Advances in Fungicides and Fungicide Mixtures
1882 - Bordeaux mixture was discovered by chance...in 1870 American grape nursery stock was imported into France to help combat grapevine phylloxera, but introduced grapevine downy mildew, *Plasmopara viticola*. Millardet noticed that grapes treated with an ‘ugly’ mixture of lime and copper sulfate to prevent grape thieves, also were not affected by downy mildew...
Bordeaux mixture was the first fungicide used in turf, in 1917 originally for brown patch disease (Piper and Coe, USDA).

1913 - first organic mercury fungicides were introduced, but not used in turf until later in the 1920’s; the first was Semesan (chlorophenol mercury) for dollar spot control.
History of Fungicide Development

- 1927 - organic and inorganic mercury compounds became standard turf disease control materials.
- 1934 - the first synthetic organic fungicides, the dithiocarbamates, were discovered. These materials were developed for vulcanization of rubber...
- The first was ‘tetramethylthiuram’ or Thiram. The black iron salt was ‘Ferbam’ and the white zinc salt was ‘Ziram’.
History of Fungicide Development

- **1943** - ethylene bis dithiocarbamates were discovered. The zinc salt was Zineb, the first stable EBDC fungicide. The manganese salt was Maneb, and eventually a manganese-zinc complex EBDC was Mancozeb (1961)

- **1952** - the first carboximide fungicides, Captan and Folpet, were discovered.
History of Fungicide Development

- 1964-1975 - the first ‘systemic’ fungicides were developed.
- 1964 - oxathiin fungicides, carboxin and oxycarboxin were developed. Use as seed treatments mostly.
- 1969 - benzimidazole fungicides, including thiabendazole, benomyl, and later, thiophanate ethyl and methyl fungicides.
- 1972 - chorothalonil, from Diamond Alkali Co. was developed.
History of Fungicide Development

• 1973 - the first SBI fungicide, triadimenol, was developed. Soon after, triadimefon (Bayleton) was developed.
• 1974-75 – dicarboximides: iprodione and vinclozolin
• 1979 - propiconazole (Banner)
• 1982 - cyproconazole (Sentinel)
• 1986 - myclobutanil (Eagle) and tebuconazole (Lynx)
History of Fungicide Development
- Interspersed in the ‘70’s were:

- 1977 - fosetyl Al (Aliette) - phosphonate class
- 1977 - metalaxyl (Subdue, Ridomil) - phenylamide class
- 1978 - propamocarb (Banol) - carbamate class
Development - Next Generation Fungicides:

- 1993 - flutolanil (Prostar) - benzamide fungicide, narrow spectrum of activity for Basidiomycete fungi
- 1996 - first strobilurin fungicide, azoxystrobin, sold for turf disease control
- 1999 - second strobilurin fungicide, trifloxystrobin (Compass)
- 2003 - third strobilurin, Insignia
- 2006 – fourth strobilurin, fluoxastrobin (DisArm 480 SC – from Arysta)
- 2007 – triticonazole and metconazole
Modern Fungicide Development

**Sources from natural products:**

- Antibiotics, such as cyclohexamide (Actidione-thiram)
- Polyoxin D (Endorse) – discovered in 1970 from Streptomyces in Japan
- Phenylpyrrole fungicides – Medallion, derived from a Pseudomonas species
- Strobilurin fungicides – azoxystrobin, trifloxystrobin, pyraclostrobin – active moiety discovered as a natural fungicide from Strobilurus tenacellus
Fungicides - characteristics of importance

- Fungicide Chemical Family
- Modes of Action - topical or physical (contact or penetrant) activity of the fungicide
- Biochemical or physiological modes of action
- Strengths/ weaknesses for particular diseases
- Potential for resistance/tolerance
- Non target effects, if any
<table>
<thead>
<tr>
<th>Chemical Class</th>
<th>Examples</th>
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<tbody>
<tr>
<td>Aromatic Hydrocarbons</td>
<td>Ethazole, PCNB, chloroneb</td>
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<tr>
<td>Benzimidazoles</td>
<td>Benomyl, thiophanate methyl</td>
</tr>
<tr>
<td>Carboximides</td>
<td>Flutolanil, carboxin, oxycarboxin, boscalid</td>
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<tr>
<td>Demethylation Inhibitors (DMI) Fungicides</td>
<td>Triadimefon, propiconazole, cyproconazole, myclobutanil, tebuconazole, triticonazole, metconazole, fenarimol</td>
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<tr>
<td>Dicarboximides</td>
<td>Iprodione, vinclozolin</td>
</tr>
<tr>
<td>Dithiocarbamates and carbamates</td>
<td>Captan, maneb, mancozeb, propamocarb, thiram</td>
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<tr>
<td>Nitriles</td>
<td>Chlorothalonil</td>
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<tr>
<td>Phenylamides</td>
<td>Metalaxyl, mefanoxam</td>
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<tr>
<td>Phenylpyrrole</td>
<td>Medallion</td>
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<tr>
<td>Phosphonates</td>
<td>Fosetyl Al, generic phosphite fungicides</td>
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<tr>
<td>Strobilurins (Qoi, methoxyacrylates)</td>
<td>Azoxystrobin, trifloxystrobin, pyraclostrobin, fluoxastrobin...</td>
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<tr>
<td>Cyanoimidazole (Qii)</td>
<td>Cyazofamid (Segway)</td>
</tr>
<tr>
<td>Carboxilic acid amide</td>
<td>Fluopicolide (with propamocarb in Stellar)</td>
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</table>
Fungicide Topical (Physical) Modes of Action -

- Contact - remains on outside of plant

- Penetrant - gets into plant in some fashion
Fungicide Topical (Physical) Modes of Action - Penetrants

- acropetal penetrant, xylem mobile, - upwardly mobile
- localized penetrant - penetrates plant surfaces but does not move in xylem
- Systemic - mobile throughout the plant; xylem and phloem mobile
Fungicide Topical (Physical) Modes of Action

- Other physical attributes of some fungicides includes movement in vapor phase (gas)…some DMI’s, chlorothalonil, strobilurins to various degrees: trifloxystrobin (Compass), pyraclostrobin
- Affinity for waxes on/in leaves – trifloxystrobin (Compass), pyraclostrobin (Insignia)
Transportation in Xylem

- Distribution pattern and extent of movement is determined by the gradient in the water potential between soil and air...evapotranspiration

- Factors controlling the intensity of transpiration: relative humidity, temperature, light, phytohormones...
Transportation in Xylem

- Substances are accumulated at sites of high transpiration – at tips and leaf margins
- Transport into plant organs with negligible transpiration (fruits and young leaves) is limited
- Xylem-mobile substances do not move downward from expanded leaves
DMI or SBI Fungicides - characteristics

- broad spectrum of activity, but especially strong against ascomycete fungi
- rapid xylem-mediated translocation (51% of $^{14}$C-labeled triadimefon to upper leaf in 12 days)
- rainfast – only 40% triadimefon was removable with water 45 minutes after application
# Sterol Biosynthesis Inhibitors (SBI’s) - subclasses

<table>
<thead>
<tr>
<th>Subclass</th>
<th>Turf Fungicide</th>
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<tr>
<td><strong>Pyrimidines</strong></td>
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<tr>
<td>fenarimol</td>
<td>Rubigan</td>
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<tr>
<td>fluorprimidol</td>
<td>Cutless</td>
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<tr>
<td><strong>Triazoles</strong></td>
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<tr>
<td>paclobutrazol</td>
<td>Turf Enhancer, Trimmit</td>
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<td>metconazole</td>
<td>Tourney</td>
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<td>tebuconazole</td>
<td>Lynx</td>
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<td>triticonazole</td>
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<tr>
<td><strong>Imidazoles</strong></td>
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<td>- none-</td>
</tr>
<tr>
<td>prochloraz</td>
<td>- none-</td>
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</table>
Triadimefon - trade name Bayleton

Chemical Class:
SBI (DMI), subclass triazole

labeled for dollar spot,
brown patch suppression, copper
spot, powdery mildew, rusts,
southern blight, anthracnose, stripe smut,
Fusarium blight, summer patch,
large patch of zoysia, bermudagrass decline,
Fusarium patch, Typhula
blight, red thread, take-all patch, and fairy ring

Upwardly mobile in plant
Propiconazole - trade name *Banner Maxx*

Chemical Class: SBI (DMI), subclass triazole

labeled for dollar spot, anthracnose, powdery mildew, brown patch, stripe smut, gray leaf spot, melting out and leafspot, summer patch, necrotic ring spot, Fusarium patch, Typhula blight, red thread, take-all patch, spring dead spot

\[ \text{CH}_3\text{CH}_2\text{CH}_2 \]

Upwardly mobile in plant
Myclobutanil - trade name *Eagle*

**Chemical Class:**
SBI (DMI), subclass triazole

labeled for anthracnose, dollar spot, copper spot, brown patch, necrotic ring spot, powdery mildew, rusts, red thread, spring dead spot

Upwardly mobile in plant
Fenarimol - trade name *Rubigan*

Chemical Class:
DMI, subclass pyrimidine

labeled for dollar spot, copper spot, brown patch, necrotic ring spot, Fusarium blight, Fusarium patch, Typhula blight, red thread, take-all patch, spring dead spot

Upwardly mobile in plant
Metconazole - trade name Tourney

Chemical Class:
DMI, subclass triazole

labeled for dollar spot, brown patch, anthracnose, necrotic ring spot, Fusarium patch, Typhula blight, red thread, fairy ring

Upwardly mobile in plant
Triticonazole - trade names ‘Trinity’, Triton Flo, and Chipco Triton

Chemical Class:
DMI, subclass triazole

Dollar spot, anthracnose, brown patch, Rust, powdery mildew, red thread, pink Patch, leaf spot, summer patch, take-all Patch, necrotic ring spot, yellow patch, Large patch, brown ring patch, algae & Summer decline

Upwardly mobile in plant
Tebuconazole - trade name ‘Lynx’

Chemical Class:
DMI, subclass triazole

* Not labeled in turf to date
Upwardly mobile in plant
# Spectrum of Activity/Labels

<table>
<thead>
<tr>
<th>Disease</th>
<th>Banner</th>
<th>Bayleton</th>
<th>Eagle</th>
<th>Rubigan</th>
<th>Tourney</th>
<th>Trinity</th>
<th>Triton Flo</th>
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<td>Eagle</td>
<td>Rubigan</td>
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</table>
Non-target Effects of Fungicides

- Increase in non-target diseases
- Fungicide-enhanced disease resurgence
- Hormonal effects of fungicides
- Phytotoxic effects
Non-target Effects of Fungicides – positive physiological effects

- benzimidazoles – showed anti-senescence activity in vegetables, wheat and oats
- benzimidazoles inhibit degradation of chlorophyll
- benzimidaoles showed an increase in yield of wheat (3%) in absence of disease – concluded cytokinin and anit-oxidant activity
Non-target Effects of Fungicides – DMI fungicides

- block gibberellic acid biosynthesis
- inhibit plant sterol biosynthesis, which retards growth
- so, DMI’s typically increase leaf thickness, increase epicuticular wax, increase chloroplasts, change root/shoot ratios
- some of these effects are positive – increased stress tolerance in some plants
Non-target Effects of Fungicides – negative physiological effects of DMI’s

- thinning of bentgrass, Poa, and bermudagrass turf which can lead to increased algae

- inhibition of seed germination with some DMI’s (Rubigan, Sentinel)
## 2006 Dollar Spot Trial/ Crenshaw

<table>
<thead>
<tr>
<th>No.</th>
<th>Name</th>
<th>Rate</th>
<th>Rate Unit</th>
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## Tourney + Daconil/ Dollar Spot

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<td>0.5 c</td>
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<td>4.8 b</td>
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Prevention of fairy ring caused by *Lycoperdon perlatum* in ‘A-1’ creeping bentgrass with DMIs. 2007

**Data is averaged across all application timings**

Miller and Tredway, 2007
Fungicides Currently Labeled for Fairy Ring

- Azoxystrobin (Heritage)
- Flutolanil (Prostar)
- Pyraclostrobin (Insignia)
- Fluoaxostrobin (DisArm)
- Polyoxin D (Endorse)
- Bayleton Flo
- Triticonazole (Trinity)
- Metconazole (Tourney)
**Boscalid** – trade name *Emerald*

Class: Carboxamide or anilide  
MOA: inhibits succinate ubiquinone reductase (complex II) in respiration pathway

Systemic activity (xylem mobile)

Diseases:  
Dollar spot and dead spot  
Rates: 0.13-0.18 oz/1000 sq.ft.

Limited to 1.1 oz/1000 sq.ft./year  
(= 6 apps at 0.18 oz rate)
All strobilurin fungicides work by inhibition of cellular respiration -

these fungicides bind to the $Q_o$ site of cytochrome b of the respiration cytochrome bc1 complex on the outside of mitochondrial membranes

these strobilurin fungicides belong to the $Q_o$I ‘cross resistance’ group
Strobilurin fungicides developed from natural fungicides produced by certain mushroom fungi (*Strobilurus tenacellus*, *Oudemansiella mucida*).

Strobilurin A

Active moiety

Natural products degraded rapidly by sunlight
Figure 12. Phosphor image showing redistribution of radiolabelled strobilurins in wheat following application 3 days previously.
Physical Modes of Action of Strobilurins

- Azoxystrobin (Heritage) is xylem-mobile (acropetal penetrant)... it is gradually taken into plant surfaces, with 3-25% taken into the plant within 24 hours of application.

- Trifloxystrobin (Compass) is not xylem-mobile; mode of action described as 'mesostemic', but it is strongly lipophilic and has activity via vapor activity.
Physical Modes of Action of Strobilurins

- Pyraclostrobin (Insignia) is similar to trifloxystrobin (Compass) - not xylem mobile, but very strongly lipophilic. Described as ‘locostemic’, pyraclostrobin is strongly bound to leaf waxes, and is very strongly rainfast.

- Fluoxastrobin (DisArm) is also xylem-mobile
Azoxystrobin - Heritage

Chemical Class: strobilurines

labeled for anthracnose, brown patch, yellow patch, Fusarium patch, gray snow mold, leaf spot, melting out, necrotic ring spot, pink snow mold, Pythium blight, Pythium root rot, red thread, large patch, spring dead spot, summer patch, take-all patch

Upward mobility in plant

* 1st penetrant with Rhizoctonia and Pythium activity
Trifloxystrobin - trade name *Compass*

Chemical class: strobilurins

Brown patch, anthracnose, red thread, pink patch, leaf spot, fusarium patch, summer patch

local penetrant ("mesostemic")
Pyraclostrobin (BAS 500F) - trade name *Insignia*

Chemical class - strobilurins
translaminar absorption/locosystemic

Turf diseases: brown patch, large patch,
Yellow patch, Pythium blight, pink snow mold,
Fusarium patch, gray snow mold, gray leaf spot,
anthracnose, take-all patch, summer patch, spring
dead spot, red thread, leaf spot (Helminthosporium), rusts,
suppression of dollar spot

Proposed use rates - 0.5 to 0.9
oz prod/M (max. 5.5 oz/season)
Chemical Class: strobilurines

labeled for anthracnose, brown patch, large patch, Fusarium patch, gray snow mold, leaf spot, melting out, pink snow mold, Gray snow mold, Pythium blight, Pythium root rot, red thread, pinkpatch, spring dead spot, summer patch, take-all patch and southern blight

Use rates: 0.18-0.37 oz/1000 sq.ft
Max of 64 oz/acre/year

Upward mobility in plant
Disarm formulations for brown patch in A1 bentgrass

Martin, 2009
Pythium fungicides

- Phospites (many labels)
- Segway (cyazofamid)
- Stellar (fluopicolide + propamocarb)
Cyazofamid – trade name **Segway** (3.33 lb/gal SC)

Class: cyanoimidazole
MOA: mitochondrial complex III at Qi center

Pythium blight
Pythium damping-off
Pythium root dysfunction

Label indicates “limited systemic activity”

Label rates:
0.45-0.9 fl oz/1000 sq.ft., 14-21 day
≤ 3 sequential applications
Segway (cyazofamid) for Pythium blight control (ryegrass)

Martin, 2009
Fludioxonil (Medallion) - phenylpyrrole fungicide developed by Ciba (Syngenta), early 1990’s

- derived from the antifungal compound pyrrolnitrin, produced by Pseudomonas pyrocinia
- active for bentgrass dead spot
Other Fungicides of Interest in Turf

- Polyoxin - discovered in Japan, labeled as Endorse (W.A. Cleary)
- Work by inhibition of fungal cell wall chitin synthesis
- Good curative control of Rhizoctonia brown patch; residual control is poor
- Recently found to be active for anthracnose; supplemental labeling for that purpose
Non Target Effects that are beneficial to disease control and turf health

- Proprietary pigment added to Bayer products (StressGard technology)
- Broader spectrum of control of phosphonate fungicides than only for Pythium: anthracnose
- Investigations of Insignia (pyraclostrobin) for positive plant physiological effects (anti-oxidant activity, elicitation of anti-stress enzymes)
Brown Patch Control - Bentgrass 1995

Turf Quality


B. Martin, 1995
Comparison of Chipco Signature and a Phosphite in a Program Approach – Fungicide Schedule

<table>
<thead>
<tr>
<th>Prog</th>
<th>May 24</th>
<th>June 8</th>
<th>June 22</th>
<th>July 6</th>
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<td>2</td>
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<td>Sig + 26 GT</td>
<td>Sig + Compass</td>
<td>Sig + Daconil</td>
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<td>26 GT</td>
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Martin, 2004
Comparison of Chipco Signature and a PHOSPHITE in a Program Approach - Brown Patch

Martin, 2004
Comparison of Chipco Signature and a PHOSPHITE in a Program Approach – Turf Quality

Martin, 2004

Diagram showing the comparison of percent disease over time between programs and check groups.
Turf Fungicide Program Trial

May 22: Tartan 2.0 fl oz

June 5: Insignia 0.9 oz

June 19: Spectro 90 5.76 oz

July 3: Signature 4.0 oz + Daconil Ultrex 3.2 oz

July 17: Insignia 0.9 oz

July 31: Signature 4.0 oz + Daconil Ultrex 3.2 oz

August 14: Chipco 26GT 4.0 fl oz

August 28: Tartan 2.0 fl oz

Clemson Program (13)

August 21, 2007
Pee Dee Research Center, Florence, SC

Dr. Bruce Martin, Clemson
Effect of Strobilurins in Program ‘13’

AUTQ curve:
13: 7.18.95 a  Insignia 0.9 oz
14: 661.1 ab  Heritage TL 2 fl oz
15: 681.86 ab  Disarm 0.37 fl oz
Tactics for Minimizing Potential for Resistance

- Do not use the product in isolation - apply it as a mixture with one or more fungicides of a different type (preferably one with no history of resistance) or as one component in a rotation or alternation of different fungicide treatments.

- Use of a fungicide tank-mix partner or rotation partner with similar mode of action or known to be a single-site resistance risk by increase the risk of selecting dual-resistant strains.
Tactics for Minimizing Potential for Resistance

- Restrict the number of treatments applied per season and apply only when strictly necessary. Use other fungicides subsequently.
- Strategy aims at reducing the total number of applications of the at-risk fungicide.
- Maintain manufacturers’ recommended dose
- Avoid eradicant (curative) use - attempt to keep populations of pathogens low
Tactics for Minimizing Potential for Resistance

- Use integrated pest management - for economic, environmental, and resistance management reasons.
- Utilize chemical diversity - in this regard, a new fungicide does not necessarily have to be superior to existing ones in order to be of value...
Pre-mix Products
Recent Premix Products

- **Stellar** - 5.54% fluopicolide + 55.4% propamocarb
- **Headway** - 5.73% azoxystrobin + 9.54% propiconazole
- **Concert** - 2.9% propiconazole + 38.5% chlorothalonil
- **Instrata** - 29.9% chlorothalonil + 4.7% propiconazole + 12% fludioxonil
- **Renown** - azoxystrobin + chlorothalonil
- **Honor** - 16.8% pyraclostrobin + 11.2% bosalid
Recent Premix Products

- Tartan/Armada – 4.17% trifloxystrobin + 20.86% triadimefon + StressGuard
- Interface SC(Bayer) – 23.1% iprodione + 14.4% trifloxystrobin + StressGuard
- Reserve SC(Bayer) – 5% triticonazole + 40% chlorothalonil
- Disarm C – 2.44% fluoxastrobin + 38.4% chlorothalonil
- Disarm M – myclobutanil + fluoxastrobin
Summary

- 2 new DMI fungicides: triticonazole (Trinity, Triton) and metconazole (Tourney)
- 1 new strobilurin: fluoxastrobin (Disarm)
- 2 new Pythium fungicides: cyazofamid (Segway) and propamocarb+fluopicolide (Stellar)
- Numerous premix products on market now or in development
- Granular strobilurin fungicides on market or in development