Paladin® Soil Fumigant

- **Registration** – July 9, 2010
  - Arkema
    - World’s largest producer of thiochemicals
- **Development & Marketing**
  - United Phosphorus, Inc.
    - Global supplier of proprietary and post patent crop protection technologies
Paladin® Soil Fumigant

• Product Information
  – Active Ingredient
    • Dimethyl disulfide
  – Molecular formula
    • $C_2H_6S_2$
  – Molecular weight
    • 94.2
Paladin® Soil Fumigant

• Physical & Chemical Properties
  – Color
    • Yellow
  – Physical State
    • Liquid
  – Specific Gravity
    • 1.062 (68°F)
  – Vapor pressure
    • 22.5 mmHg (68°F)
      – Vapor pressure reference
        » Water = 17.5
        » Ethanol = 67.5
        » Propane = 16,500
Paladin® Soil Fumigant

- P.Chem. (continued)
  - Solubility in water
    - 2.7 g/L (68°F)
  - Flash point
    - closed cup (65.3°F)
      - Reference
        - Ethanol (70%) = 61.9°F
  - Odor
    - Garlic-like
      - 8-10 ppb threshold
Paladin® Soil Fumigant

• Signal Word
  – Warning
    • Only currently registered fumigant with this signal wording

• Restricted Use Pesticide
  – Certified applicators only
    • Nasal irritation
Paladin® Soil Fumigant

• Mode of Action
  – Causes mitochondrial dysfunction and activation of K-ATP channels
    ▪ Blocks cytochrome oxydase
      ▪ Complex IV
    ▪ Acts on K-ATP channels
    ▪ hyperpolarization
Paladin® Soil Fumigant

• Toxicological Information
  – Oral
    • Moderately toxic (rat)
      – LD50 = 290-500 mg/kg
  – Dermal
    • Slightly toxic (rabbit)
      – LD50 >2,000 mg/kg
  – Inhalation
    • Practically nontoxic (rat)
      – 4 h LC50 = 5.24 mg/l (1310 ppm)
      – 24 h NOAEL = 0.05 mg/l (12 ppm)
    » Signs: Degeneration of nasal epithelium
Paladin® Soil Fumigant

• Toxicological Information
  – Eyes
    • Slightly to moderately irritating (rabbit)
      – Index: 7-20/110
  – Skin Irritation
    • Slightly irritating (rabbit)
      – Index: 1.5-2.5/8.0 (4 h)
  – Skin sensitization
    • No skin allergy observed (guinea pig)
Paladin® Soil Fumigant

• Toxicological Information (cont.)
  – Genetic toxicity
  – Developmental toxicity
  – Reproductive toxicity
    • No effects observed
Paladin® Soil Fumigant

• Ecological Effects
  – Chemical fate
    • Not readily biodegradable
      – 28 d < 10%
  – Atmospheric half-life
    • Hours
      – ozone depleting potential
        » zero
Paladin® Soil Fumigant

• Ecological Effects
  – Algae
    • Slightly toxic
      – Pseudokirchneriella subcapitata
        » 72 h EC50 = 14-26 mg/l
      – Skeletonema costatum
        » 96 h EC50 = 1.2-3.9 mg/l
Paladin® Soil Fumigant

• Ecological Effects
  – Aquatic toxicity
    • Moderately toxic
      – Zebra fish 96 h LC50 = 5 mg/l
    • Highly toxic
      – Trout 96 h LC50 = 0.97 mg/l
Paladin® Soil Fumigant

• Ecological Effects
  – Aquatic invertebrates
    • Moderately toxic
      – Daphnia 48 h EC50 = 1.8 mg/l
      – Mysid shrimp 96 h LC50 = 5 mg/l
    • Slightly toxic
      – Oysters 96 h LC50 = 14 mg/l
Dimethyl Disulfide

- **Industrial Uses**
  - Oil refining
    - Activates catalysts which remove sulfur
  - Petrochemicals
    - Coke inhibiting agent
Dimethyl Disulfide

- **Food Uses**
  - FDA approved additive
  - Flavor Use for onion, garlic & savory flavor in cheese, meat
    - 0.02-10 ppm
Dimethyl Disulfide

- Environmental Occurrence
  - Water
    - Salt
    - Brackish
    - Fresh
  - Sediment
  - Soil
  - Atmosphere
    - Sulfur cycle
Dimethyl Disulfide

• Biological Presence
  – Bacteria
  – Fungi
  – Animals
  – Plants
    • Cole crops, bulb crops,
    • tomatoes, others
FORMULATIONS
ACTIVE INGREDIENT..........98.8%
For Shank Injection
Raised Beds, Broadcast/Flatfume Applications
ACTIVE INGREDIENT .......... 93.8%
Emulsifiable Concentrate for Preplant Soil Chemigation
Crops

Fruiting Vegetables
Tomatoes
Peppers
Eggplant

Cucurbit Crops
Cucumbers
Squash (all)
Melons (all)

Small Fruit Crops
Strawberries
Blueberries

Field Grown Ornamentals

Forestry Nursery Crops
Pests

Weeds such as-
Nutsedge (purple & yellow), Chickweed, Lambsquarters, Purslane, grasses

Soil Borne Plant Pathogens such as-
Verticillium, Fusarium, Pythium, Sclerotinia, Rhizoctonia

Nematodes such as-
Root Knot (Southern, Northern and Colombia), Stubby Root, Lesion, Stunt, Sting
RATES
<table>
<thead>
<tr>
<th>Crops</th>
<th>Pests 1</th>
<th>Broadcast Application Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fruiting Vegetables</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tomatoes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peppers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eggplant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cucurbit Crops</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cucumbers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Squash (all)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melons (all)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Small Fruit Crops</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Strawberries</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blueberries</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Field Grown Ornamentals</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Forestry Nursery Crops</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Weeds such as:</strong></td>
<td><strong>Soil Borne Plant Pathogens such as:</strong></td>
</tr>
<tr>
<td></td>
<td>Nutsedge (purple &amp; yellow), Chickweed, Lambsquarters, Purslane, grasses</td>
<td>Verticillium, Fusarium, Pythium, Sclerotinia, Rhizoctonia</td>
</tr>
<tr>
<td></td>
<td>51.3</td>
<td>40-51.3</td>
</tr>
<tr>
<td></td>
<td>455</td>
<td>355-455</td>
</tr>
<tr>
<td></td>
<td></td>
<td>42.3-54.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>347-479</td>
</tr>
<tr>
<td></td>
<td><strong>Nematodes 2 such as:</strong></td>
<td><strong>Nematodes 2 such as:</strong></td>
</tr>
<tr>
<td></td>
<td>Root Knot (Southern, Northern and Colombia), Stubby Root, Lesion, Stunt, Sting</td>
<td>Root Knot (Southern, Northern and Colombia), Stubby Root, Lesion, Stunt, Sting</td>
</tr>
<tr>
<td></td>
<td>35-51.3</td>
<td>37-54.2</td>
</tr>
<tr>
<td></td>
<td>310-455</td>
<td>326-479</td>
</tr>
</tbody>
</table>

1 Use the higher rate of product when there is a combination of these pests
2 Use the higher rate for cyst forming nematodes
BUFFER ZONES
Paladin® Soil Fumigant

Buffer zones

- Buffer zones determined by
  1. Area treated
  2. Application method
     - Broadcast
     - Raised bed
  3. Application rate of Paladin
Paladin® Soil Fumigant
Broadcast/Flat Fume Shank Applications

Example Buffer Zones for low/high or ≈100 pounds, Paladin
1-40 Acres (10 acre increments)
buffer zones < 250 feet = blue, >250 ft = red

<table>
<thead>
<tr>
<th>Application Rate</th>
<th>Application Block size (Acres)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lbs/A</td>
<td>Gal/A</td>
</tr>
<tr>
<td>199</td>
<td>22.4</td>
</tr>
<tr>
<td>290</td>
<td>32.7</td>
</tr>
<tr>
<td>380</td>
<td>42.9</td>
</tr>
<tr>
<td>455</td>
<td>51.3</td>
</tr>
</tbody>
</table>

Buffer zone in feet

1The Paladin product label contains detailed tables for determining buffer zone distances with broadcast applications.
Paladin® Soil Fumigant
Raised Bed Shank Applications

Example¹ Buffer Zones for low/high or ≈50 pounds, Paladin
1-40 Acres (10 acre increments)
buffer zones 25 feet = blue, <100 ft = green; <200 ft = yellow, 200 ft or greater =red

<table>
<thead>
<tr>
<th>Application Rate</th>
<th>Application Block size (Acres)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Lbs/A</td>
<td>Gal/A</td>
</tr>
<tr>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>112</td>
<td>12.8</td>
</tr>
<tr>
<td>152</td>
<td>17.2</td>
</tr>
<tr>
<td>200</td>
<td>22.5</td>
</tr>
<tr>
<td>251</td>
<td>28.3</td>
</tr>
<tr>
<td>300</td>
<td>34.0</td>
</tr>
</tbody>
</table>

¹The Paladin product label contains detailed tables for determining buffer zone distances with raised bed applications.
Calculating Prepared / Raised Bed Application Amounts

Bed top Width (inches) \times \text{Row spacing (center to center in inches)} = \text{Effective broadcast equivalent rate}

Example calculation for Paladin

\[
\frac{30''}{48''} \times 455 \text{ lb} = 284 \text{ lb}
\]

\(^1\)From the rate table in the Paladin product label use instructions
PERSONAL PROTECTIVE EQUIPMENT (PPE)
• Handlers with potential contact with Paladin liquid
  – Loose fitting or well ventilated long sleeved shirt and long pants
  – Chemical resistant footwear
  – Socks
  – Full face shield or safety glasses
  – If odor detected,
    • Half or full face air-purifying respirator
      – May be removed if no odor detected
        » two consecutive air sampling events at 15 minute intervals
Paladin® Soil Fumigant
PPE

• Handlers with no potential for contact with Paladin liquid
  – Loose fitting or well ventilated long sleeved shirt and long pants
  – Socks
  – If odor detected,
    • Half or full face air-purifying respirator
      – May be removed if no odor detected
        » two consecutive air sampling events at 15 minute intervals
TARPS
barrier mulch films
Paladin® Soil Fumigant TARPS

• Low density polyethylene (LDPE)
  – Approximately four times more permeable than higher density barrier films (Tarps).

• Only VIF films are approved for use with Paladin
Paladin® Soil Fumigant TARPS

- High Barrier Tarps (VIF) required and listed on the Paladin labels
  - Olefinas Embossed VIF
  - Klerks VIF
  - Pliant Blockade (1.25 mil)
    - black or white
  - XL Blockade (0.00125)
  - Pliant Metalized black VIF
  - Canslit Metalized (1.25 mil)
    - high barrier black or white
  - FilmTec VIF (1.25 mil)
  - Ginegar VIF Embossed
  - Cadillac VIF
  - Guardian VIF (1.2 mil)
  - Mid-South Extrusion VIF
  - Bromostop (1.38 mil)
Paladin® Soil Fumigant
TARPS

• Tarp installation
  – Immediately after application
    • Kept in place
      – Minimum of 12 days
Paladin® Soil Fumigant
Plant Back Intervals

- Application to planting interval determined by average low soil temp$^1$ at an 8” depth

<table>
<thead>
<tr>
<th>Soil Temperature</th>
<th>Application to planting interval (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>71° F and higher</td>
<td>21 days</td>
</tr>
<tr>
<td>61° - 70° F</td>
<td>28 days</td>
</tr>
<tr>
<td>55° - 60° F</td>
<td>35 days</td>
</tr>
<tr>
<td>50° - 54° F</td>
<td>42 days</td>
</tr>
</tbody>
</table>

- Circumstances such as heavy soils & high soil moisture can also lengthen the plant back interval. See also Paladin label.

$^1$The soil temperature at the depth of injection must not be less than 45° F or exceed 90° F at the beginning of the application.
FMPs
fumigation management plans
• **SITE-SPECIFIC FUMIGATION MANAGEMENT PLAN (FMP)**
  – Prior to the start of fumigation, the Certified Applicator supervising the application must verify that a site-specific FMP exists for each application block.
  – Each site-specific FMP must contain date of completing registrant training program.
Efficacy
Paladin® Soil Fumigant

• Field Trials
  – 2004 to 2010
  • efficacy and crop safety assessments
    – Approximately
      » 250 field trials
      » 15 countries
Combinations of Paladin® Soil Fumigant With Chloropicrin
Paladin® Soil Fumigant
With and without Chloropicrin

Equivalent rates of DMDS active ingredient

Paladin
51 GPA

UTC

Paladin® Pic
60 GPA

UTC
Paladin® Soil Fumigant
Average of three trials 2008 & 2009
BURIED BAG ASSAYS
Dr. Gary E. Vallad  University Of Florida, IFAS, Gulf Coast REC

*F. oxysporum f.sp. lycopersici* (causal agent of Fusarium wilt of tomato)

Average CFU/g soil (cfu) per gram of soil for each bag was calculated and log transformed.
2009 University of Georgia
Fall Root Knot Nematode Trial

UTC Nematode Count/100cm³ 786.5
Evaluation of Paladin and Paladin Pic With and Without soil applied herbicide (napropamide – (Devrinol)) Dr. Andrew MacRae UFL Grass Control

Average Weed Count Per Plot

- Non-treated Control
- Paladin @ 51.4 gal/A
- Paladin Pic @ 60 gal/A
- Methyl Bromide 67:33 @ 175 lbs/A

Devrinol=Devrinol+ # compound for nut sedge control
Evaluation of Paladin and Paladin Pic With and Without soil applied herbicide (napropamide – (Devrinol))

Dr. Andrew MacRae UFL

Broadleaf Control

平均杂草数量

<table>
<thead>
<tr>
<th>处理类型</th>
<th>平均杂草数量</th>
</tr>
</thead>
<tbody>
<tr>
<td>未处理控制</td>
<td>70</td>
</tr>
<tr>
<td>Paladin @ 51.4 gal/A</td>
<td>60</td>
</tr>
<tr>
<td>Paladin Pic @ 60 gal/A</td>
<td>50</td>
</tr>
<tr>
<td>Methyl Bromide 67:33 @175 lbs/A</td>
<td>40</td>
</tr>
</tbody>
</table>

Devrinol=Devrinol+ # compound for nutsedge control
Paladin® Soil Fumigant

- Experimental Use Permit
  - On farm evaluation of Paladin
    - 2007 to 2010
Efficacy % of MB / Standard
Paladin EUP Trials 2007 - 2009

PaladinPic Vs MB / Standard

% of MB / Standard

- Amaranth
- Amaranth
- Cyperus
- Digitaria
- Eleusine
- Geraniun
- Ipomea
- Melilotus
- Polygonum
- Rumex
- Sesbania
- Solanum
- Vicia
- Weeds
- Radish
- Vorticillium
- Root Gall Ing
Last comment…

• Could everyone *please* take a deep breath and exhale slowly
• Everyone exhaling has just produced a small quantity of DMDS