Fluid Starter Fertilizer Sources

RD Lohry
D Zabel
Two Distinct Fluid Starter types

- Ammonium polyphosphates
- 100% orthophosphates
Two Distinct Fluid Starter Types

• With exception of nitrogen, the two types made from different sets of P & K raw materials
• Different marketing techniques
Plant Food Madness

- The market is becoming more diverse with blends
  - 30/70 ortho/poly—typical high polyphosphate
  - 50/50 ortho/poly
  - 60/40 ortho/poly
  - 70/30 ortho/poly
  - 80/20 ortho/poly
  - 100/0 ortho/poly
- We’re no longer “purists”

Blends are the growth area. K source can be KCl or KOH.
High Ortho  High Poly

- N from ammonia, urea
- P from very (clean) orthophosphoric acid
- K from KOH
- S from ATS
- Micros from EDTA chelated sources
<table>
<thead>
<tr>
<th>High Ortho</th>
<th>High Poly</th>
</tr>
</thead>
<tbody>
<tr>
<td>N from ammonia, urea</td>
<td>N from ammonia, UAN</td>
</tr>
<tr>
<td>P from high grade orthophosphoric acid</td>
<td>P from polyphosphate (converted from ortho)</td>
</tr>
<tr>
<td>K from KOH</td>
<td>K from KCl</td>
</tr>
<tr>
<td>S from ATS</td>
<td>S from ATS + other</td>
</tr>
<tr>
<td>Micros from EDTA chelated sources</td>
<td>Micros from ammoniated complexes, sulfates, chlorides and chelates</td>
</tr>
</tbody>
</table>
Nitrogen Sources

• Nitrogen – N
  – Ammonia NH$_3$
  – Urea CO(NH$_2$)$_2$
  – UAN
  – Complexed N
    • Ammonium phosphate
    • Ammonium (thio) sulfates
    • Ammonium nitrates
All N comes from Atmosphere

- Earth’s atmosphere is 78% nitrogen.
- 1884—Development of the theoretical principles for combining hydrogen and atmospheric nitrogen to form ammonia.
- Hydrogen (natural gas) + air and under high pressure (2200 psi) and temperature (400-500 C) + catalyst = Ammonia.
- 33,000 cubic feet of natural gas is needed to supply hydrogen for 1 ton of ammonia.
Ammonia NH₃ 82-0-0

- Used to make all other forms of nitrogen fertilizer.
- Both of our starter types use ammonia (sometimes called ammonium hydroxide when dissolved in water) ammoniacal
Urea CO(NH\textsubscript{2})\textsubscript{2} 46-0-0

- Ammonia is reacted with carbon dioxide in the presence of a catalyst.
- Less corrosive than some other N fertilizers
- Most likely to be included in the high ortho mixes to adjust pH
Nitric Acid

• Not used directly as fertilizer, but is necessary to produce certain N fertilizers.

• Nitric acid (HNO$_3$) is produced by the oxidation of Ammonia with air in the presence of a catalyst, usually platinum.
Ammonium Nitrate

• Nitric acid and ammonia are reacted to produce ammonium nitrate (NH₄NO₃).
• 34-0-0. (20-0-0 in solution)
Ready to make 32% UAN

- We made urea from ammonia and CO2
  - In solution urea might be 20 – 23% N
- Made Ammonium nitrate from nitric acid and ammonia
  - In solution about 20% N
- Time to combine them
When ammonium nitrate and urea in more or less equal proportions are mixed with water, the solubility of the combination is greater than the solubility's of the individual components.

32%, 28% (urea ammonium nitrate) are stable solutions.

What a happy outcome!
Phosphates
Fluid Phosphate Source

• Tricalcium phosphate rock (fluoroapatite)
• “Rock phosphate” in the “old days”
• Needed Bray II P test to measure it in the soil after application
• Turn phosphate rock into phosphoric acid
Phosphoric Acid Sources

Wet, Thermal & Kiln Process Acid
Wet Process (Ortho)

- Made by reacting finely ground tricalcium phosphate rock (fluoroapatite—a naturally occurring mineral) with sulfuric acid.
- (Green or black acid) Used directly for production of Ammonium polyphosphate such as 10-34-0, 8-24-0, 9-30-0 and 11-37-0
- Can be further purified by removing fluorine—Animal grade acid
- Solvent extraction and arsenic removal to make food grade acid
Thermal or "Dry" Process

- Burn dry, rock phosphate in furnace: (furnace grade or "white" acid)
- Very pure—food grade—additional arsenic removal may be needed for critical industrial applications.
- Clear in color because all impurities that give color to P acid have been removed
- Ortho form
Kiln Process Acid

- New process called “Improved Hard Process”
- Makes low grade phosphate rock reserves commercially viable
- Increase phosphate recovery from existing reserves
- May significantly extend commercial viability of phosphate reserves
Phosphate Types

- **Orthophosphates**
  - Simplest form of liquid phosphate

- **Polyphosphates**
  - Complex phosphate chains (polymer)
  - Formed by removing water from ortho

- **Monopotassium Phosphate**
  - Phos acid reacted with potassium hydroxide
  - Can be ortho and/or poly
Polyphosphates

What are they?
How they are produced?
What do they do?
Precautions
What is a polyphosphate?

• Polyphosphates are molecules containing more than one phosphorus atom
  – Prior to the advent of the TVA pipe reactor process they were very difficult to make
  – Only source lay in “high poly” superacids (which are very corrosive)
    • Required high heat and high vacuum conditions
    • 50% poly was about the most that could be achieved
Why develop Poly P?

• Industry wanted higher P grades
• Save on transportation—more P per load
TVA PIPE REACTORS

How they work
TVA PIPE REACTOR PROCESS SCHEMATIC
Benefits of the TVA pipe reactor process
(Developed in the mid-60’s)

1. Allowed production of High poly ammonium phosphate solutions
2. Eliminated the need for high poly superacids
3. Higher grades of phosphates—saved on shipping P
The basic building block for polyphosphates
Where does the heat come from?
Ah-ha! An Exothermic Reaction

600 to 700°F
The overall process

AMMONIA + SUPER ACID =

HEAT + AMMONIUM POLYPHOSPHATE + WATER

Figure 8
Potassium

- Widely distributed in earth’s crust
- Mined, brines in saline lakes and seas
- Underground deposits
- 60% of world’s reserves are in North America—most in Western Canada
Monopotassium Phosphate
High OrthoP/KOH ‘low salt’

- React KOH with Phos acid
- Exothermic reaction—heat released 220°F
- Minimizes escape of ammonia when reacted with urea and ammonium phosphates
- Ortho and/or poly P
- Used in production of low-salt starter and foliar fertilizers, fungicides (powdery mildew), buffering agents and food additives (Gatorade) and for greenhouse and hydroponics nutrient source
Monopotassium Phosphate

- 6-24-6 high orthophosphate starter contains 3 kinds of potassium phosphate
  - Potassium orthophosphate monobasic (predominate form)
  - Potassium orthophosphate dibasic
  - Dipotassium pyrophosphate
- Very low corrosion on mild steel
- Can have K included and still have salt index less than APP 10-34-0—K source for seed placement
Potash sources for fluids

- Potassium chloride 0-0-60 (62)
- Monopotassium phosphate 0-52-35
- Potassium carbonate 0-0-30 (32)
- Potassium thiosulfate 0-0-25-17
- Potassium sulfate 0-0-50-18
- Potassium nitrate 13-0-45
Most Common K Sources
In our corner of the universe

• KCl - Blend with APP and UAN to make 7-21-7 and similar grades

• KOH – blend with ammonia, urea, ortho and poly phosphates, thiosulfates to make an array of low-salt affect grades of fertilizer (potassium phosphates)
Fluid Sulfur Sources

- Ammonium thiosulfate  12-0-0-26
- Potassium thiosulfate  0-0-25-17
- Ammonium sulfate      21-0-0-24
- Potassium sulfate     0-0-52-18
- Urea-sulfuric acid   


Micronutrient Sources

• EDTA chelated micros used for all fluids, necessary for high ortho P products
• HEEDTA, NTA, DTPA and EDDHA
• Ammoniated zinc complexes—intended for products with high poly P content
• Sulfate, chloride or oxide forms
• Borates and Molybdates
Agronomic Considerations

• Or, does corn care? Yes, it just might!
• Handling, storage (sludge) and ease of use may be just as important to the grower as agronomic differences.
• Low salt index important for seed placement—lean to potassium hydroxide (monopotassium phosphate) for K source
• Low salt index important for maximum P uptake when K is added
• Growers and their dealers have choices
Phosphorus Uptake by Corn as Affected by the Potassium Salt Added to Phosphate-Nitrogen Mixture in Band

<table>
<thead>
<tr>
<th>Formula</th>
<th>Compound</th>
<th>Salt Index (SI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KH₂PO₄</td>
<td>Potassium Phosphate</td>
<td>0.10</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>Potassium Sulfate</td>
<td>0.85</td>
</tr>
<tr>
<td>KCl</td>
<td>Potassium Chloride</td>
<td>1.94</td>
</tr>
</tbody>
</table>

Source - How Roots Tap a Fertilizer Band by Prof. A.J. Ohlrogge
National Plant Food Institute, Washington, D.C.

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### Salt Index Values of Fertilizer Materials

<table>
<thead>
<tr>
<th>Material and analysis</th>
<th>Salt Index</th>
<th>Per equal wts of materials</th>
<th>Per unit of nutrients*</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NITROGEN/SULFUR</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonia, 82% N</td>
<td>47.1</td>
<td>0.572</td>
<td></td>
</tr>
<tr>
<td>Ammonium nitrate, 34% N</td>
<td>104.0</td>
<td>3.059</td>
<td></td>
</tr>
<tr>
<td>Ammonium sulfate, 21% N, 24% S</td>
<td>68.3</td>
<td>3.252</td>
<td></td>
</tr>
<tr>
<td>Ammonium thiosulfate, 12% N, 26% S</td>
<td>90.4</td>
<td>7.533</td>
<td></td>
</tr>
<tr>
<td>Urea, 46% N</td>
<td>74.4</td>
<td>1.618</td>
<td></td>
</tr>
<tr>
<td>UAN, 28% N (39% a. nitrate, 31% urea)</td>
<td>63.0</td>
<td>2.250</td>
<td></td>
</tr>
<tr>
<td>32% N (44% a. nitrate, 35% urea)</td>
<td>71.1</td>
<td>2.221</td>
<td></td>
</tr>
<tr>
<td><strong>PHOSPHORUS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>APP, 10% N, 34% P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>20.0</td>
<td>0.455</td>
<td></td>
</tr>
<tr>
<td>DAP, 18% N, 46% P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>29.2</td>
<td>0.456</td>
<td></td>
</tr>
<tr>
<td>MAP, 11% N, 52% P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>26.7</td>
<td>0.405</td>
<td></td>
</tr>
<tr>
<td>Phosphoric acid, 54% P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td></td>
<td>1.613&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>72% P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td></td>
<td>1.754&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td><strong>POTASSIUM</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monopotassium phosphate, 52% P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;, 35% K&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>8.4</td>
<td>0.097</td>
<td></td>
</tr>
<tr>
<td>Potassium chloride, 62% K&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>120.1</td>
<td>1.936</td>
<td></td>
</tr>
<tr>
<td>Potassium sulfate, 50% K&lt;sub&gt;2&lt;/sub&gt;O, 18% S</td>
<td>42.6</td>
<td>0.852</td>
<td></td>
</tr>
<tr>
<td>Potassium thiosulfate, 25% K&lt;sub&gt;2&lt;/sub&gt;O, 17% S</td>
<td>68.0</td>
<td>2.720</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Salt index per 100 lbs of H<sub>3</sub>PO<sub>4</sub>.<sup>*</sup>One unit equals 20 lb.

Mortvedt, “Calculating Salt Index”
## Salt Index of Some Common Liquid Formulations

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Salt index</th>
<th>Salt index per unit of plant nutrient (20 lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-20-20</td>
<td>7.2</td>
<td>0.17</td>
</tr>
<tr>
<td>3-18-18</td>
<td>8.5</td>
<td>0.22</td>
</tr>
<tr>
<td>6-24-6</td>
<td>11.5</td>
<td>0.32</td>
</tr>
<tr>
<td>6-30-10</td>
<td>13.8</td>
<td>0.30</td>
</tr>
<tr>
<td>9-18-9</td>
<td>16.7</td>
<td>0.48</td>
</tr>
<tr>
<td>10-34-0</td>
<td>20.0</td>
<td>0.45</td>
</tr>
<tr>
<td>7-21-7</td>
<td>27.8</td>
<td>0.79</td>
</tr>
<tr>
<td>4-10-10</td>
<td>27.5</td>
<td>1.18</td>
</tr>
<tr>
<td>28%UAN</td>
<td>63.0</td>
<td>2.25</td>
</tr>
</tbody>
</table>

\( ^{a} \) These grades are formulated using potassium phosphate as the K source.

\( ^{b} \) Use in seed-row placement with caution.

\( ^{c} \) Not suggested for use in seed-row placement.

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**Mortvedt, “Calculating Salt Index”**
## Calculating Salt Index of 7-21-7

<table>
<thead>
<tr>
<th>Material</th>
<th>% Nutrient</th>
<th>lbs/ton</th>
<th>N</th>
<th>P$_2$O$_5$</th>
<th>K$_2$O</th>
<th>Salt index per unit (20 lb)$^a$</th>
<th>Salt index in formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-34-0</td>
<td>10% N, 34% P$_2$O$_5$</td>
<td>1,235</td>
<td>6.2</td>
<td>21.0</td>
<td>—</td>
<td>0.455</td>
<td>12.4</td>
</tr>
<tr>
<td>UAN</td>
<td>28% N</td>
<td>57</td>
<td>0.8</td>
<td>—</td>
<td>—</td>
<td>2.250</td>
<td>1.8</td>
</tr>
<tr>
<td>KCl</td>
<td>62% K$_2$O</td>
<td>226</td>
<td>—</td>
<td>—</td>
<td>7.0</td>
<td>1.936</td>
<td>13.6</td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td>482</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2,000</td>
<td>7.0</td>
<td>21.0</td>
<td>7.0</td>
<td>27.8$^b$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Salt index per unit (20 lb) of plant nutrients, listed Table 1, also called the partial salt index.

$^b$ 0.79 SI/unit plant nutrient

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Mortvedt, “Calculating Salt Index”
# Calculating Salt Index of 6-24-6

<table>
<thead>
<tr>
<th>Material</th>
<th>% Nutrient</th>
<th>lbs/ton</th>
<th>N</th>
<th>Nutrient units</th>
<th>_____</th>
<th>_____</th>
<th>Salt index per unit (20 lb)</th>
<th>in formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1)</td>
<td>(2)</td>
<td>(3)</td>
<td>(4)</td>
<td>(5)</td>
<td>(6)</td>
<td>(7)</td>
<td>(8)</td>
</tr>
<tr>
<td>NH₃</td>
<td>82%N</td>
<td>146</td>
<td>6.0</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>— b</td>
<td>—</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>54% P₂O₅</td>
<td>666</td>
<td>—</td>
<td>18.0</td>
<td>—</td>
<td>1.613</td>
<td>10.7</td>
<td></td>
</tr>
<tr>
<td>Potassium</td>
<td>22% K₂O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.097</td>
<td>1.2</td>
</tr>
<tr>
<td>Phosphate</td>
<td>22% P₂O₅</td>
<td>546</td>
<td>—</td>
<td>6.0</td>
<td>6.0</td>
<td>6.0</td>
<td>0.097</td>
<td>1.2</td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td>642</td>
<td>—</td>
<td></td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2,000</td>
<td>6.0</td>
<td>24.0</td>
<td>6.0</td>
</tr>
</tbody>
</table>

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a Salt index per unit (20 lb) of plant nutrients, listed in Table 1, also called the partial salt index.
b Ammoniation of phosphoric acid to a 1-3-0 ratio forms a mixture of MAP and DAP.
c 0.32 SI/unit plant nutrient.

Mortvedt, “Calculating Salt Index”
Caution: This chart contains information based on the opinions of people in the fluid fertilizer industry. This information has been compiled as a general guide only. Neither the Fluid Fertilizer Foundation or contributors guarantee the accuracy of the information. Please refer to manufacturer/supplier product information and also perform a small jar compatibility test prior to final mixing.

Compatible, results in generally acceptable mixture.
Limited Compatibility, generally compatible within solubility limits.
Very Limited Compatibility, generally unsuitable mixtures.
Incompatible, unsuitable mixture and/or hazardous combination.
Δ Significant heat generated.

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3/1/09
The End