MICHAEL ORR
“THE BROTHER FROM ANOTHER MOTHER”
MONTANA GROW
SPECIALTY PROCESS CONSULTING

FLUID FERTILIZER FOUNDATION
TECHNOLOGY ROUNDUP
COUNCIL BLUFFS, IOWA
DECEMBER 6-7, 2016
Agricultural Outlook

**Global Population Growth:**

- Gerald Nelson, University of Illinois:
  - The world’s population will continue growing through at least 2050, barring a major war or the widespread outbreak of a serious disease.

- Chairman & CEO, ADM:
  - Population is projected to grow by 33% in the next 20 years, from 6 to 8 billion people, while food demand increases 50% due to higher living standards and more demand for protein.
The Drought Monitor focuses on broad-scale conditions. Local conditions may vary. See accompanying text summary for forecast statements.
• Improving crop nutrient demand drivers and outlook
  • Upturn in the global economic outlook
  • Constructive agricultural fundamentals
• Tighter phosphate fundamentals begins to take hold
  • Low stocks from producer warehouses to farm field
  • Demand recovery underway
• Potash shipments remain slow
  • Waiting for a China settlement and price discovery
  • Strong demand recovery expected in 2018
  • Demand recovery at what price?
• Unpredictable factors to watch
  • Agricultural commodity prices and farm economics
  • Macroeconomic conditions
  • Government policies
U.S. Nitrogen Fertilizer Consumption
Tons N/year

- Anhydrous Ammonia: -30,800 Tons N/year
- UAN: +51,000 Tons N/year
- Urea: +60,100 Tons N/year
- Ammonium Nitrate: -14,400 Tons N/year
USA Evolution of N Fertilizer Consumption

- Urea
- Ammonium nitrate
- Nitrogen solutions
- Anhydrous ammonia
- Total compound N

Millions of tonnes

1973 / 74
2004 / 08

www.fertilizer.org
Nutrient Demand of a 225 bu/a Corn Crop and Nutrient Supply from the Soil

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>Demand (lb/a)</th>
<th>Interception</th>
<th>Mass Flow</th>
<th>Diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium</td>
<td>250</td>
<td>6</td>
<td>34</td>
<td>210</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>254</td>
<td>3</td>
<td>206</td>
<td>45</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>60</td>
<td>2</td>
<td>3</td>
<td>55</td>
</tr>
<tr>
<td>Sulfur</td>
<td>30</td>
<td>2</td>
<td>28</td>
<td>0</td>
</tr>
</tbody>
</table>
As a rule, elements as you move upper left are more soluble with elements as you move upper right.
Unocal Compatibility Chart

- An NH3
- Aqua NH3
- Urea soln
- AN-20
- UAN-32
- AS soln
- 8-24-0
- 10-34-0
- APS
- ATS
- US 28/27
- US 15/49
- US 10/55
- CAN-17
- HNO3
- Grn P acid
- Wht P acid
- Sulf acid
- water
- Urea dry
- AN dry
- MAP
- DAP
- CN dry
- KCl dry

Legend:
- ▲: heat generation
- Green: compatible
- Yellow: compatible within certain limits
- Red: incompatible
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 relatively stable 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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- Green: 'Compatible', results in generally acceptable mixture.
- Yellow: 'Limited Compatibility', generally compatible within solubility limits.
- Blue: 'Very Limited Compatibility', generally unsuitable mixtures.
- Red: 'Incompatible', unsuitable mixture and/or hazardous combination.
- Δ: Significant heat generated.
“Any chemical reaction that proceeds smoothly under normal conditions can proceed violently in the presence of an idiot!”

This usually is preceded by the words:

“Hey Bubba watch this!”
## CHEMICAL COMPATIBILITY FOR LIQUIDS FERTILIZERS

### Table Key:
- **A-** Acceptable if compatible with container or appurtenances
- **N-** Not acceptable because of chemical compatibility
- **1-** Acceptable if product is treated with corrosion inhibitor
- **2-** Acceptable if warranted by equipment manufacturer for the intended use
- **3-** Acceptable if cleaned after seasonal use and is used to store materials less than three months (cumulative) annually

<table>
<thead>
<tr>
<th>Product</th>
<th>Urea Ammonia Nitrate</th>
<th>Ammonium Thiosulfate</th>
<th>Ammonium Poly-phosphate</th>
<th>Potassium Phosphate</th>
<th>Potassium Hydroxide</th>
<th>Potash Solutions</th>
<th>Mixed Fertilizers, Starters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Container Material</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stainless Steel</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>Mild Steel</td>
<td>1</td>
<td>1</td>
<td>A</td>
<td>A</td>
<td>N</td>
<td>N</td>
<td>3</td>
</tr>
<tr>
<td>Mild Steel with Liner</td>
<td>2</td>
<td>2</td>
<td>A</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Aluminum</td>
<td>A</td>
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<td>N</td>
<td>N</td>
<td>N</td>
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<td>A</td>
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<tr>
<td>Poly or Plastic</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>2</td>
<td>A</td>
<td>A</td>
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<tr>
<td>Brass or Copper Alloys</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
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<tr>
<td><strong>Plugs, Valves, Tank Inserts</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>Nickel Stainless Insert</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>2</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>Fully Lined Metal</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Stainless Insert</td>
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<td>A</td>
<td>A</td>
<td>A</td>
<td>N</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>Nylon Ball Valve</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
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<td>A</td>
<td>A</td>
</tr>
<tr>
<td>Forged Steel</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>2</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>Cast Iron/Mild Steel</td>
<td>N</td>
<td>N</td>
<td>A</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
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<tr>
<td>Poly or Plastic</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
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<tr>
<td>Brass or Copper Alloys</td>
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<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td><strong>Plumbing</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stainless Steel</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
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<tr>
<td>Forged Steel</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>2</td>
<td>N</td>
<td>A</td>
<td>A</td>
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<tr>
<td>Cast Iron/Mild Steel</td>
<td>1</td>
<td>1</td>
<td>A</td>
<td>2</td>
<td>N</td>
<td>3</td>
<td>3</td>
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<tr>
<td>Galvanized</td>
<td>N</td>
<td>N</td>
<td>A</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>3</td>
</tr>
<tr>
<td>PVC/Other Synthetic</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>A</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

Source: Wisconsin Department of Agriculture, Trade and Consumer Protection
What is a BTU?

- A BTU, short for British Thermal Unit, is a basic measure of thermal (heat) energy. One BTU is the amount of energy needed to heat one pound of water one degree Fahrenheit, measured at its heaviest point. In other words, if you placed 16 ounces of water at 59°F into a stovetop pan and turned on the gas burner, it would take one BTU to raise the temperature of the water to 60°F.
UAN PRODUCTION

• AN Liquor + Urea Liquor

• Nitric acid + Ammonia + Urea Liquor

• Melt

• Adjust concentration
Composition of UAN 28% N

- 14% N from Ammonium Nitrate
  - 7% ammonium N
  - 7% nitrate N
- 14% N from Urea
- 30% water
- + small amounts of inhibitors to inhibit corrosion of mild steel
ADJUST UAN

• Addition of Urea-summer, winter blend
• Addition of Ammonia to adjust pH
• Addition of one or the other also impacts salt out temperature
• Addition of water to cut concentration impacts salt out
• Inhibitor addition impacts salt out temperature
<table>
<thead>
<tr>
<th>pH</th>
<th>% Free NH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 6.30</td>
<td>0.00</td>
</tr>
<tr>
<td>6.31 - 6.85</td>
<td>0.01</td>
</tr>
<tr>
<td>6.86 - 7.10</td>
<td>0.02</td>
</tr>
<tr>
<td>7.11 - 7.25</td>
<td>0.03</td>
</tr>
<tr>
<td>7.26 - 7.35</td>
<td>0.04</td>
</tr>
<tr>
<td>7.36 - 7.45</td>
<td>0.05</td>
</tr>
<tr>
<td>7.46 - 7.52</td>
<td>0.06</td>
</tr>
<tr>
<td>7.53 - 7.57</td>
<td>0.07</td>
</tr>
<tr>
<td>7.58 - 7.61</td>
<td>0.08</td>
</tr>
<tr>
<td>7.62 - 7.67</td>
<td>0.09</td>
</tr>
<tr>
<td>7.68 - 7.72</td>
<td>0.10</td>
</tr>
<tr>
<td>7.73 - 7.75</td>
<td>0.11</td>
</tr>
<tr>
<td>7.76 - 7.80</td>
<td>0.12</td>
</tr>
<tr>
<td>7.81 - 7.83</td>
<td>0.13</td>
</tr>
<tr>
<td>7.84 - 7.86</td>
<td>0.14</td>
</tr>
<tr>
<td>7.87 - 7.88</td>
<td>0.15</td>
</tr>
<tr>
<td>OVER 7.88</td>
<td>TITRATE</td>
</tr>
</tbody>
</table>
Eutectic Point – point of maximum solubility

32% UAN contains:
- approximately 35% ammonium nitrate, 45% urea and 20% water at eutectic point

28% UAN contains 30% water
The Ratio of AN to Urea in UAN Determines the Salt Out Temperature

The ideal ratio range is 1.1 to 1.4
<table>
<thead>
<tr>
<th>% N</th>
<th>Freezing Temperature °F</th>
<th>28-0-0</th>
<th>32-0-0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>gal per 100 gal water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>32</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>29</td>
<td>6.1</td>
<td>5.2</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>13.1</td>
<td>11.2</td>
</tr>
<tr>
<td>6</td>
<td>22</td>
<td>21.5</td>
<td>18.2</td>
</tr>
<tr>
<td>8</td>
<td>19</td>
<td>31.5</td>
<td>26.2</td>
</tr>
<tr>
<td>10</td>
<td>15</td>
<td>43.7</td>
<td>35.6</td>
</tr>
<tr>
<td>12</td>
<td>12</td>
<td>59.0</td>
<td>47.2</td>
</tr>
<tr>
<td>14</td>
<td>9</td>
<td>78.7</td>
<td>61.2</td>
</tr>
</tbody>
</table>
Appearance Value – Cross Contamination

- A Product Is Only As Good As The Skill It Was Made
- Contamination Can Be Disastrous To A Blend
- Dries That Go Into Blends Must Be Segregated
- Alley Ways Must Not Be Allowed To Co-Mingle
Salt-out is an issue in many environments

- Warm water has ability to dissolve more salts than cold water
- Salt-out occurs when salt content exceeds solubility at a given product temperature
- Crystals form on tank walls as temperature cools
- Eventually salts accumulate at tank bottom
- Salts will re-dissolve with sufficient heat and recirculation
- There is very little water in UAN solution.
Do you Circulate Continuous?
Receiving and Unloading Materials Into the Plant

• HAVE ALL PERTINENT SHIPPING INFORMATION, BOLs, DOT requirement, etc.

• REVIEW AND UNDERSTAND SDS AND RMP/PSM REQUIREMENTS

• HAZARDOUS MATERIALS RECEIVING
Filling Liquid Storage Tanks

- Make Sure Inbound Transport Is Connected to the Correct Storage Tank
- Open All Appropriate Valves and Close Others
- Contain All Leaks
- Check Tank Inventory Prior To Transfer
- Wear Proper PPE
- Close All Appropriate Valves Upon Completion Of Transfer
- Complete All Documentation and Record Ending Inventory
BLENDING LIQUID FERTILIZERS

• Solubility

• Order of Addition

• Stability
CHANGING NITROGEN SUPPLY

• Ammonium nitrate
• Increased importation of UAN
• pH variation in UAN
• AN/Urea ratio
• Supply
• Discoloration
Source and Quality of Water

• Major concern is Water Quality
• pH and Bicarbonates (HCO$_3^-$)
• Treat water with acid bring to pH 6.5
• Electrical Conductivity (EC)
• Snow melt and rain fed lake water
• Need gypsum if EC is < 0.3 dS/m
• Or EC is < 0.3 mmhos/cm
Order of Addition

- Water (Hot / Cold)
- Chelating / Complexing Agent
- Nitrogen
- Phosphates
- pH adjustment (initial)
- Micronutrients for Chelating / Complexing
- Potash
- Additional Micronutrients
- Calcium Nitrate / Chloride
- ATS / Pot Carbonate / SRN’s
- Final pH Adjustment
Order of Addition

- Suspend Solids While Mixing
- Chelating / Complexing
- pH
- Temperature
- Reaction / Compatibilities
- Foaming / Air Entrapment

Many exceptions to Rules of Addition
LABELING

• Use Placards, NFPA, and Caution Labels & Symbols

• Label All Containers Properly

Avoid trade symbols: KOH, MOP, APP
Summary of ammonia loss from UAN???

• Urea in UAN does not hydrolyze in the fertilizer tank.
• The NH$_4^+$ from the ammonium nitrate portion of the UAN cannot be lost as NH$_3$.
• The amount of NH$_3$ added to some UAN to inhibit corrosion is very small, around 10 lb per ton. A small portion of this NH$_3$ may be lost during application.
Effect of Temperature on Conversion of Aqueous NH$_3$ to Gaseous NH$_3$
So Why Do Tanks Fail?

- Improper Construction
- Corrosion
- Specific Gravity of fluid incompatible with tank wall
- Internal/External forces or events (fire, flood, impact, etc.)
- Age/UV related issues – Poly & Fiberglass
- Seismic zone design not compatible with area
UAN Corrosion Management Should Be Taken Seriously by Every UAN Tank Owner

• All UAN producers strive to make quality material, that is clean, bright and only minimally corrosive.
• However, you should not depend solely on the UAN producer to manage your corrosion concerns.
• Some producers have gone to lined tanks, or use epoxy coatings extensively. Their piping is all stainless.
• UAN corrosiveness can vary:
  • producer to producer,
  • plant to plant,
  • and even day to day in the same plant
If a UAN tank located on your property leaks, you may be liable for contamination in ground and surface water...

You may lose significant amounts of product and property

The EPA and OHSA might become your new business partners

Your business reputation may be put at risk
**Key UAN Corrosion Mechanisms**

**Surface Corrosion in UAN**

- \[ \text{NH}_4\text{NO}_3 \rightarrow \text{NH}_4^+ + \text{NO}_3^- \]
- \[ \text{NH}_4^+ \leftrightarrow \text{NH}_3 + \text{H}^+ \]
- \[ \text{H}^+ + \text{NO}_3^- \rightarrow \text{HNO}_3 \]

Easy mass transfer of ammonia through the thin UAN film results in acid build up and surface corrosion. This reaction is strongly driven by temperature.

**Pitting Corrosion in UAN**

**Crevice or Under-Deposit Corrosion**

- \[ \text{Fe}^{+2} \rightarrow \text{Fe}^{+3} \]
- \[ \text{Fe}^{+3} + 3\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 3\text{H}^+ \]

**Solution**

- \[ \text{NH}_4\text{NO}_3 \rightarrow \text{NH}_4^+ + \text{NO}_3^- \]
- \[ \text{NO}_3^- + \text{H}^+ \rightarrow \text{HNO}_3 \]

The \( \text{H}^+ \) can’t diffuse out of the crevice fast enough. To remain electrically neutral, \( \text{NO}_3^- \) ions come in and in effect make Nitric Acid resulting in low pH inside the crevice, resulting in accelerated (pitting) corrosion.

**UAN “Thin Film”**

Easy mass transfer of ammonia through the thin UAN film results in acid build up and surface corrosion. This reaction is strongly driven by temperature.

**Heat Affected Zone on Bottom Welded Plates**

The \( \text{H}^+ \) can’t diffuse out of the crevice fast enough. To remain electrically neutral, \( \text{NO}_3^- \) ions come in and in effect make Nitric Acid resulting in low pH inside the crevice, resulting in accelerated (pitting) corrosion.
Tank Failure Background & History

• Storage tank failure is not a new phenomenon in fact...

On January 15, 1919 a United States Industrial Alcohol Company’s distilling tank which recently had received a shipment of molasses in from Puerto Rico, exploded. At about 12:40 p.m. the giant tank ruptured, emptying its entire contents of about 2.5 million gallons of molasses, into Commercial Street in the space of a few seconds. The tank, a 90’-0 diameter x 50-foot high cast iron tank was filled to the top with molasses. Upon failure, a 15-foot high wave of dark molasses moving about 35 miles per hour swallowed the streets of Boston's North End. Almost 150 people lie injured in the streets with the final death toll being 21. A Massachusetts court determined that insufficient safety inspections had played a part in the accident. In time, after 3,000 witnesses testify during 300 days of hearings, the courts found the company liable, concluding shoddy construction and overfilling of the tank was to blame, along with the apparent sudden expansion of the molasses -- the temperature had only been 2 degrees above zero the previous day. The company paid almost $1 million to settle the claims.
• 3/1997 – Washington, a 500k gallon storage tank of Potassium Thiosulfate has a weld rupture resulting in loss of 100k gallons of material.
• 3/1997 – Iowa, a 1M gallon ammonium phosphate tank ruptures and in turn damages two other liquid fertilizer tanks
• 7/1999 – Michigan, a 1M gallon APP ruptures and damages 3 adjacent tanks
• 1/2000 – Ohio, a 1M gallon fertilizer tank ruptures and damages 4 adjacent tanks and 5 tractor trailer rigs. More than 800k gallons spills into the Ohio River.
• 3/2000 – Ohio, a 1.5M gallon ammonium phosphate tank ruptures and damages 2 adjacent tanks. Some of the released liquid flows into nearby creeks.
• 10/2000 – Montana, a 2M gallon nitrogen fertilizer intermediate tank has a massive roof failure, no loss of product, but tank is damaged significantly.
UAN Corrosion Management Should Be Taken Seriously by Every UAN Tank Owner

• Purchasing UAN from multiple sites, may result in mixed inhibitors
  – These different inhibitors, (now diluted), may not be as effective together as they are by themselves when at full strength

• Purchasing quality UAN, from a trusted source, may be worth a little extra in price
  – You should monitor what you receive
  – Look closely at the quality of the UAN you are buying and the assets that will be exposed to that UAN
Excess NH3 Controls the pH and also the Corrosivity

At Excess NH3 Below 0.008 wt %, UAN pH Goes Down Sharply Resulting in Extremely High Corrosion Rates!
Considerations

• Systematic approach
• Compatible components
• Short term vs. long term
• Plan ahead for future expansion
Floor Failure Prevention

• Concrete Foundations

• Internal Coatings

• Full draining of liquids/thorough circulation of liquids

• Routine solids removal

• Cathodic protection
HOUSEKEEPING

• Keep the Place Clean
• Plumbing
• Pumps
• Gaskets
• Etc.
## Open vs. closed impeller design pumps

<table>
<thead>
<tr>
<th>Open</th>
<th>The fluid enters the eye of the impeller where the turning vanes add energy to the fluid and direct it to the discharge nozzle. A close clearance between the vanes and the pump volute, or back plate in a few designs, prevents most of the fluid from recirculating back to the eye of the impeller. (L) shows the leading edge or higher-pressure side of the impeller. (T) describes the trailing edge of the impeller.</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Open Impeller" /></td>
<td><img src="image" alt="Open Impeller" /></td>
</tr>
<tr>
<td>Closed</td>
<td>The fluid enters the eye of the impeller where the vanes add energy to the fluid and direct it to the discharge nozzle. There is no impeller to volute or back plate clearance to set. Wear rings restrict the amount of discharge fluid that recirculates back to the suction side of the impeller. When this wear ring clearance becomes excessive the wear rings must be replaced.</td>
</tr>
<tr>
<td><img src="image" alt="Closed Impeller" /></td>
<td><img src="image" alt="Closed Impeller" /></td>
</tr>
</tbody>
</table>
Doubling the diameter of a pipe increases its capacity four times.
SAFETY

Special Situations

• Respirators
• Confined Space Entry
• Forklifts/Loaders/Shuttle Trucks
• Elevated Work / Maintenance
  • Harnesses
  • Safety Cages
  • Rest Platforms
  • Ladders & Man Lifts/Boom Trucks
SAFETY

• Our Most Important Priority
• Every Employee Goes Home Safe
  – Training – Documented
  – PPE when you can’t eliminate hazards
  – Regular Tailgate & Huddles Meetings
  – Policies, Procedures, Work Directions
  – Develop Culture of Safety in
  – Environmental Safety
  – Facility / Equipment Safety
Training

- Haz-ops Trained. What Level?
- PPE
- Safety Meetings/Documentation
- Understanding Of the Process
- Response To Releases, etc.
- Understanding Of Chemistry
PERSONNEL RESPONSIBILITIES

• Safety And Quality Are Everyone's Business
• Be Properly Trained
• Understand All Products
• Chemistry (basic understanding)
SECURITY

• Site & Transportation Security
  • Homeland Security Compliance
    • Hazmat Railcar Training
  • Security Fencing
• Restricted Entry
Supervision

• If You Are Not Committed To Training
• If You Are Not Committed To Proper Equipment
• If You Are Not Committed To Safety
• Don’t Make These Products And Have Someone Toll Them For You
Key Take Aways…

- Training and Safety is Paramount
- Take Pride in Your Operation
- Quality Inputs make Quality Products
- Stored Liquid Can be Corrosive
- But **YOU** can manage this risk:
  - Manage Risk
  - Control Your UAN chemistry
  - Proper Tank Design and Maintenance Practices

Questions?