethyl)-2,4-dioxo-1-imidazolidine carboxamide (Iprodione), 1-[2-(2,4dichlorophenyl)4-propyl-1,3-dioxolan-2-yl methyl]-1H-1,2,4-triazole (Propicona-

zole) 1-(4-chlorophenoxy)-3,3-dimethyl-1(1H-1,2,4-triazol-

1-yl)-2-butanone (Triadimafon) or other fungicides, either to complete the range of activity of the compounds according to the invention or to increase their persistence.

The synergistic combinations according to the invention may also be mixed with other fungicidal, anti-mildew phosphorus derivatives, especially 2-hydroxy-1,3,2-dioxaphospholanes, β -hydroxy ethyl phosphites and phosphorous acid and its salts.

For their practical application, the active ingredients in the synergistic combinations are used as part of a formulated ¹⁰ product which, as a rule, contains a support and/or a surfactant in addition to the active material according to the invention.

In the context of the invention, a support is an organic or mineral, natural or synthetic material with which the active 15 material is associated to facilitate its application to plants, seeds or soil, or its transportation and/or handling. The support can be solid (clays, natural or synthetic silicates. resins, waxes, solid fertilizers) or fluid (water, alcohols, ketones, petroleum fractions. chlorinated hydrocarbons, liquefied 20 gases).

The surfactant can be an ionic or non-ionic emulsifier, dispersant or wetting agent such as, for example, salts of polyacrylic acids and lignin-sulphonic acids, condensates of ethylene oxide with fatty alcohols, fatty acids or fatty amines.

The compositions according to the invention can be prepared in the form of wettable powders, soluble powders, dusting powders, granulates, solution, emulsifiable concentrates, emulsions, suspended concentrates and aerosols.

The wettable powders according to the invention can be ³⁰ prepared in such a way that they contain from 20 to 95% by weight of the active material, and they normally contain, in addition to a solid support, from 0 to 5% by weight of a wetting agent, from 3 to 10% by weight of a dispersant and, when necessary, from 0 to 10% by weight of one or more ³⁵ stabilizers and/or other additives, such as penetration agents, adhesives or anti-lumping agents, colorants, etc.

One example of the compositions of a wettable powder is given in Table 1 below:

TABLE 1

Compound	% by wt.
active material	80
sodium lignosulphonate (deflocculant)	5
inionic wetting agent	1
antilumping silica	5
kaolin (filler)	9

Powders soluble in water are obtained by mixing from 20 50 to 95% by weight of the active material, from 0 to 10% of an antilumping agent, the remainder being a hydrosoluble filler mainly a salt.

An example of a composition of the present invention as a soluble powder is given in Table 2 below:

TABLE 2

% by wt.
70
0.5
5
24.5

Aqueous dispersions and emulsions, for example compositions obtained by diluting with water a wettable powder or an emulsifiable concentrate according to the invention, are

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included within the general scope of the invention. These emulsions can be of the water-in-oil type or of the oil-in-water type, and can have a thick consistency resembling that of a "mayonnaise".

The compositions according to the invention can contain other ingredients, for example protective colloids, adhesives or thickeners, thixotropic agents, stabilizers or sequestrants, as well as other active materials known to have pesticidal properties, especially acaricides or insecticides.

The present invention can be practiced with all turfgrasses, including cool season turfgrasses and warm season turfgrasses. Examples of cool season turfgrasses are Bluegrasses (Poa L.), such as Kentucky Bluegrass (Poa pratensis L.), Rough Bluegrass (Poa trivialis L.), Canada Bluegrass (Poa compressa L.), Annual Bluegrass (Poa annua L.), Upland Bluegrass (Poa glaucantha Gaudin), Wood Bluegrass (Poa nemoralis L.). and Bulbous Bluegrass (Poa bulbosa L.); the Bentgrasses and Redtop (Agrostis L.), such as Creeping Bentgrass (Agrostis palustris Huds.), Colonial Bentgrass (Agrostis tenius Sibth.), Velvet Bentgrass (Agrostis canina L.), South German Mixed Bentgrass (Agrostis L.), and Redtop (Agrostis alba L.); the Fescues (Festuca L.), such as Red Fescue (Festuca rubra L.). Chewings Fescue (Festuca rubra var. commutata Gaud.), Sheep Fescue (Festuca ovina L.), Hard Fescue (Festuca ovina var. duriuscula L. Koch), Hair Fescue (Festuca capillata Lam.). Tall Fescue (Festuca arundinacea Schreb.), Meadow Fescue (Festuca elanor L.); the Ryegrasses (Lolium L.), such as Perennial Ryegrass (Lollium perenne L.), Italian Ryegrass (Lolium multiflorum Lam.); the Wheatgrasses (Agropyron Gaertn.), such as Fairway Wheatgrass (Agropyron cristatum (L.) Gaertn.), Western Wheatgrass (Agropyron smithii Rydb.). Other cool season turfgrasses include Beachgrass (Ammophila Host.), Smooth Brome (Bromus inermis Leyss.), Timothy (Phleum L.). Orchardgrass (Dactylis glomerata L.), Crested Dog's-Tail (Cynosurus cristatus L.). Examples of warm season turfgrasses are the Bermudagrasses (Cynodon L. C. Rich), Zoysiagrasses (Zoysia Willd.), St. Augustinegrass (Stenotaphrum secundatum (Wait.) Kuntze), Centipedegrass (Eremochioa ophiuroides (Munro.) Hack.), Carpetgrass (Axonopus Beauv.), Bahiagrass (Paspalum notalum Flugge.), Kikuyugrass (Pennisetum clandestinum Hochst. ex Chiov.), Buffalograss (Buchloe dactyloides (Nutt.) Engelm.), Blue Grama (Bouteloua gracilis (H.B.K.) Lag. ex Steud.), and Sideoats Grama (Bouteloua curtipendula (Michx. Torr.). Cool season 45 turfgrasses are preferred. More preferred is Bluegrass, Bentgrass and Redtop, Fescue, and Ryegrass. Bentgrass is most preferred.

The active materials are, in general, applied to turfgrass either together or separately by spraying a liquid formulation (e.g., an aqueous formulation, including emulsions, or an oil-based formulation) thereof on the turfgrass. The ethylenebisdithiocarbamate contact fungicide is typically applied in an amount of from 10 to 25 pounds per acre (about 10 to 25 Kilograms per Hectare), more preferably in an amount of from 15 to 20 pounds per acre (about 15 to 20 Kg per hectare), and still more preferably in an amount of from 17 to 18 pounds per acre (about 17 to 18 Kg per Hectare). The compound of Formula (I) is, in general, applied in an amount of from about 5 to 17 pounds per acre.

The following examples are provided to illustrate the present invention, and should not be construed as limiting thereof.

EXAMPLES 1-3

These examples were carried out to identify fungicide and combinations thereof which will improve turf quality and

color, and have activity against crown and root rot and brown patch. Fungicides were evaluated on a one-year-old stand of the bentgrass cultivar "Penncross" planted in Raleigh, N.C., U.S.A. The bentgrass was planted in native soil and maintained under conditions similar to a golf green with a mowing 5 height of 0.635 cm (.25 inches). The fungicides which have activity against Pythium species include KOBANTM (active ingredient: etridiazole) obtained from Grace-Sierra, ALIETTETM (active ingredient: fosetyl-Al) obtained from Rhone-Poulenc. and SUBDUETM (active ingredient: metal- 10 axyl) obtained from Ceba-Giegy. The fungicides which have activity against Pythium and Rhizoctonia species is FORETM (active ingredient: mancozeb also including Pigment Blue 15) obtained from Rhom and Haas, MANZATETM (active ingredient: mancozeb) obtained from DuPont, LESCO 15 MN80TM (active ingredient: mancozeb) obtained from Lesco, PENCOZEB DF 75TM (active ingredient: mancozeb) obtained from Elf Atochem, PROTECT DG 80TM (active ingredient: mancozeb) obtained from W. A. Cleary, and DITHANETM (active ingredient: mancozeb) obtained from 20 Rhom and Haas.

The fungicides were applied separately and in combination at labelled rates to 1.5 m×1.5 m (5 ft×5 ft) plots of bentgrass prior to evidence of any decline in turf quality due to crown and root rot. A CO₂ backpack sprayer was used to apply the 25 fungicide treatments at (30 lbs psi) using TEEJETTM 8004 nozzles to apply 9.5 liters (2.5 gallons) of fungicide dilutions per 93 square meters (1000 sq ft). The fungicides were initially applied and subsequently reapplied according to a 14 day schedule. In some experiments, an electrical pump 30 sprayer was used to apply the treatments at 30 psi using a Teejet 8004 nozzle.

Turf quality, color and percent disease ratings were recorded weekly, based on a scale from 1-9, with 9 being ideal turf quality and color and 1 being all turf dead. The percent 35 disease ratings were calculated based on the percent of area in each plot showing symptoms of brown patch. Turf quality and color ratings were used as an indicator of the health of the bentgrass and the amount of decline associated with crown and root rot. Pythium and Rhizoctonia species of fungi were 40 isolated from the bentgrass in the experiment during the test period.

Table 1 below indicates that an improvement in turf quality and color was observed from application of ALIETTETM+ FORETM (treatment #4), with a turf quality of 7.5 and a turf

color of 7.8 with 9 being ideal. The combination of ALIETTETM+MANZATETM had a lower turf quality rating of 6.8 and a turf color of 7.0.

TABLE 1

			Turf		%		
Trt.		Pesticide		Qual-	Turf	Brown	Dis- ease
No.	Name	Formu.	LBai/A	ity	Color	Patch	Con- trol
01	CHECK			4.5	5.3	50.0	0
02	ALIETTE TM	W DG 80	8.712	6.5	6.8	0	100.0
	CHP26019	W DG 50	2.72				
03	ALIETTE TM	WDG 80	8.712	6.8	7.0	0	100.0
	MANZATE	\mathbf{WP}	16.34				
		70 TM					
04	ALIETTE TM	W DG 80	8.712	7.5	7.8	0	100.0
	FORE TM	WP	17.42				
		80 TM					
05	FORE TM	W DG 80	17.42	6.8	7.0	2.5	91.7
06	ALIETTE TM	W DG 80	8.712	5.0	5.8	26.3	38.0
07	ALIETTE TM	W DG 80	4.356	6.8	7.5	0	100.0
	FORE TM	WP	8.712				
		80 TM					
	LSD	0(0.05) =	1.0	.8	9.1	23.5	
	STANDARI	DEVIATIO	N =	.7	.5	6.2	16.1
	COEFF. OF	VARIABILIT	Y =	10.8	8.2	71.2	19.9

Table 2 below indicates that similar results were observed in a second test. The data demonstrate that ALIETTETM+ FORETM (treatment #8) gave better turf quality of 7.8 and 8.0 than ALIETTETM+mancozeb+AURAGREENTM (another type of green dye) (treatment #5) of 7.0 and 7.3. The combination of the experimental formulation of ALIETTETM and the blue pigment EXP 10622)+mancozeb (treatment#10) gave higher turf quality ratings of 7.5 and 8.0 than treatment #5. and ratings as high as the ratings for ALIETTETM+ FORETM.

TABLE 2

ALIETTE TM/FORE TM Interaction													
	Pesticide		Application	Phyto	Turf	% Brown	Turf	Turf	% Brown				
o. Name Formu. LBai/A Type		rating	Qual.	Patch	Qual.	Color	Patch						
CONTROL				1.0	5.0	25.0	5.3	6.3	15.0				
NCAD 1	SG 100	0.545	14 DAY	1.0	4.8	21.3	5.0	7.5	16.3				
NCAD 1	SG 100	0.545	14 DAY	1.8	5.8	15.0	6.3	7.5	5.0				
ALIETTE TM	WDG 80	8.712	14 DAY										
NCAD 1	SG 100	0.545	14 DAY	1.3	6.3	7.5	6.8	7.8	0				
MANCOZEB	WDG 80	17.43	14 DAY										
NCAD 1	SG 100	0.545	14 DAY	5.5	7.0	2.5	7.3	6.8	0				
MANCOZEB	WDG 80	17.43	14 DAY										
ALIETTE TM	WDG 80	8.712	14 DAY										
ALIETTE TM	WDG 80	8.712	14 DAY	2.5	5.3	16.3	6.0	6.3	25				
MANCOZEB	WDG 80	17.43	14 DAY	2.0	6.0	13.8	6.5	6.8	8.8				
ALIETTE TM	WDG 80	8.712	14 DAY	1.0	7.8	0	8.0	8.0	0				
FORE TM	WP 80 TM	17.43	14 DAY										
EXP10622	WDG 80	8.712	14 DAY	15	5.8	10.0	6.5	6.8	6.3				
	CONTROL NCAD 1 NCAD 1 ALIETTE TM NCAD 1 MANCOZEB NCAD 1 MANCOZEB ALIETTE TM ALIETTE TM ALIETTE TM ALIETTE TM HANCOZEB ALIETTE TM COZEB ALIETTE TM	Name Formu. CONTROL — NCAD 1 SG 100 NCAD 1 SG 100 ALIETTE ™ WDG 80 NCAD 1 SG 100 MANCOZEB WDG 80 NCAD 1 SG 100 MANCOZEB WDG 80 ALIETTE ™ WDG 80 MANCOZEB WDG 80 ALIETTE ™ WDG 80 ALIETTE ™ WDG 80 FORE ™ WP 80 ™	Name Formu. LBai/A CONTROL — — NCAD 1 SG 100 0.545 NCAD 1 SG 100 0.545 ALIETTE ™ WDG 80 8.712 NCAD 1 SG 100 0.545 MANCOZEB WDG 80 17.43 NCAD 1 SG 100 0.545 MANCOZEB WDG 80 17.43 ALIETTE ™ WDG 80 8.712 MANCOZEB WDG 80 17.43 ALIETTE ™ WDG 80 8.712 MANCOZEB WDG 80 8.712 FORE ™ WP 80 ™ 17.43	Pesticide Application Name Formu. LBai/A Type CONTROL — — — NCAD 1 SG 100 0.545 14 DAY NCAD 1 SG 100 0.545 14 DAY ALIETTE ™ WDG 80 8.712 14 DAY NCAD 1 SG 100 0.545 14 DAY MANCOZEB WDG 80 17.43 14 DAY MANCOZEB WDG 80 8.712 14 DAY ALIETTE ™ WDG 80 8.712 14 DAY MANCOZEB WDG 80 8.712 14 DAY MANCOZEB WDG 80 8.712 14 DAY ALIETTE ™ WDG 80 8.712 14 DAY ALIETTE ™ WDG 80 8.712 14 DAY FORE ™ WP 80 ™ 17.43 14 DAY	Pesticide Application Phyto Name Formu. LBai/A Type rating CONTROL — — — 1.0 NCAD 1 SG 100 0.545 14 DAY 1.0 NCAD 1 SG 100 0.545 14 DAY 1.8 ALIETTE ™ WDG 80 8.712 14 DAY 1.3 MANCOZEB WDG 80 17.43 14 DAY 5.5 MANCOZEB WDG 80 17.43 14 DAY 4 ALIETTE ™ WDG 80 8.712 14 DAY 2.5 MANCOZEB WDG 80 8.712 14 DAY 2.5 MANCOZEB WDG 80 8.712 14 DAY 2.0 ALIETTE ™ WDG 80 8.712 14 DAY 1.0 FORE ™ WP 80 ™ 17.43 14 DAY 1.0	Pesticide Application Phyto Turf Name Formu. LBai/A Type rating Qual. CONTROL — — — 1.0 5.0 NCAD 1 SG 100 0.545 14 DAY 1.0 4.8 NCAD 1 SG 100 0.545 14 DAY 1.8 5.8 ALIETTE ™ WDG 80 8.712 14 DAY 1.3 6.3 MANCOZEB WDG 80 17.43 14 DAY 5.5 7.0 MANCOZEB WDG 80 8.712 14 DAY 2.5 5.3 MANCOZEB WDG 80 8.712 14 DAY 2.5 5.3 MANCOZEB WDG 80 17.43 14 DAY 2.0 6.0 ALIETTE ™ WDG 80 8.712 14 DAY 1.0 7.8 FORE ™ WP 80 ™ 17.43 14 DAY 1.0 7.8	Pesticide Application Phyto Turf % Brown Name Formu. LBai/A Type rating Qual. Patch CONTROL — — — 1.0 5.0 25.0 NCAD 1 SG 100 0.545 14 DAY 1.0 4.8 21.3 NCAD 1 SG 100 0.545 14 DAY 1.8 5.8 15.0 ALIETTE ™ WDG 80 8.712 14 DAY 1.3 6.3 7.5 MANCOZEB WDG 80 17.43 14 DAY 5.5 7.0 2.5 MANCOZEB WDG 80 8.712 14 DAY 2.5 5.3 16.3 MANCOZEB WDG 80 8.712 14 DAY 2.5 5.3 16.3 MANCOZEB WDG 80 17.43 14 DAY 2.0 6.0 13.8 ALIETTE ™ WDG 80 8.712 14 DAY 1.0 7.8 0 FORE ™ WP 80 ™ 17.43 14 DAY 1.	Pesticide Application Phyto Turf % Brown Turf Name Formu. LBai/A Type rating Qual. Patch Qual. CONTROL — — — 1.0 5.0 25.0 5.3 NCAD 1 SG 100 0.545 14 DAY 1.0 4.8 21.3 5.0 NCAD 1 SG 100 0.545 14 DAY 1.8 5.8 15.0 6.3 ALIETTE ™ WDG 80 8.712 14 DAY 1.3 6.3 7.5 6.8 MANCOZEB WDG 80 17.43 14 DAY 5.5 7.0 2.5 7.3 MANCOZEB WDG 80 8.712 14 DAY 2.5 5.3 16.3 6.0 MANCOZEB WDG 80 8.712 14 DAY 2.5 5.3 16.3 6.0 MANCOZEB WDG 80 8.712 14 DAY 2.0 6.0 13.8 6.5 ALIETTE ™ WDG 80 8.712	Pesticide Application Phyto Turf % Brown Turf Turf Name Formu. LBai/A Type rating Qual. Patch Qual. Color CONTROL — — — 1.0 5.0 25.0 5.3 6.3 NCAD 1 SG 100 0.545 14 DAY 1.0 4.8 21.3 5.0 7.5 NCAD 1 SG 100 0.545 14 DAY 1.8 5.8 15.0 6.3 7.5 ALIETTE ™ WDG 80 8.712 14 DAY 1.3 6.3 7.5 6.8 7.8 MANCOZEB WDG 80 17.43 14 DAY 5.5 7.0 2.5 7.3 6.8 MANCOZEB WDG 80 8.712 14 DAY 2.5 5.3 16.3 6.0 6.3 MANCOZEB WDG 80 8.712 14 DAY 2.5 5.3 16.3 6.0 6.3 MANCOZEB WDG 80 8.712 <td< td=""></td<>				

TABLE 2-continued

		ALI	ETTE TM/FOR	E TM Inte	eraction				
		7 11.71	ETTE TOR		<u> </u>				
Trt	Pesticide		_Application	Phyto	Turf	% Brown	Turf	Turf	% Brown
No. Name	Formu.	LBai/A	Type	rating	Qual.	Patch	Qual.	Color	Patch
10 EXP10622 MANCOZEB	WDG 80 WP 80 TM	8.712 17.43	14 DAY 14 DAY	3.3	7.5	0	8.0	7.5	0
	LDS (0.05)		.8	1.0	9.4	.6	1.0	6.8	
STAN	NDARD DEV	=	.6	.7	6.5	.4	.7	4.7	
COEF	FF. OF VARIA	=	27.2	11.0	58.4	5.9	9.4	87.3	

Table 3 is a comparative study of the effects of different formulations of mancozeb. The formulations of FORETM 15 WP80TM and FL4.0TM, which contain mancozeb +Pigment Blue 15. gave better turf quality and turf color than other formulations of mancozeb without the Pigment Blue 15. Treatment #7 of ALIETTETM+FORETMFL4.0+BLEN-DEXTM (a blending agent) gave better results. Treatment #7 20 contains more Pigment Blue 25 than treatment #2.

$$\begin{bmatrix} R - O - P - O \end{bmatrix}_n Me^{n+1}$$

TABLE 3

	ALIETTE TM/MANCOZEB Interactions														
Trt.		Pesticide		Appli- cation	Turf Qual-	Turf Col-	% Brown	Turf Qual-	Turf Col-	% Brown	Turf Qual-	Turf Col-	% Brown	Turf Qual-	Turf Col-
No.	Name	Formu.	LBai/A	Type	ity	or	Patch	ity	or	Patch	ity	or	Patch	ity	or
01	CONTROL				3.8	4.5	60.0	3.3	4.0	67.5	2.8	3.8	75.0	4.8	6.3
02	ALIETTE TM	WDG~80	8.712	14 DAY	7.0	7.0	10.0	7.8	7.5	5.0	7.3	7.0	5.0	7.0	6.8
	FORE TM	WP 80	17.42	14 DAY											
03	ALIETTE TM	WDG 80	8.712	14 DAY	6.0	6.3	12.5	6.0	6.0	1.3	6.0	6.0	8.8	5.8	53
	LESCO MN	DG 80	17.42	14 DAY											
04	ALIETTE TM	WDG 80	8.712	14 DAY	6.3	6.5	13.8	6.0	6.0	2.5	6.0	6.3	12.5	6.0	5.5
	PENCOZES	DF 75	17.42	14 DAY											
05	ALIETTE TM	WDG 80	8.712	14 DAY	6.0	6.5	11.3	6.3	6.3	5.0	6.3	6.3	8.8	5.8	5.3
	PROTECT	DG 80	17.42	14 DAY											
06	ALIETTE TM	WDG~80	8.712	14 DAY	6.8	7.0	6.3	6.8	6.8	7.5	7.3	7.8	3.8	7.5	7.5
	FORE TM	F1 4.0 TM	17.42	14 DAY											
07	ALIETTE TM	WDG 80	8.712	14 DAY	7.0	7.3	5.0	8.5	7.8	0	8.0	8.0	1.3	8.0	8.0
	FORE TM	F1 4.0 TM	17.42	14 DAY											
	BLENDEX	% C		14 DAY											
08	ALIETTE TM	WDG 80	8.712	14 DAY	4.3	4.8	46.3	5.8	6.0	2.5	5.8	5.8	17.5	6.0	5.5
	DITHANE	WDG 75	17.42	14 DAY											
09	LESCO MN	DG 80	17.42	14 DAY	4.8	5.5	21.3	5.0	5.3	8.8	4.8	4.8	22.5	5.8	6.0
		LDS(0.05) =	:		1.0	.7	21.3	.5	.7	10.3	.7	.6	9.1	.7	1.1
	STA	NDARD DEVIA	TION =		.7	.5	14.6	.4	.5	7.0	.5	.4	6.2	.5	.7
	COE	FF. OF VARIAB	ILITY =		11.7	8.3	70.6	5.8	7.4	63.3	8.5	6.6	36.1	7.6	11.6

Overall, the results indicate that the combination of ALIETTETM+FORETM. containing the Pigment Blue 15. provides a better improvement in turf quality and color over other combinations of ALIETTETM and mancozeb without the Pigment Blue 15. The results demonstrate that the presence of the Pigment Blue 15, enhances the activity of the ALIETTETM and mancozeb in a synergistic interaction.

The foregoing is illustrative of the present invention and is not to be construed as limiting thereof. The invention is defined by the following claims, with equivalents of the claims to be included therein.

That which is claimed is:

- 1. A method of combatting fungi and enhancing turf quality in turfgrass which comprises applying to said turfgrass synergistic fungicidally effective amounts of:
 - (a) a first active agent selected from the group consisting of 65 cyanine compound is Pigment Blue 15.
 - (i) 1 part by weight of a monoester salt of a phosphorous acid of Formula (I):

wherein:

R is an alkyl radical having 2 to 4 carbon atoms,

Me is an alkali metal, alkaline earth, or aluminum atom, and

n is a whole number from 1 to 3 equal to the valence of Me;

- (ii) phosphorous acid or an alkali or alkali earth metal salt thereof; and
- (b) from 0.01 to 0.1 parts by weight of a phthalocyanine compound,
- wherein said method does not include the application of an ethylenebisdithiocarbamate contact fungicide.
- 2. The method according to claim 1, wherein said step of applying comprises applying 1 part by weight of said first active agent, and 0.05 parts by weight of said phthalocyanine compound.
- 3. The method according claim 1, wherein said phthalocyanine compound is Pigment Blue 15.
- 4. The method according to claim 1, wherein said phthalocyanine compound is not Pigment Blue 15.

- 5. The method according to claim 1, wherein said step of applying is carried out by applying said first active agent and said phthalocyanine compound to said turfgrass together in a common carrier.
- 6. The method according to claim 1, wherein said turfgrass 5 is bentgrass.
- 7. The method according to claim 1, wherein said turfgrass is bermudagrass.
- 8. The method according to claim 1, wherein said first active agent is applied to said turfgrass in an amount of from about 8 to about 16 pounds active ingredient per acre, and said phthalocyanine compound is applied to said turfgrass in an amount of from about 0.2 to about 0.8 pounds per acre.
- [9. The method according to claim 1 consisting essentially of applying to said turfgrass, said first active agent in an amount of from about 8 to about 16 pounds active ingredient per acre, and said phthalocyanine compound in an amount of from about 0.2 to about 0.8 pounds per acre.]
- 10. A fungicidal composition [tier] for enhancing turf quality [which comprises] wherein the active material present in synergistic fungicidally effective amounts [of an active material comprising] consists essentially of:
 - (a) 1 part by weight of a first active agent selected from the group consisting of
 - (i) a monoester salt of a phosphorous acid of Formula (I):

$$\begin{bmatrix} R - O - P - O \end{bmatrix}$$

$$\begin{bmatrix} R - O - P - O \end{bmatrix}$$

$$\begin{bmatrix} Me^{n+} \\ 0 \end{bmatrix}$$

wherein:

R is an alkyl radical having 2 to 4 carbon atoms,

Me is an alkali metal, alkaline earth, or aluminum atom, and

- n is a whole number from 1 to 3 equal to the valence of Me; and
- (ii) phosphorous acid or an alkali or alkali earth metal salt thereof; and
- (b) from 0.01 to 0.1 parts by weight of a phthalocyanine compound

wherein the composition does not include an ethylenebis- 45 dithiocarbamate contact fungicide.

- 11. The composition according to claim 10, wherein said first active agent is said monoester salt of phosphorous acid, and R is selected from the group consisting of ethyl, propyl, and butyl.
- 12. The composition according to claim 10, wherein said first active agent is said monoester salt of phosphorous acid, and Me is selected from the group consisting of aluminum, calcium, magnesium, and sodium.
- 13. The composition according to claim 10, wherein said 55 first active agent is said monoester salt of phosphorous acid, and said compound of Formula (I) is selected from the group consisting of calcium ethyl phosphite, sodium ethyl phosphite, aluminum ethyl phosphite, magnesium isopropyl phosphite, calcium isopropyl phosphite, aluminum isopropyl phosphite, magnesium ethyl phosphite, magnesium isobutyl phosphite, aluminum N-butyl phosphite, aluminum sec-butyl phosphite, aluminum N-butyl phosphite, aluminum sec-butyl phosphite, and aluminum isobutyl phosphite.
- 14. The composition according to claim 10, wherein said 65 first active agent is said monoester of phosphorous acid, and said compound of Formula (I) is aluminum ethyl phosphite.

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- 15. The composition according to claim 10, wherein said phthalocyanine compound is selected from the group consisting of Pigment Blue 16, Vat Blue 29, Pigment Blue 15, Heliogen Green GG. Ingrain Blue 14, Ingrain Blue 5, Ingrain Blue 1, Pigment Green 37, and Pigment Green 7.
- 16. The composition according to claim 10, wherein said phthalocyanine compound is Pigment Blue 15.
- 17. The composition according to claim 14, wherein said phthalocyanine compound is not Pigment Blue 15.
- [18. The composition according to claim 10, comprising 1 part by weight of said first active agent and between about 0.01 and about 0.1 parts by weight of said phthalocyanine compound.]
- [19. The composition according to claim 10, consisting essentially of 1 part by weight of said first active agent and between about 0.01 and about 0.1 parts by weight of said phthalocyanine compound.]
- 20. The composition according to claim 10, wherein said composition is an aqueous suspension.
- 21. The composition according to claim 10, wherein said composition is a wettable powder.
- 22. The method according to claim 1, wherein said first active agent comprises ethyl aluminum phosphite and said phthalocyanine compound comprises Pigment Blue 15.
 - 23. The composition according to claim 10, wherein said first active agent comprises ethyl aluminum phosphite and said phthalocyanine compound comprises Pigment Blue 15.
- 24. A method of combatting fungi and enhancing turf quality in turfgrass which comprises applying to said turfgrass synergistic fungicidally effective amounts of:
 - (a) I part by weight of a first active agent selected the group consisting of phosphorous acid or an alkali or alkali earth metal salt thereof; and
 - (b) from 0.01 to 0.1 parts by weight of a phthalocyanine compound,
 - wherein said method does not include the application of an ethylenebisdithiocarbamate contact fungicide.
- 25. The method according to claim 24, wherein said step of applying comprises applying 1 part by weight of said first active agent, and 0.05 parts by weight of said phthalocyanine compound.
 - 26. The method according claim 24, wherein said phthalocyanine compound is Pigment Blue 15.
 - 27. The method according to claim 24, wherein said phthalocyanine compound is not Pigment Blue 15.
- 28. The method according to claim 24, wherein said step of applying is carried out by applying said first active agent and said phthalocyanine compound to said turfgrass together in a common carrier.
 - 29. The method according to claim 24, wherein said turfgrass is bentgrass.
 - 30. The method according to claim 24, wherein said turfgrass is bermudagrass.
 - 31. The method according to claim 24, wherein said first active agent is applied to said turfgrass in an amount of from about 8 to about 16 pounds active ingredient per acre, and said phthalocyanine compound is applied to said turfgrass in an amount of from about 0.2 to about 0.8 pounds per acre.
 - 32. A fungicidal composition for enhancing turf quality wherein the active material present in synergistic fungicidally effective amounts consists essentially of:
 - (a) I part by weight of a first active agent selected from the group consisting of phosphorous acid or an alkali or alkali earth metal salt thereof; and
 - (b) from 0.01 to 0.1 parts by weight of a phthalocyanine compound, and

wherein the composition does not include an ethylenebisdithiocarbamate contact fungicide.

- 33. The composition according to claim 32, wherein said phthalocyanine compound is selected from the group consisting of Pigment Blue 16, Vat Blue 29, Pigment Blue 15, Heliogen Green GG, Ingrain Blue 14, Ingrain Blue 5, Ingrain Blue 1, Pigment Green 37, and Pigment Green 7.
- 34. The composition according to claim 32, wherein said phthalocyanine compound is Pigment Blue 15.

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- 35. The composition according to claim 32, wherein said phthalocyanine compound is not Pigment Blue 15.
- 36. The composition according to claim 32, wherein said composition is an aqueous suspension.
- 37. The composition according to claim 32, wherein said composition is a wettable powder.

* * * *