What’s Going On in the Spray tank?

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The spray tank mix:

- Carrier (usually water)
- Formulation ingredients – “inerts”
- Spray adjuvant(s)
- Active ingredient(s)

Adjuvant: broadly defined as any substance added to the spray tank, separate from the pesticide formulation, that will improve the performance of the pesticide
Types of formulations

- Solutions
- Emulsions (EC=emulsifiable concentrate)
- Wettable Powders (WP)
- Flowable suspensions (F)
- Ultralow volume concentrates (ULV)
- Granules (G)
- Dispersible granules (DG)
- Aerosols
- Encapsulated (ME=microencapsulated)
Spray-tank adjuvants

• Spray-tank adjuvants usually are added to the spray tank at the time of mixing.

• They are meant to complement the formulation adjuvants – the “other” (inert) ingredients in the pesticide formulation.
Spray-tank adjuvants

- oils
- petroleum oils (paraffin and naphtha based)
- crop oil concentrate (vegetable oil base with 15 to 20% surfactant/emulsifier)
- surfactants (wetting agents, spreaders, penetrants)
- stabilizing agents (emulsifiers, dispersants, anti-flocculating agents, compatibility agents)
- solvents (co-solvents, coupling agents)
- hygroscopic agents (humectants)
- deposit builders (stickers, film formers)
- antifoam agents
- buffering agents
Spray-tank adjuvants

- Retailers sell ~ 300 registered adjuvants in Washington State.

- In other Pacific Northwest states where registration is not required, retailers sell from 400 to 500 adjuvants.

- Terminology not standardized and often confusing.

- Adjuvant label claims often market driven, may not be validated by research.

- Not regulated by EPA other than being exempt from the requirement of a tolerance under CFR 40 180, or when mentioned on a pesticide product label.
Pesticide formulation “inerts”

- Provide:
  - Formulation stability: must not separate when stored for long periods or at extreme temperatures.
  - Dispersibility: Product should disperse readily in spray tank water (not flocculate, aggregate, sink, or float.)
  - Emulsifiability: oil-based products require emulsifying surfactants and co-solvents to “bridge” between oil and water (micelles).
  - Efficacy: spread an active ingredient or enhance its penetration into the plant cuticle.
Spray-tank adjuvants: value added?

- Improve dispersion
- Inhibit pesticide re-crystallization on the leaves
- Slow droplet volatilization
- Slow dry-down time
- Speed chemical diffusion across the cuticle
- Solubilize leaf waxes and partition into the cuticle
- Modify droplets to optimum size
- Adjust the pH
- Defoam the spray mixture
Sprayed without a surfactant

Sprayed with a mixture containing a nonionic surfactant
Transfer of agrochemicals to the target

R. Pontzen, Pflanzenschutz-Nachrichten Bayer 59/2006, 1, p 63-72
Spray deposit of thiacloprid on a barley leaf (electron micrograph).

R. Pontzen, Pflanzenschutz-Nachrichten Bayer 59/2006, 1, p 63-72
Agrochemical Spray deposit on the leaf surface
Interpretation of label information:

- Specific recommendations
- Suggested recommendations
- No recommendations
- Specific prohibitions
- Tank-mix recommendations
Spray tank buffers

- Water hardness and pH often cause confusion.
- Hardness refers to the minerals in the water.
- pH measures the degree of acidity or alkalinity.
Spray tank buffers

- The pH of natural waters in the Pacific Northwest generally ranges between 4 and 10.
- The pH of waters west of the Cascades generally ranges from 4 to 7.
- The pH of waters east of the Cascades generally ranges from 7.2 to 9.6.
- Hard water is alkaline and typically contains high levels of carbonate and bicarbonate (> 300 ppm).
Effect of pH and water hardness on the diluted formulation

How do pesticides degrade in the spray tank?

The predominant pathway of degradation in the spray tank is by hydrolysis.
Pesticides containing the following functional groups are known to be susceptible to hydrolysis:

- Amides
- Carbamates
- Epoxides
- Esters
- Halides
- Nitriles
- Phosphate esters
Hydrolysis of Dursban

\[
\text{chlorpyrifos} \quad \xrightarrow{\text{H}_2\text{O}} \quad 3,5,6 \text{ Trichloro-2-pyridinol}
\]
Hydrolysis of 2,4 DB

2,4 D butyl ester \xrightarrow{\text{H}_2\text{O}} \text{2,4 dichlorophenol}
Half-life = the amount of time it takes the parent compound to decay to half its original concentration.

How fast a pesticide is degraded by hydrolysis depends on pH, temperature, and to a lesser degree water hardness.
Hydrolysis *Half-life* based on first-order reaction rate kinetics

\[
\frac{C_t}{C_0} = 0.5 = e^{-kt_{1/2}}
\]

\[
t_{1/2} = 0.639/k
\]

\[C_0 = \text{concentration at time 0}\]
\[C_t = \text{concentration at time } t\]
Pesticide hydrolysis half-life ($t_{1/2}$)

- **Cythion**: pH 9, $t_{1/2} = 12$ hours
- **Imidan**: pH 7, $t_{1/2} = 9.4$ hours, pH 9, $t_{1/2} = 5.5$ minutes
- **Fusilade**: pH 9, $t_{1/2} = 9$ hours
- **Captan**: pH 7, $t_{1/2} = 8$ hours, pH 9, $t_{1/2} = 4$ minutes
- **2,4 D ester**: pH 6, $t_{1/2} = 4$ years, pH 9, $t_{1/2} = 37$ hours
Guthion hydrolysis as a function of pH
Guthion hydrolysis half-life as a function of pH at 25 °C (77 °F)

pH 1-7: half-life = 69 days
pH 7.5: half-life = 46 days
pH 8.0: half-life = 11 days
pH 8.5: half-life = 6 days
pH 9.0: half-life = 4 days
Guthion hydrolysis rate as a function of Temperature

Guthion hydrolysis rate at pH 7

Temperature C

k (days) at pH 7
Guthion hydrolysis rate at pH 7 as a function of temperature

- 6 °C (43 °F): half-life = 231 days
- 25 °C (77 °F): half-life = 69 days
- 37 °C (99 °F): half-life = 16.5 days
- 50 °C (122 °F): half-life = 3.7 days
Guthion hydrolysis rate at pH 9 and 37 °C (99 °F)

Half-life = 22 hours
<table>
<thead>
<tr>
<th>Trade name</th>
<th>Common name</th>
<th>Effect of pH on half-life</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4 D</td>
<td></td>
<td>pH 6 half-life = 4 y; pH 9 half-life = 37 h</td>
</tr>
<tr>
<td>Agri-Mek, Avid</td>
<td>abamectin</td>
<td>pH 5–9 stable</td>
</tr>
<tr>
<td>Ambush, Pounce</td>
<td>permethrin</td>
<td>optimum pH 4</td>
</tr>
<tr>
<td>Ammo, Cymbush</td>
<td>cypermethrin</td>
<td>pH 9 half-life = 35 h</td>
</tr>
<tr>
<td>Asana XL</td>
<td>esfenvalerate</td>
<td>pH 5–9 stable</td>
</tr>
<tr>
<td>Benlate</td>
<td>benomyl</td>
<td>do not mix with alkaline materials</td>
</tr>
<tr>
<td>(Bacillus thuringiensis)</td>
<td></td>
<td>incompatible with highly alkaline materials</td>
</tr>
<tr>
<td>Captan</td>
<td>captan</td>
<td>pH 7 half-life = 8 h; pH 9 half-life = 4 m</td>
</tr>
<tr>
<td>Carzol</td>
<td>formetanate</td>
<td>pH 5 half-life = 4 d; pH 7 half-life = 14 h;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pH 9 half-life = 3 h</td>
</tr>
<tr>
<td>Counter</td>
<td>terbufos</td>
<td>hydrolyzes under alkaline conditions</td>
</tr>
<tr>
<td>Chemical</td>
<td>Active Ingredient</td>
<td>pH 6 half-life</td>
</tr>
<tr>
<td>----------------</td>
<td>-----------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>Cygon</td>
<td>dimethoate</td>
<td>12 h</td>
</tr>
<tr>
<td>Cythion</td>
<td>malathion</td>
<td>7.8 d</td>
</tr>
<tr>
<td>Daconil</td>
<td>chlorothalonil</td>
<td></td>
</tr>
<tr>
<td>Diazinon</td>
<td></td>
<td></td>
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<tr>
<td>Dibrom</td>
<td>naled</td>
<td></td>
</tr>
<tr>
<td>Di-Syston</td>
<td>disulfoton</td>
<td>32 h</td>
</tr>
<tr>
<td>Ficam</td>
<td>bendiocarb</td>
<td></td>
</tr>
<tr>
<td>Guthion</td>
<td>azinphos-methyl</td>
<td>69 d</td>
</tr>
<tr>
<td>Imidan</td>
<td>phosmet</td>
<td>12 h</td>
</tr>
<tr>
<td>Product</td>
<td>Active Ingredient</td>
<td>pH Conditions</td>
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<tr>
<td>---------------</td>
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<td>---------------------------------</td>
</tr>
<tr>
<td>Kelthane</td>
<td>dicofol</td>
<td>pH 7 half-life = 5 d; pH 9 half-life = 15 m</td>
</tr>
<tr>
<td>Kocide</td>
<td>copper hydroxide</td>
<td>incompatible with acids</td>
</tr>
<tr>
<td>Larvin</td>
<td>thiodicarb</td>
<td>rapidly hydrolyzes at pH 9</td>
</tr>
<tr>
<td>Malathion</td>
<td>malathion</td>
<td>pH 6 half-life = 7.8 d; pH 7 half-life = 3 d; pH 8 half-life = 19 h</td>
</tr>
<tr>
<td>Mocap</td>
<td>ethoprophos</td>
<td>rapidly hydrolyzes at pH 9</td>
</tr>
<tr>
<td>MSR</td>
<td>oxydemeton-M</td>
<td>pH 6 half-life = 12.3 h; unstable in alkaline conditions</td>
</tr>
<tr>
<td>Omite, Comite</td>
<td>propargite</td>
<td>pH 7 half-life = 120 d; pH 9 half-life = 1 d</td>
</tr>
<tr>
<td>Pydrin</td>
<td>fenvalerate</td>
<td>optimum stability at pH 4</td>
</tr>
<tr>
<td>Insecticide</td>
<td>Active Ingredient</td>
<td>Stability Conditions</td>
</tr>
<tr>
<td>------------</td>
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</tr>
<tr>
<td>Rovral</td>
<td>iprodione</td>
<td>hydrolyzes in alkaline pH</td>
</tr>
<tr>
<td>Talstar</td>
<td>bifenthrin</td>
<td>pH 5–9 stable</td>
</tr>
<tr>
<td>Thimet</td>
<td>phorate</td>
<td>subject to hydrolysis under alkaline conditions</td>
</tr>
<tr>
<td>Thiodan</td>
<td>endosulfan</td>
<td>pH 8 half-life = 7 d; pH 9 half-life = 0.5 d</td>
</tr>
<tr>
<td>Tospin M</td>
<td>thiophanate</td>
<td>pH 5 stable; pH 9 half-life = 17 h</td>
</tr>
<tr>
<td>Vapam</td>
<td>metam-sodium</td>
<td>pH 5–7 half-life = 2 d; pH 9 half-life = 4 d</td>
</tr>
<tr>
<td>Vendex</td>
<td>fenbutatin oxide</td>
<td>pH 5–9 stable</td>
</tr>
<tr>
<td>Ziram</td>
<td>ziram</td>
<td>decomposes in acidic media</td>
</tr>
</tbody>
</table>
Buffers and pH

Buffer is defined as a solution that will maintain a reasonably constant pH when relatively large amounts of either acid or base are added.
Water hardness

Hard water is alkaline and typically contains high levels (> 300 ppm?) of carbonate and bicarbonate.
Water hardness

- Alkaline pH may affect those pesticides susceptible to alkaline hydrolysis
- Calcium and magnesium may reduce effectiveness of surfactants
Summary

• Know your spray adjuvants.

• Test the pH and hardness of your diluent.

• Best way to determine compatibility is the “jar test”.
Dodine (Cyprex 65W) + Karathane WP + Multi-Film L

Surfactant
The information presented here and more in the section on spray-tank adjuvants at:


Also see National Pesticide Information Center fact sheets:

Inert or Other Ingredients: http://npic.orst.edu/factsheets/inerts.pdf